EXPERIMENTAL ORGANIC CHEMISTRY

James F. Norris

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BY
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PREFACE TO THE SECOND EDITION

The appearance of the second edition of the author's "Textbook of Organic Chemistry" made it advisable to prepare a revision of this laboratory guide, in order that the references given to the text should refer to the new edition of the latter.

Advantage has been taken of the opportunity to give improved directions for a number of experiments and to incorporate new material of importance. Some additions have been made to the chapter on laboratory methods, and directions for a few new preparations have been given. These include the preparation of normal butyl chloride from the alcohol and aqueous hydrochloric acid, of triphenylmethane directly from benzene, carbon tetrachloride, ether, and aluminium chloride, of an amylene from secondary amyl alcohol, and of a secondary alcohol from pentene-2.

The author will be glad to receive suggestions from teachers who use the book with their classes.

JAMES F. NORRIS.

CAMBRIDGE, MASS.
April, 1924.

PREFACE TO THE FIRST EDITION

This book is designed primarily to be used as a laboratory guide in connection with courses in organic chemistry in which the student follows in the laboratory the subject as developed in the class-room. An attempt has been made to furnish directions for experiments to illustrate the methods of preparation and the chemical properties of the more important classes of organic compounds. As a consequence, the student following the work as given, comes in contact with many substances of importance which are not handled by one whose laboratory work consists solely in the preparation of a few compounds. For example, directions are given in considerable detail for experiments which illustrate the properties of fatty amines, hydroxy acids, carbohydrates, fats, proteins, etc., subjects which receive scant, if any, attention in many laboratory courses in organic chemistry.

Directions for a large number of preparations are also given. These serve to illustrate the more important synthetic methods and the different kinds of laboratory technique with which the student should become acquainted. In connection with the directions for the preparation of typical compounds, experiments are given which illustrate the properties of the compounds made. These experiments include in each case a study of the reactions of the substance which are of particular value in the identification of the characteristic group present.

No attempt has been made to introduce novel preparations; the ones given are, in the main, those commonly used. These have been selected on account of their simplicity and the fact that they illustrate the principles to be taught; they are as novel to the student as any that could be devised. Although the older preparations are used, the laboratory details are, in many cases, different from those commonly employed. The changes have been the result of a detailed study of the preparations which, in many cases, resulted in simplification and improvement. A few new preparations are described; these are to illustrate, in most cases, the properties of compounds that have not been studied commonly in laboratory courses in organic chemistry.

A feature of the book is the introduction of directions for the preparation of certain compounds on a very small scale. Students often acquire the habit of careless work in the laboratory practice in organic chemistry. Preparation-work on the small scale serves to counteract this effect and to develop a technique that is valuable. Such work is often necessary in the identification of unknown compounds when a small amount only of the substance is available. In many cases a crystalline derivative whose melting-point can be determined, can be prepared in a pure condition from but two or three drops of a substance. Among the examples of work of this kind which are given are the preparation of acetanilide from acetic acid, glyceryl tribenzoate from glycerol, dinitrobenzene from benzene, and dibenzalacetone from acetone. In order to facilitate such work, a section in the first chapter is devoted to a consideration of the technique used in the manipulation of small quantities of substances.

The final chapter of the book deals with the methods used to identify organic compounds by a study of their chemical behavior and physical properties. The method is outlined only, since the pedagogical value of the work depends largely upon giving the student opportunity to apply the knowledge he has gained throughout the course in the study of the behavior of the typical classes of organic compounds. It has been the experience of the author for a number of years, that laboratory practice of this kind undertaken at the end of the course, is of great value to the student, on account of the fact that it gives him an opportunity to review, correlate, and apply many of the facts he has learned. The practical application of his knowledge is evident. When a student has been able to identify definitely a number of compounds which were unknown to him, he feels that he has gained power in handling problems in organic chemistry.

A chapter of the book is devoted to detailed directions for carrying out the simpler operations used in laboratory work in organic chemistry. In order that the student may make use of this information when it is necessary, references are given throughout the book to the paragraph and page where the particular process to be employed is described. It is impossible to repeat in the laboratory directions details for these processes, and if the student does not have these details before him he is apt to carry out the operation in a careless manner. It is believed that a definite reference to the place where the process is described may be useful.

The book contains directions for more work than can be done in a laboratory course of the usual length. An opportunity is thus given the teacher to select the work that is best adapted to the needs of his students. The method of numbering and lettering the experiments makes it possible to assign readily the work to be done by the class.

The author has consulted all the well-known texts on laboratory work in organic chemistry in the preparation of the book. In writing the directions for the preparation of compounds on a small scale, valuable help was obtained from S. P. Mulliken's "The Identification of Pure Organic Compounds." A number of experiments on fats, carbohydrates, and proteins have been adapted, with the permission of the author, from a laboratory manual in descriptive organic chemistry prepared for the use of students of household economics, by Professor Alice F. Blood, of Simmons College. The author wishes to express his thanks for the courtesy shown in granting permission to make use of this material.

All the figures in the book were prepared from drawings made by the wife of the author; for this help and for assistance in reading the proof he is deeply grateful.

The author will be pleased to have called to his attention any mistakes which may be discovered by those who use the book; any suggestions as to improved directions for the experiments will also be gladly received.

JAMES F. NORRIS

BOSTON, MASS.
April, 1915.

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CHAPTER I

LABORATORY METHODS

1. General Directions to the Student.—Before beginning an experiment read through to the end the directions which are to be followed. Many mistakes which involve additional work can be prevented by understanding beforehand just what is to be done. The import of the experiment should be clear, and the chemical reactions involved at each step should be understood before the work is started.

References are given in each experiment to the section in the author's textbook "The Principles of Organic Chemistry" in which the chemical reactions involved are discussed. These references are given in bold-face type thus, (SECTION **359).** References to paragraphs in this book are indicated thus, §64, page 42.

Keep a clear and concise record of the laboratory work. The notes should be written as soon as the experiment has been performed, and care should be taken to have the original record, made during the course of the experiment, of such a character that it serves as the permanent record of the work. Notes should not be taken on loose pieces of paper and afterward written out in the notebook; they should be written carefully in good English, and should state briefly what was done and what was observed. It is necessary for the student to recognize what the experiment is to teach—why he was asked to do it. If the work consists in the preparation of some compound the details for which are given in the laboratory guide, it is not advisable to take time to copy these details in the notebook. References to the pages in the book where the preparation is described should be given, and a statement made of the amounts of the substances used. If any unexpected difficulties arose, or if any improvement in the way of carrying out the preparation was used, these facts should be noted. Write equations for all reactions taking place in the experiment, and record the yield of the compound obtained. The substance should be put in a clean, dry, glass-stoppered bottle of appropriate size, and be labeled. The student's name, the name, weight, and the boiling-point or melting-point of the substance should be recorded on the label. The boiling-point or melting-point should be that observed by the student for the sample itself, and not the points recorded in the book.

The student should use reasonable care in his manipulations. He should endeavor to get as large a yield as possible of the product sought, but should use judgment as to whether it is advisable to spend a large amount of time to increase by a small amount the yield of the product. The processes should not be carried out in the manner used with a quantitative analysis—a few drops may be lost here and there if they form but a very small portion of the total amount formed, and their recovery entails the expenditure of much extra time. It is not meant by this that the student be careless; be should develop judgment as to the relative value of a slightly higher yield of product and the time required to obtain it.

2. Calculation of Yield.—The student should calculate in each preparation the percentage yield obtained. From the chemical equation for the reaction can be calculated the so-called theoretical yield. The percentage of this obtained is called the percentage yield. The latter is never equal to 100 per cent for many reasons. It is often advisable to use an excess over the theoretical amount of one of the substances used in the preparation. The student should, before calculating the percentage yield obtained, determine whether an excess of one reagent has been employed. When one substance used in a preparation is much more expensive than the rest, it is customary to take the substances in such amounts that the largest yield possible calculated from the more expensive substance is obtained. For example, preparations involving the use of iodine are so carried out that the largest amount of the halogen possible is obtained in the substance prepared. In this case the test of the skill with which the preparation is carried out is determined by this fact; the percentage yield should be calculated, accordingly, from the weight of iodine used.

3. Integrity in Laboratory Work.—The student should record in his notebook his own observations only, and the results he has obtained himself, unless there is a definite statement to the contrary. If a student has carried out an experiment along with another student a statement to this effect should be put into the notes.

4. Cautions in Regard to Laboratory Work.—A student uses in laboratory work in organic chemistry inflammable liquids and substances like sodium and phosphorus which have to be handled with great care. Unless care is exercised fires may happen. The laboratory should be provided with buckets of sand and a fire-extinguisher. A heavy woolen blanket should be near at hand to be used in case the clothing catches fire.

Inflammable liquids such as ether, alcohol, and benzene should not be poured into the jars provided for acids.

Only cold solutions should be extracted with ether, and the process should be carried out at least twelve feet from a flame.

When carrying out a reaction in a test-tube, care should be taken to hold the tube in such a position that if the contents are violently thrown out, they will not come in contact with the experimenter or any one in the neighborhood. If the odor of a substance in the tube is to be noted, do not look down into the tube. If this is done and a violent reaction takes place suddenly, the material in the tube may be thrown into the eye.

CRYSTALLIZATION

5. When an organic compound has been prepared it must be purified from the by-products which are formed at the same time. In the case of solid substances crystallization is ordinarily used for this purpose, although with certain compounds purification can be more readily effected by sublimation or distillation, processes which are described below.

Choice of Solvent.—The separation of two substances by means of crystallization is based on the fact that they are present in the mixture to be separated into its constituents in different amounts, or on the fact that the two substances possess different solubilities in the liquid used as a solvent. When it is desired to purify a substance by crystallization a solvent should be selected, if possible, in which the impurity is readily soluble, and in which the substance sought is more or less difficultly soluble. Purification is effected most easily when the substance to be purified is appreciably soluble in the hot solvent, and much less soluble in it when cold. If the two conditions stated above can be combined—and this is possible in many cases—purification is readily accomplished.

The solvents most commonly used in crystallization are water, alcohol, ether, benzene, petroleum ether, ligroin, carbon bisulphide, chloroform, acetone, and glacial acetic acid. In certain cases hydrochloric acid, carbon tetrachloride, ethyl acetate, toluene, and nitrobenzene have been found of particular value as solvents.

In order to crystallize a compound the solubility of which is not known, preliminary tests should be made with the solvents enumerated above; about 0.1 gram or less of the substance should be used in each test. The solid is placed in a small test-tube, and the solvent is added a drop at a time and the tube is shaken. After the addition of about 1 cc. of the liquid, if the substance has not dissolved, the tube should be heated until the liquid boils. If the substance does not dissolve, more liquid should be added in small quantities until solution occurs. If a very large amount of the liquid is required for solution, or the substance proves insoluble, another solvent must be used. When solution takes place the tube is cooled by running water. If the substance separates, it is redissolved by heating, and the contents set aside to cool slowly, when crystals will probably form.

If the substance does not separate to a considerable degree when the hot solution is cooled, similar tests should be made with other liquids. If none of the solvents can be used in this way, either the substance must be obtained by spontaneous evaporation, or a mixture of liquids must be used—a method described below.

If the compound is to be crystallized by spontaneous evaporation, cold saturated solutions, prepared by dissolving about 0.1 gram or less of the substance in a number of solvents, are poured onto watch-glasses and left to evaporate slowly.

6. Some substances form solutions from which the first crystals separate with difficulty. In such cases the solution is "seeded" by adding a trace of the solid substance; a piece the size of the bead of a small pin is sufficient. Crystallization of such substances can often be brought about by scratching with a glass rod the side of the vessel containing the solution; the rough surface so formed assists materially in the formation of the first crystal, after which crystallization proceeds readily.

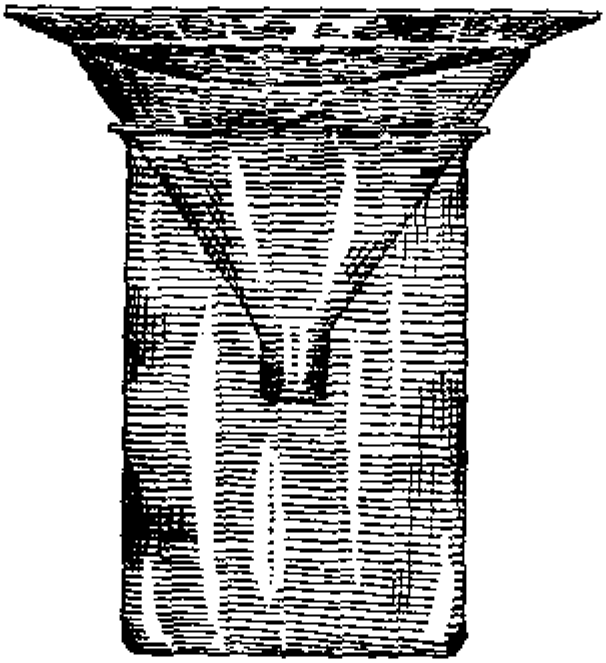
The liquid finally selected for the solvent should be one which yields well-formed crystals, and does not evaporate too slowly.

7. Use of Freezing Mixtures in Crystallization.—It often happens that substances which do not separate from their hot solutions when the latter are cooled with water, crystallize out well when the solutions are allowed to stand for some time in a freezing mixture. For this purpose, a mixture consisting of equal weights of sodium chloride and *finely divided* ice or snow, is commonly used; with snow, a temperature of -17° is obtained. A mixture of equal weights of crystallized calcium chloride and snow gives the temperature -48°. A convenient freezing mixture is made by covering finely divided ice with commercial concentrated hydrochloric acid.

8. Preparation of Crystals.—When a satisfactory solvent has been selected, the material to be crystallized is placed in a beaker and covered with the liquid. The mixture is heated to boiling over a free flame or on a steam-bath if the solvent used is inflammable. It is essential to avoid the presence of a free flame when alcohol, benzene, ether, or petroleum ether are used as solvents. The beaker is covered with a watch-glass, and the solvent is added in small portions at a time until the substance to be crystallized has passed into solution. It may happen that a small amount of a difficultly soluble impurity is present; in this case it is not advisable to add enough solvent to dissolve the impurity.

When the substance to be crystallized has been dissolved, the solution is filtered while hot through a fluted filter-paper into a beaker. Crystallizing dishes should not be used. If the substance crystallizes out during the filtration, either a hot-water funnel can be used, or enough of the solvent can be added to prevent crystallization. In the latter case, and whenever an excess of solvent has been used, it is advisable to concentrate the solution to crystallization after filtration.

9. The solution is evaporated to crystallization by boiling it gently. Tests are made from time to time to determine whether crystals will form when the solution cools. This can be readily done by placing a glass rod in the hot solution and then withdrawing it; if crystals appear when the drop of the liquid which adheres to the rod cools, the solution should be set aside and covered with a watch-glass or filter-paper. If crystals are not formed, the evaporation should be carried further.



A hot-water funnel is at times very useful if crystals form during the filtration. It consists of a funnel surrounded by a metal jacket in which is placed water that can be heated to its boiling-point by means of a Bunsen burner. When inflammable liquids are used as solvents, the water should be heated and the burner extinguished before filtration. Disregard of this precaution has frequently led to fires.

10. It is advisable to cut off the stems of the funnels to be used in the preparation of organic compounds. This eliminates the clogging of the funnel as the result of crystallization of solids in the stem. It also makes it unnecessary, in most cases, to use filter-stands as the funnel can be supported by the beaker which is to hold the filtrate; if the beaker is too large for this, the funnel can be supported on a clay triangle placed on the beaker. The arrangement represented in Fig. 1 is especially convenient for filtering solutions which deposit crystals on cooling slightly. During filtration the beaker is heated on the steam-bath or over a flame; the vapor which rises heats the funnel. The latter should be covered during filtration with a watch-glass to prevent loss of heat from the liquid that it contains.

11. The Use of a Mixture of Two Liquids as the Solvent in Crystallization.—It is advisable to use as a solvent in purifying a substance a liquid in which the substance is readily soluble when heated and difficultly soluble in the cold. If such a solvent can not be found, a mixture of two miscible liquids is often used—one in which the substance is readily soluble, and one in which it is insoluble or difficultly soluble. In crystallizing a substance in this way it is first treated with the hot liquid which dissolves it; to the solution is then added the second liquid, also hot, until the mixture begins to cloud. A little of the solvent is added to clear up the solution, which is then covered to prevent too rapid evaporation, and the mixture is set aside to crystallize. Pairs of liquids which are valuable for crystallization in this way are alcohol and water, alcohol and benzene, petroleum ether and benzene, and alcohol and carbon disulphide.

12. Separation of Crystals.—The separation of crystals from the mother-liquor is effected by filtration under diminished pressure. A funnel is attached to a filter-bottle by means of a rubber stopper. A perforated plate about 4 cm. in diameter is placed in the funnel and covered with a circular piece of filter-paper the diameter of which is about 6 mm. greater than that of the plate. This paper is moistened with the solvent. The bottle is connected with the suction-pump, and air is drawn through the apparatus. The paper is fitted into place so that it covers the joint between the filter-plate and funnel. If a crust has formed around the beaker at the surface of the liquid from which the crystals to be separated have formed, it should be carefully removed, as it will probably contain some of the impurities present. The remaining solution and crystals are then poured into the funnel, and the suction applied. When all the liquid has been drawn off the solid should be pressed down tightly with a spatula. The connection with the pump is broken, and the solid on the funnel is moistened with some of the pure solvent used for crystallization. The crystals are allowed to absorb the solvent and to stay in contact with it for about half a minute. The suction is then applied and the crystals drained as fully as possible from the liquid. The filter-bottle is again disconnected from the pump, and the crystals covered again with the solvent, and washed as before. Crystals should never be washed by pouring the solvent over them while the filter-bottle is connected with the pump. If this is done a large amount of liquid is required to wash the crystals, and there is great loss due to the solution of the crystals in the solvent.

When the crystals have been freed by suction as much as possible from the liquid used to wash them, they should be removed to a porous plate and allowed to dry spontaneously in the air.

13. In the preparation of many compounds tarry substances are often obtained along with the compound desired. In this case the crystals first obtained from solution are often mixed with these substances. The tar may be removed by pressing the crystals on a porous plate and allowing them to stand undisturbed for some time. The residue, from which the tar has been largely removed as the result of absorption into the porous plate, is transferred to a clean part of the plate and is moistened with the solvent. The substance is left until the solution of the tarry product clinging to the crystals is absorbed. A second crystallization and treatment with the porous plate generally yields a pure compound.

When the crystals are thoroughly dry a melting-point determination (§49, page 33) should be made; if this is not sharp the substance should be recrystallized.

14. Decolorization of Solutions.—If a substance contains tarry materials which impart to it a color it can be purified usually by boiling a solution of it for some time with bone-black, and filtering the hot solution. The efficiency of the process and the amount of bone-black required are markedly affected by the quality of the latter. As an approximation about 1 gram should be used for a solution of 250 cc. which is moderately colored.

DISTILLATION

15. Liquids are purified by distillation. The form of apparatus ordinarily used is represented in Fig. 2. In setting up the apparatus the details noted below should be considered.

The distilling flask should be supported by a clamp placed *above* the side-arm, and the condenser by a clamp placed at its middle point. The side-arm of the distilling flask should extend for about one-half its length into the inner tube of the condenser.

16. Preparation of Corks.—Before being used corks should be softened. This can be done by means of a press, which is made for this purpose, or the cork can be rolled on the desk while it is being pressed firmly by means of a block of wood. It is, in most cases, not advisable to use rubber stoppers as they may be attacked by the vapor of the liquid during distillation. Sharp cork borers should be used to make the holes of such a size that the tubes to pass through fit snugly. In boring corks it is advisable first to push the borer with a rotary motion half way through the cork, taking care that the hole is bored through the center of the cork, the borer is then removed and a hole made from the center of the other end of the cork to meet that first made. By proceeding in this way the edges of the holes on the two sides of the cork will be clean cut, and thus make a tight joint with the tube to be passed through the hole; and the latter will run evenly through the axis of the cork.

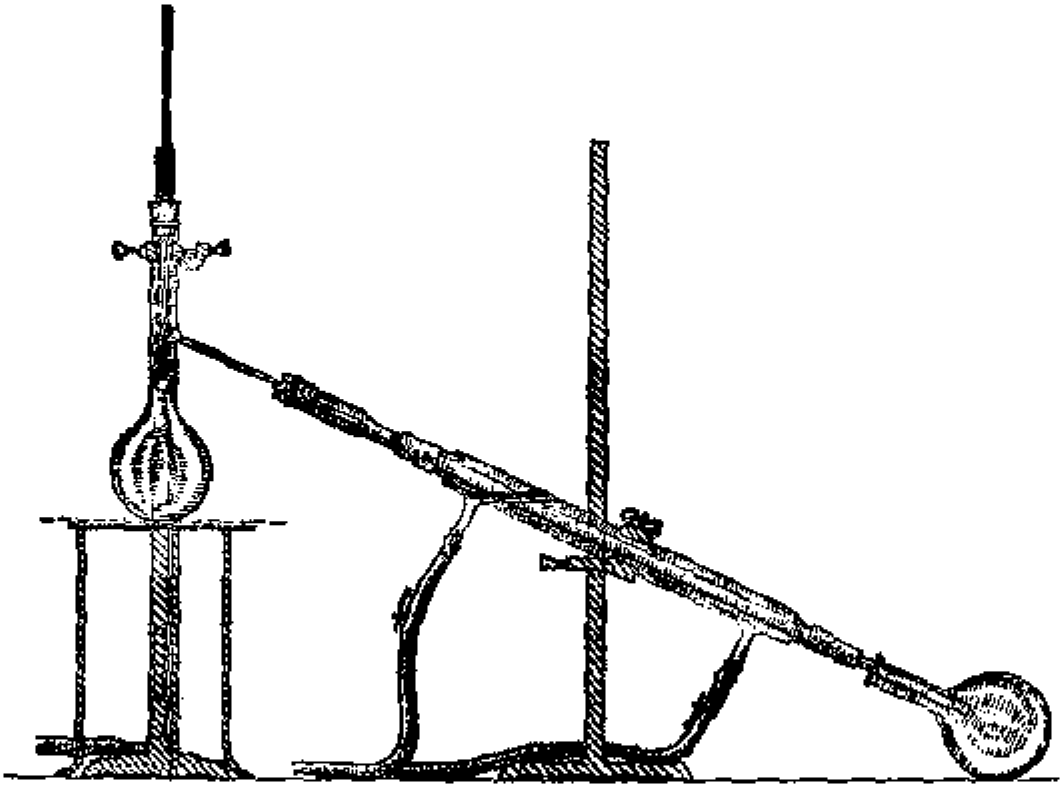


FIG. 2.

17. Position of the Thermometer.—The bulb of the thermometer should be so placed that it is about 1 inch below the side-arm of the distilling flask. If the liquid boils at such a point that the end of the thread of mercury is hidden by the cork during the boiling, the position of the thermometer can be shifted downward, or the upper or lower end of the cork can be cut away. The bulb should never be placed above the side-arm, since it is essential that it be covered completely by the vapor during the distillation.

18. Heating the Flask.—The best way of heating the distilling flask is determined by the boiling-point of the liquid to be distilled. If the liquid has a low boiling-point, up to about 80° or 90°, the flask should be placed *in* a water-bath in such a position that the level of the water is just below that of the liquid in the flask. Toward the end of the distillation the flask should be raised in order to prevent superheating the vapor of the liquid. With very volatile liquids great care is necessary to prevent this superheating.

Another method which is often used is to place the flask on an asbestos board in which a hole is bored having a diameter about one-half that of the flask. The smallest flame which will furnish heat enough to boil the liquid is used. This method can be used for distilling in general, whatever the boiling-point of the liquid.

If a flask of 250-cc. capacity or greater is used, it is advisable to support it on a wire gauze. This precaution is also advisable when the burner is put in place, and the distillation allowed to take place of itself. It is often better to hold the burner in the hand and keep the flame in motion during the distillation. In this way the process is more carefully watched and the rate of distilling can be controlled.

The heating of the flask should be discontinued before all of the liquid has distilled; it is customary to leave a residue of 2 to 5 cc. in the flask.

19. Rate of Distillation.—The distilling flask should be heated in such a way that the distillate falls in drops from the end of the condenser at the rate of about one drop per second. Care should be taken to avoid the rapid distillation of very volatile, inflammable liquids, such as ether, alcohol, and carbon disulphide. If such liquids are distilled very rapidly, a part of the vapor is not condensed, and a fire may result when this vapor comes in contact with a near-by flame. In order to prevent accidents the method of collecting such liquids which is described in §34, page 23, should be used.

20. Distillation of High-boiling Liquids.—When a liquid boils above 150° an "air-condenser" should be used instead of the kind shown in Fig. 2, which is supplied with a water-jacket. If one of the latter type is used, the inner tube, cooled by running water, is apt to crack when the vapor of the high-boiling liquid comes in contact with it. The inner tube without a jacket is used as an air-condenser. When a substance which boils at a high temperature (above 300°) and solidifies readily is distilled, it is customary to use no condenser, but to collect the distillate directly at the end of the side-arm of the distilling flask. If, in this case, or when an air-condenser is used, the distillate solidifies before it reaches the receiver, the tube should be gently heated by passing the flame of a burner slowly along its length. It is necessary to prevent the filling of the side-arm of the flask with solid; if this occurs and boiling is continued, the vapor produced soon reaches a sufficient pressure to cause an explosion. When this method is unsatisfactory on account of the high melting-point of the substance, it is advisable to distil from a retort. On account of the large diameter of the neck of the retort, a considerable quantity of the solid can be collected in it. Before the solid fills the neck at any point, the distillation is stopped, the neck of the retort is heated, and the liquid collected in a beaker; the distillation is then continued.

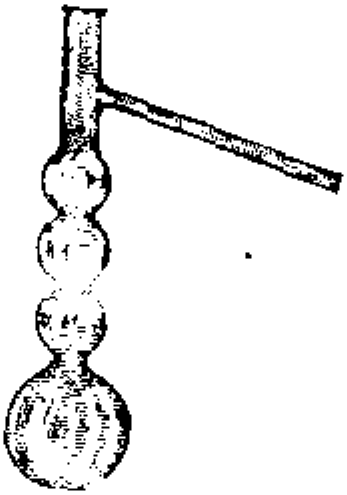


FIG. 3.

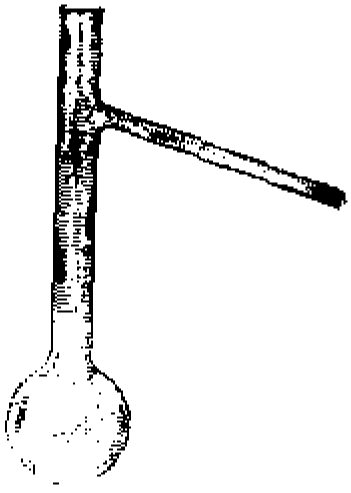


FIG. 4.

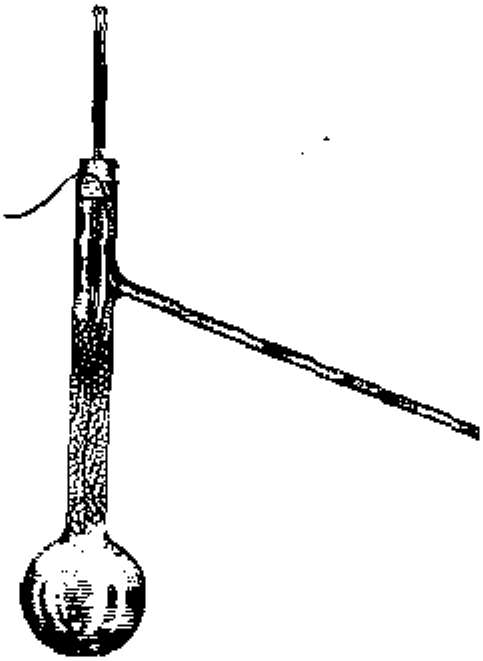


FIG. 5.

21. Fractional Distillation.—When it is necessary to separate two or more liquids by distillation, special forms of distilling flasks should be used. These are so constructed that they decrease materially the time required to effect a separation. This is accomplished by subjecting the vapor to gradual cooling before it is finally condensed. In this way the less volatile constituents of the vapor are condensed and returned to the flask, while the more volatile parts pass on through the condenser. The types of flasks used are illustrated by Figs. 3, 4, and 5.

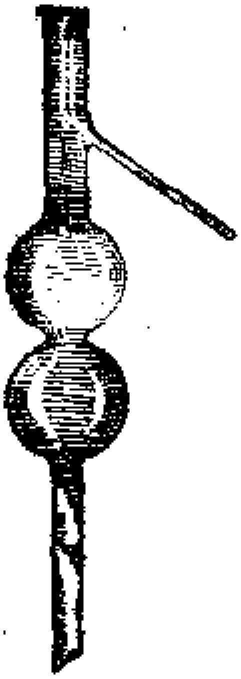


FIG. 6.

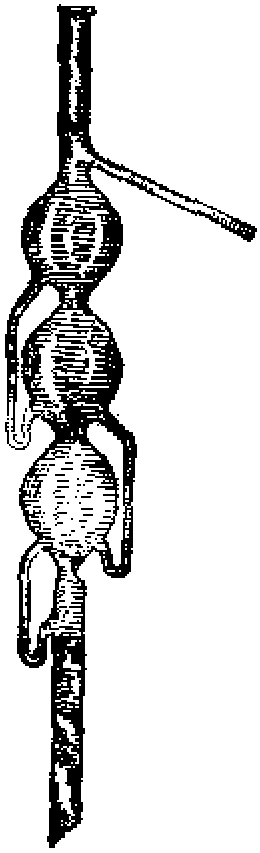


FIG. 7.

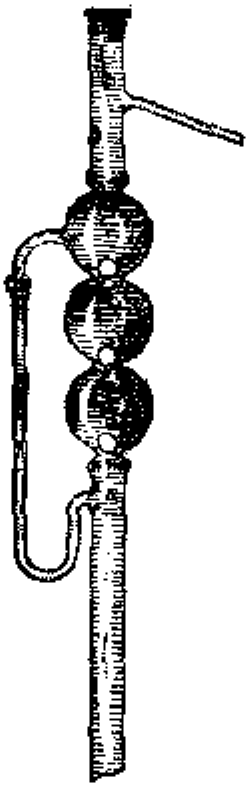


FIG. 8.

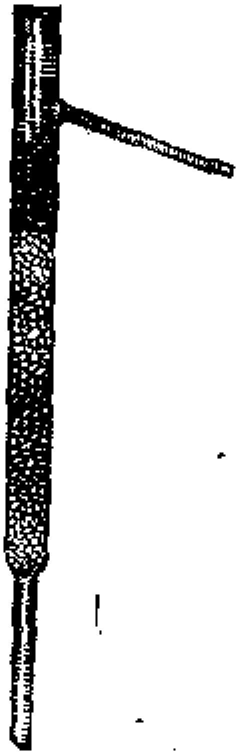


FIG. 9.

The arrangement represented in Fig. 5 is very efficient, especially when a small amount of a liquid is to be fractionated. After the liquid has been placed in the flask, a number of glass beads tied together with a cotton thread are supported by the thread, and the neck of the flask is filled to the place indicated in the diagram with glass beads.

22. The more complicated arrangements are supplied as tubes which are fitted by a cork to a round-bottomed flask. Figures 6, 7, 8, and 9 illustrate the forms commonly used.

The most efficient form is that of Hempel, Fig. 9, which consists of a tube filled with glass beads. The least efficient form is that of Wurtz, Fig. 6. The efficiency of the Lebel-Henninger tube, Fig. 7, and that of the Glinsky tube, Fig. 8, lie between the two extremes stated.

Another simple form of apparatus, for fractionating low-boiling liquids, which is especially valuable when small quantities only are available, can be constructed from a Claissen flask and a test-tube in the way illustrated in Tig. 10. The cold water enters through the long tube in the test-tube and passes upward. By regulating the flow of water the cooling effect on the vapor can be varied. The principle of fractional condensation which is used effects the separation of the vapor into low- and high-boiling constituents. The combination of a still-head of this type with a column containing short pieces of glass tubing about 15 mm. long and 3 mm. internal diameter makes, perhaps, the most efficient fractionating apparatus available for laboratory use. It is illustrated in Fig. 11.

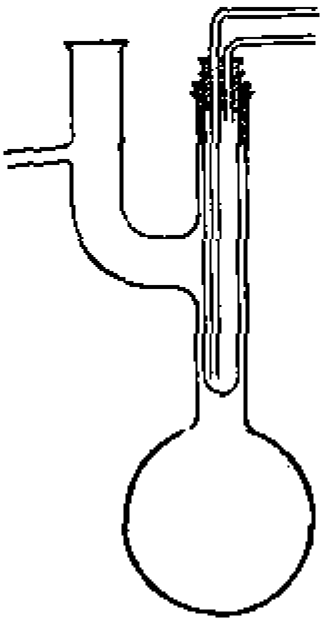


FIG. 10.

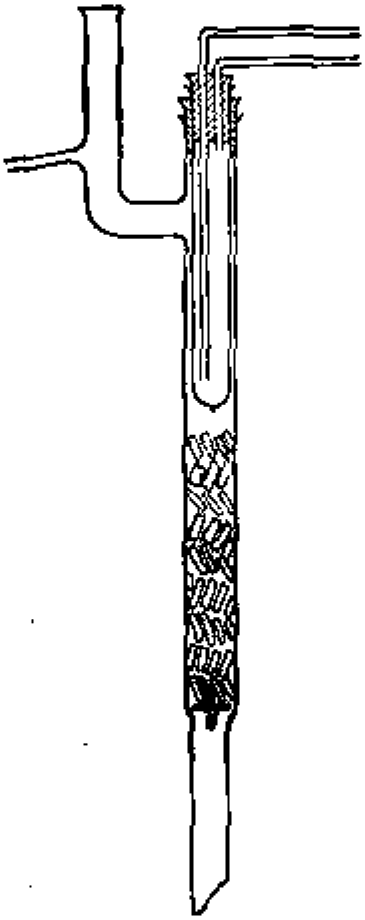


FIG. 11

23. When a mixture of two liquids which boil at different temperatures is distilled, the temperature of the vapor during the distillation rises, in most cases, from the boiling-point of one of the liquids to that of the other. The distillate which is collected first contains a large proportion of the lower boiling liquid, while that collected toward the end of the operation is rich in the higher boiling liquid. In order to separate the two, the mixture is subjected to what is called fractional distillation.

The process is carried out in the following way: The mixture is distilled slowly, and the receiver in which the distillate is collected is changed from time to time, as the boiling-point of the liquid rises. In this way the mixture is separated into what are called fractions. The number of fractions collected, and the limits of the boiling-point of the various fractions, are determined by the difficulty of separating the mixture and the purity of the products desired. The lowest boiling fraction is next placed in a clean flask and distilled. When the temperature reaches that of the upper limit of the fraction, the heating is stopped, and the second fraction added to the flask. Distillation is then continued until the upper limit of this fraction is reached, the distillate being collected in the appropriate receiver. The process is continued in this way until all the fractions have been distilled a second time. It will be found as a result of this fractionation that the distribution of the liquid in the several fractions is different from that obtained the first time. The fractions which boil at temperatures near those of the boiling-points of the constituents of the mixture increase in volume. By repeating the process a sufficient number of times, practically all of the liquid can be separated into its constituents.

In the following table are given the results of the fractional distillation of a mixture of 50 cc. of methyl alcohol and 50 cc. of water. The volumes of the fractions obtained after each of six fractionations are recorded.

	66°-68°	68°-78°	78°-88°	88°-98°	98°-100°
I	0.0	1.5	47.0	17.0	31.0
II	0.0	33.5	14.0	7.5	38.5
III	1.5	38.5	6.5	5.5	40.5
IV	15.0	24.5	5.0	3.0	43.5
V	25.0	16.0	2.5	1.0	44.5
VI	32.0	7.5	1.0	0.0	45.5

When the liquids form a constant-boiling mixture, they can not be separated in pure condition by fractional distillation. The boiling-point of a mixture of ethyl alcohol and water, which contains 96 per cent by weight of the former, is lower than that of pure alcohol. As a consequence, when a mixture of the two substances is subjected to repeated fractional distillation, the constant-boiling mixture is obtained. In order to prepare pure alcohol it is necessary to remove the water from the mixture by chemical means. Very few cases of this kind are met with in the purification of organic compounds.

DISTILLATION UNDER DIMINISHED PRESSURE

24. Many substances which decompose when distilled at atmospheric pressure, distil without decomposition when the pressure is reduced. This results from the fact that the temperature at which a substance boils is markedly affected by the pressure. For example, benzophenone boils at 306° at 760 mm. pressure, and at 170° at 15 mm. pressure. The effect of change in pressure on the boiling-point increases rapidly as the pressure decreases. Stearic acid, for example, boils at 291° at 100 mm., at 232° at 15 mm., and at 155° under the best vacuum obtainable with a mercury pump. A difference of 85 mm. in pressure from 100 mm. to 15 mm. causes a change in boiling-point of 59°, whereas a difference of 15 mm. from 15 mm. to 0 mm. lowers the boiling-point 77°.

Many substances which distill with partial decomposition at atmospheric pressure can be distilled unchanged at the pressure which can be obtained with a good water-pump. A convenient arrangement of the apparatus required for distillation under diminished pressure is represented by Fig. 12. A piece of glass tubing drawn out to a fine opening is attached to the right arm of the manometer, as indicated in the figure. This prevents the mercury from being forced out of the tube when the cock (*c*) is opened to admit air after the distillation has been completed.

The flask to contain the substance to be distilled is fitted with a thermometer and a tube (*a*) which is drawn out to a fine opening at one end; to the other end of the tube is attached a piece of rubber tubing carrying a screw-clamp (*b*). This tube is provided to prevent violent bumping during the distillation. By regulating the screw-clamp after the apparatus has been attached to the vacuum-pump, a rapid stream of air-bubbles can be drawn through the liquid. As the latter is heated the vapor formed passes into the bubbles, and superheating and the consequent bumping are largely avoided. The position of the tube is so adjusted that the fine opening almost touches the bottom of the flask. It is often advisable to replace the plain distilling flask, like the one shown in Fig. 12, by one of the Claissen type (Fig. 10). If the latter is used and bumping occurs, the material in the flask is not so apt to be forced over into the condenser.

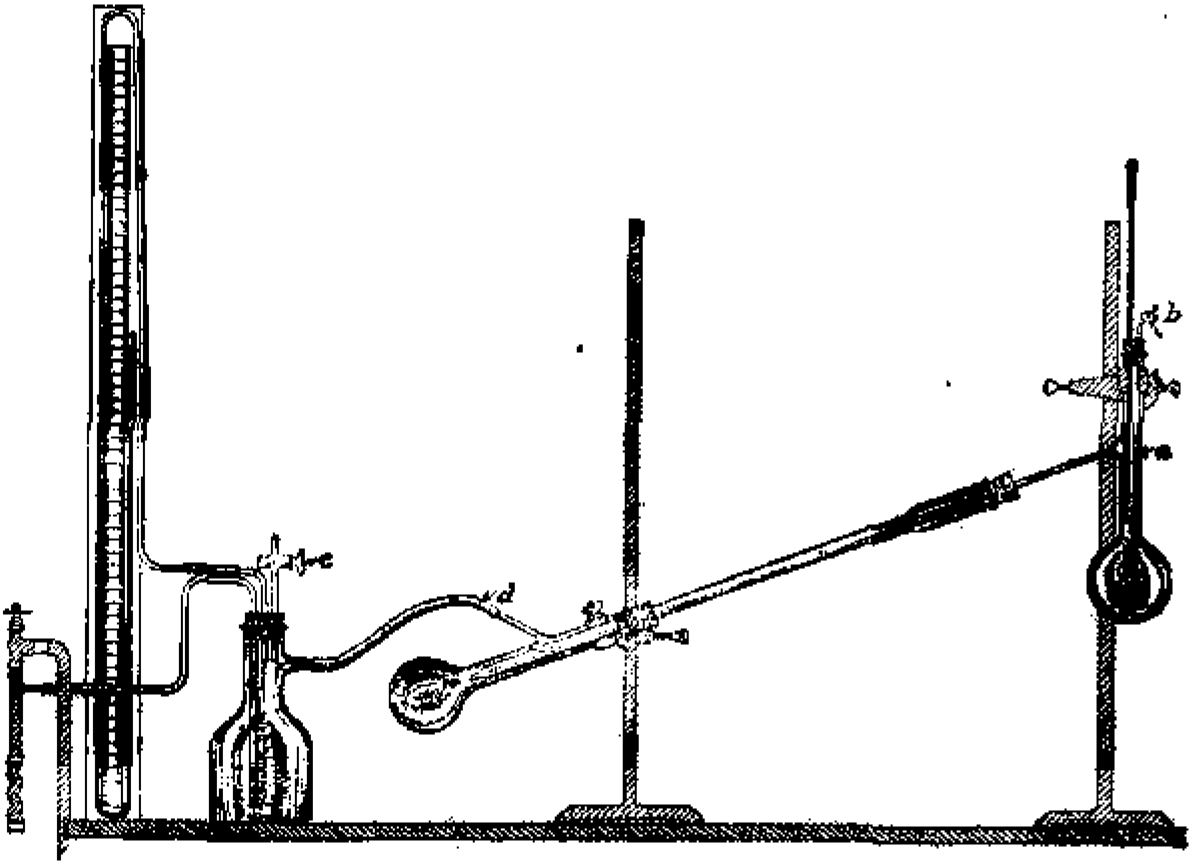


FIG. 12.

25. Other modifications of the form of the tube to admit air into the flask are often used. If the neck of the flask is small and it is impossible to insert into it both the thermometer and a glass tube of the ordinary diameter, the part of the tube which is to pass through the cork is drawn out to a capillary, and is inserted through a small hole made with a stout needle or the end of a file. One end of the tube is left with such a diameter that the rubber tubing and screw-clamp can be attached to it.

26. A second modification is often used on account of its convenience. It is illustrated in Fig. 13. A straight glass tube is selected of such a diameter that the thermometer passes into it easily. The tube is drawn out at one end to a small opening; it is then cut off at the other end at such a point that when the thermometer is placed in it and it is put into the flask, the bulb of the thermometer is in the correct position with regard to the side-arm of the flask. A piece of rubber tubing provided with a screw-clamp is attached to the upper end of the tube.

When liquids which boil at a very high temperature are distilled, it is customary not to use an air-condenser, but to connect the receiver directly with the side-arm of the flask which contains the liquid to be distilled.

In assembling the distilling apparatus, a rubber stopper may be used to attach the receiver to the condenser, provided care is taken to prevent the hot liquid from coming in contact with the rubber. Great care should be exercised in selecting the corks to be used; these should be as free as possible from holes. After the apparatus has been set up, small leaks can often be closed by painting the corks with collodion.

A convenient arrangement of the manometer and the connections between the pump and the receiver is represented in Fig. 12. A number of forms of manometers are used to register the pressure inside the apparatus. A simple form which can be readily made from a supply of mercury, a meter-stick, and a piece of glass tubing is illustrated in the figure. In order to determine the pressure in the apparatus the readings on the scale opposite the levels of the mercury in the manometer are subtracted, and this difference is subtracted from the height of the barometer.

It is necessary to insert an empty bottle between the pump and the receiver. When the apparatus has been evacuated, water may run back from the pump into the receiver as a result of a slight change in the pressure of the water caused by the opening of a cock in the neighborhood. The inserted bottle serves as a trap to catch this water. At *c* is a stop-cock through which air can be let into the apparatus. This is of value at the end of a distillation, or in case the

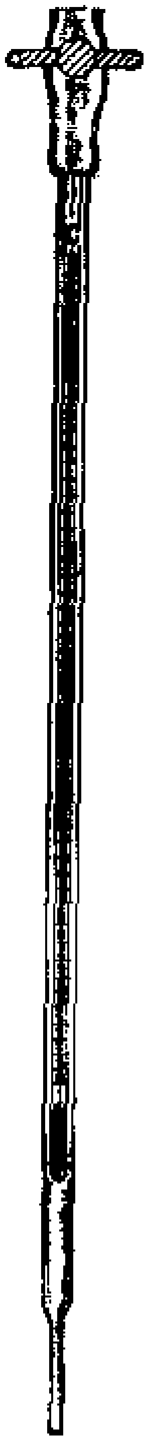


FIG. 13.

boiling liquid begins to froth or bump violently. In the latter case letting in a little air prevents the ejection of a part of the contents of the flask into the receiver.

27. Method of Distillation.—Before introducing the liquid to be distilled, the whole apparatus should be tested. The screw-clamp *b* should be closed, and the receiver connected by a heavy-walled tube to the pump. In no part of the apparatus should rubber tubing be used which collapses under diminished pressure. If no heavy tubing is available the connections can be made with glass tubing joined by ordinary rubber tubing, the ends of the glass tubes being brought together so that the connecting rubber tubes can not collapse. When the apparatus has been connected with the pump the pressure should be reduced to about 20 mm. If this can not be done, either the pump is a poor one, or the apparatus has not been well put together. The cause can be determined as follows: First, test the pump by connecting it directly with the manometer, making sure that there is not a leak in the connecting tubes. Second, disconnect the tube at *d*, and close it with a pinch-cock or glass rod. If the reduction in pressure is sufficient it will show that all the connections from the pump up to this point are tight. Next, disconnect the flask from the condenser and connect it by means of the side-arm to the pump and manometer. This will determine whether the cork provided with the thermometer and the tube to admit air is tight. It is probable that the leak will be found at this point. If everything is tight, connect the flask with the condenser, and the lower end of the latter with the pump. This will test the tightness of the joint between the flask and condenser. The apparatus is next completely adjusted, and tested again, when, if no leak has been discovered up to this point and the pressure can not be sufficiently reduced, it is evident that the connection between that condenser and receiver is at fault.

When the apparatus has been found to be tight, the product to be distilled is introduced into the flask, which should be filled to not more than one-half its capacity. The suction is applied and the screw-clamp *b* opened very slowly so that a stream of air-bubbles passes through the liquid. The flask is heated by a bath containing oil or, preferably, a low-melting alloy such as Rose's or Wood's metal. It is often better to heat the flask by means of a free flame as the amount of heat applied can be quickly regulated. When a free flame is used it should be kept in constant motion, and the surface of the liquid where it comes in contact with the flask should be heated rather than the bottom of the flask. This can be done by moving the flame around the flask and letting it come in contact with the latter at the side and not the bottom.

If frothing suddenly begins and there is a chance of the contents of the flask rushing over into the receiver, such a result can be prevented by opening the cock *c* which admits air to the apparatus.

Special forms of apparatus have been devised to fractionate a liquid by distillation under diminished pressure. It is often simpler to use the apparatus described above, and change the receiver when the limits of the fractions have been reached.

DISTILLATION WITH STEAM

28. Substances which are practically immiscible with water and have an appreciable vapor pressure at 100°, can be readily separated from those which have a very small vapor pressure at this temperature by passing steam through the mixture. The process which is of special value in separating organic compounds from tarry materials formed in their preparation, is carried out in an apparatus arranged as represented in Fig. 14.

The flask *a* is connected with a supply of steam; this can be conveniently generated in a kerosene can, which is supplied with a long glass tube reaching to the bottom of the can, to act as a safety-valve. Into the flask is put the substance to be distilled. The flask should be set up at an angle as indicated in the diagram. By placing the flask in this position any of the liquid which is violently thrown up against the flask as the result of the inrush of steam, will not be forced through the condenser into the receiver. The tube through which the steam is led should be so bent that its end almost touches the lowest point of the flask in its inclined position. By this means the steam is forced through the heavy liquid to be distilled, which is consequently kept in motion. If the liquid is not stirred up by the incoming steam distillation takes place very slowly.

29. The vapor issuing from the flask consists of a mixture of steam and the volatile substance to be distilled. When this is condensed, two layers are formed. The theory of the process is briefly as follows: When a mixture of two immiscible liquids is heated, each substance vaporizes independently of the other. When the sum of the vapor pressures of the two liquids is equal to the pressure of the atmosphere, the mixture distils. The relation between the weight of the two substances obtained is determined by their molecular weights and their vapor pressures at the temperature of distillation. The case of nitrobenzene and water is an example. When steam is passed into nitrobenzene the mixture boils at 99°, when the atmospheric pressure is 760 mm. At this temperature the pressure of water vapor is 733 mm., and of nitrobenzene 27 mm.; consequently the relation between the weight of water and that of nitrobenzene is as 18 X 733 is to 123 X 27, or approximately 4 to 1. Although the vapor pressure of nitrobenzene is small at 99°, its large molecular weight compared with that of water leads to the result that about one-fifth of the product obtained by distillation with steam consists of nitrobenzene. When the vapor pressure of a compound is as low as 10 mm. at 100°, it can be advantageously distilled with steam. Orthonitrophenol can be conveniently separated from paranitrophenol on account of the fact that the former has an

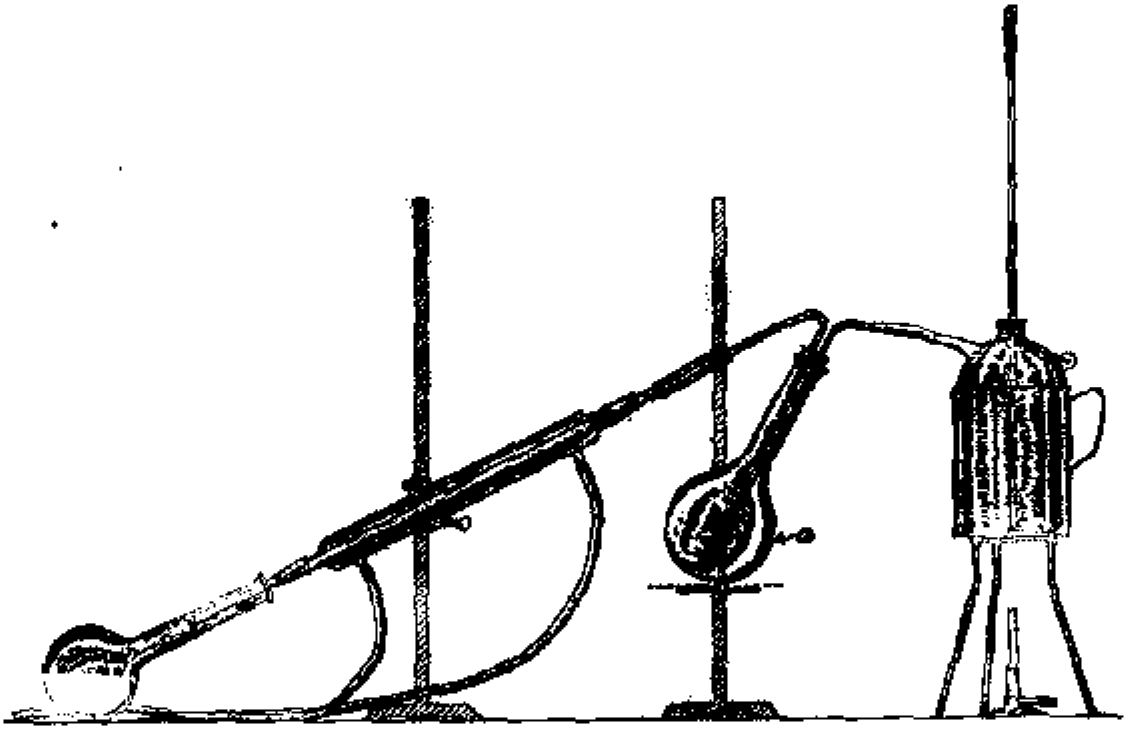


Fig. 14.

appreciable vapor pressure at 100°, and is consequently volatile with steam.

30. When the vapor pressure of a substance increases rapidly near 100°, the rate at which it distils can be markedly increased by adding to the mixture of it and water a substance soluble in water; the latter increases the boiling-point of the liquid. By saturating the water with calcium chloride a marked rise in the temperature at which distillation occurs can be effected, with the consequent increase in the vapor pressure of the organic compound undergoing distillation.

When the vapor pressure of a substance is appreciable only at a temperature considerably above the boiling-point of water, it may often be separated from less volatile compounds by distillation with superheated steam. In this case the flask containing the substance is heated in an oil-bath, and steam which has been passed through a hot coil of copper is conducted through it.

EXTRACTION

By extraction is meant the process of removing from a mixture, usually an aqueous solution, one or more substances by shaking with a liquid in which the substances to be removed are soluble. Aniline, for example, is somewhat soluble in water; when the solution is shaken with ether a large part of the aniline is removed from the water and passes into solution in the ether. As aniline can be recovered much more readily from an ethereal solution than from an aqueous solution, extraction, of such solutions is made use of in the preparation of the compound. The liquid used for extracting must be immiscible with the solution to be extracted.

31. Method of Extraction.—In extracting a solution it is shaken in a separatory funnel with a liquid in which the substance to be extracted is readily soluble. The substances commonly used for this purpose are ether, chloroform, benzene, petroleum ether or ligroin, and carbon disulphide. Ether is generally used as it is an excellent solvent for many organic compounds, and, on account of its low boiling-point, it can be readily removed. The disadvantages connected with the use of ether are its great inflammability and the fact that it is somewhat soluble in water and dissolves appreciable quantities of water. Water dissolves approximately 10 per cent of its volume of ether. When large volumes of aqueous solutions are extracted there is a loss of ether, which is an expensive substance. This loss is decreased by saturating the solution to be extracted with sodium chloride. On account of the fact that ether dissolves about 2 per cent of its volume of water, ethereal extracts have to be dried, in most cases, before the ether is removed by evaporation.

32. The relation between the volume of an aqueous solution to be extracted and the volume of the solvent used for extraction, is determined by the relative solubilities of the substances to be extracted in water and the solvent used. If an aqueous solution of a substance is extracted with ether, the amounts of the substances found in the two liquids will be proportional to the solubilities in the two solvents and to the amounts of the latter. If the substance is equally soluble in water and in ether, and the volumes of the two liquids are the same, after extraction one-half of the substance will be found in the ether. If the substance is twice as soluble in ether as in water, the relation of the amount present in the ether will be to that present in the water as two is to one, that is, two-thirds will be present in the ether and only one-third in the water. By shaking the aqueous solution with a second portion of ether, two-thirds of the substance present, that is two-thirds of one-third, or two-ninths, of the original amount will be removed and one-ninth will remain dissolved in the water. After three extractions but one twenty-seventh of the substance will remain dissolved in the water.

In the above example a certain volume of a solution was extracted three times, using each time a volume of ether equal to that of the aqueous solution. The result would have been different if the solution had been extracted with the three volumes of ether in one operation. In this case the substances would have been divided between the ether and the water in the ratio of $3 \times 2:1$; that is, one-seventh would have remained dissolved in the water. As the result of extracting the solution with the same volume of ether in three operations using one-third of the solution each time, but one twenty-seventh remains dissolved in the water. It is evident, therefore, that the most efficient way to extract a substance is to shake the solution a number of times with small amounts of the extracting agent.

33. The relation between the volumes of the extracting liquid and of the solution, and the number of times the solution should be extracted, vary widely with the relative solubility of the substance to be extracted. In general, in the case of a substance which is much more soluble in ether than in water, three extractions will be sufficient if a volume of ether equal to about one-fourth of that of the aqueous solution is used. In order to determine whether the extraction has been carried far enough, a sample of the last ethereal extract should be evaporated on a watch-glass on a steam-bath. The amount of the residue will determine whether a fourth extraction is desirable.

If a large volume of liquid is to be extracted, a separatory funnel of appropriate size is not available, the liquid can be placed in a flask and shaken with ether; the major part of the latter can be decanted off, and the rest separated in a small separatory funnel.

34. Separation of the Extracted Substance.—If the substance is a solid, and a small amount of the extracting liquid has been used, the solution can be evaporated to dryness and the residue crystallized. If it is desired to recover the ether or other solvent used in the extraction, the solution should be placed in a flask and the solvent distilled off on a water-bath as described below. When the substance to be obtained from the solution is a liquid which is to be finally distilled, it is necessary to dry the extract before the removal of the solvent. The drying agent must be selected according to the principles stated in §36, page 25. If ether has been used, the solution should not be set aside to dry in a thin-walled flask which has been stoppered; sufficient heat is at times generated as the result of the union of the water and the drying agent to break the flask. A bottle or distilling flask should be used. It is not advisable to place the extract in a beaker or other open vessel, as the solvent will be lost if the solution stands for some time.

When the solution is dry, the solvent can be removed by distillation. If ether or any other very volatile and inflammable liquid is used, the flask containing the solvent should be heated on a water-bath, and should be provided with a long water-jacketed condenser and a special form of receiver. This is made by attaching to the condenser, by means of a tightly fitting stopper, an adapter, which, in turn, is attached in the same way to a filter-bottle. The side-arm of the latter is provided with a rubber tube of such length that it reaches nearly to the floor. By taking these precautions accidents caused by fires are prevented, as the only way in which ether vapor can escape from the apparatus is through the rubber tube; as ether vapor is very heavy and as any which escapes is delivered at the level of the floor, there is little chance of its being ignited by any flames on the laboratory desks. The receiver should be dry in order that the ether which distils over may be used in transferring the residue after the distillation to a flask of appropriate size for the final distillation.

The dry ethereal extract is decanted, or, better, filtered from the drying agent into the distilling flask, great care being taken to prevent any heavy aqueous layer from getting into the flask. Such a layer is frequently formed when potassium hydroxide is used as a drying agent; the compound extracts water from the ether and forms a saturated aqueous solution. The flask is next tightly corked, attached to the condenser and receiver, and the ether distilled off on a water-bath. When all the ether has evaporated the residue is poured into a flask of appropriate size for distillation. As an appreciable amount of the substance adheres to the larger flask from which the ethereal extract was distilled, it should be washed out twice with a few cubic centimeters of the ether which have been distilled off, and these washings added to the flask from which the final distillation is to be made. In this distillation the flask should be heated slowly at first until the small amount of ether has been driven out. The final distillation should be made as described in §15.

35. Sublimation.—This process is of special value when it is desired to separate a solid which is volatile from substances which do not vaporize readily. It generally yields a very pure substance, but it often leads to loss.

The process is most easily carried out between two watch-glasses which fit closely. The substance which has been carefully dried is placed in one of the glasses. This is covered with a piece of filter-paper, in which a few small holes have been cut to allow the passage of the vapor. The second glass, placed in an inverted position, is fastened to the first by means of a specially constructed clamp. The apparatus is heated slowly on a sand-bath and the upper watch-glass is cooled by putting on it pieces of filter-paper which are kept moist with cold water. It is necessary to keep the upper watch-glass at a temperature lower than the melting-point of the substance to be sublimed.

36. Drying Agents.—Many organic substances are prepared in water solution or in their preparation are washed with water to remove soluble impurities. In this case it is necessary to dry them, if they are liquids, before they are distilled. It is necessary to select as a drying agent a substance which does not react with the compound to be freed from water. The substance generally employed is anhydrous calcium chloride, which is commonly used in a granular form; for many purposes the chloride which has been fused in the form of sticks is preferable. Calcium chloride forms addition-products with hydroxyl compounds and should not be used as a drying agent for alcohols, phenols, etc.

Alcohols are commonly dried with quicklime. Water is usually removed from basic substances by treating them with solid potassium hydroxide. Anhydrous copper sulphate is an excellent drying agent for most substances; another salt, anhydrous sodium sulphate, is frequently used. It must be remembered in the latter case that hydrated sodium sulphate loses its water of crystallization at 33°; it is evident that the salt acts as a drying agent only below this temperature.

The most powerful drying agents are sodium and phosphorus pentoxide. The use of the former is evidently limited to those substances which do not react with the metal. Sodium is used to remove the last traces of water only, the substances being previously dried with calcium chloride which removes most of the water.

37. The drying agent should remain in contact with the substances to be dried for from 2 to 3 hours, if the two are left in contact at room temperature. If convenient, the mixture should be set aside over night.

Whether the drying agent should be removed from the substance before it is distilled, is determined by the boiling-point of the substance and the stability of the compound formed between the water and drying agent. It is advisable, however, except in the case of substances which boil below 80°, to remove the drying agent before distillation.

The last traces of water may be removed from liquids which boil above 200° by drawing a current of air through them while they are gently heated.

38. Use of the Reflux Condenser.—It is often necessary to heat together two or more substances for a number of hours. If all the substances boil above the room temperature an open vessel provided with a reflux condenser is used. The arrangement of the apparatus is shown in Figs. 15 and 16.

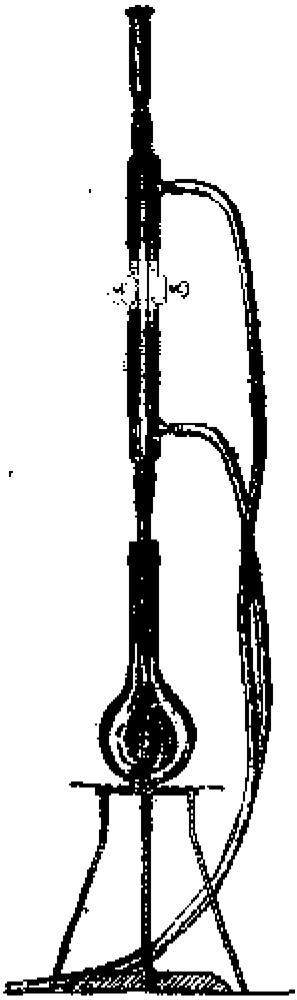


FIG. 15.

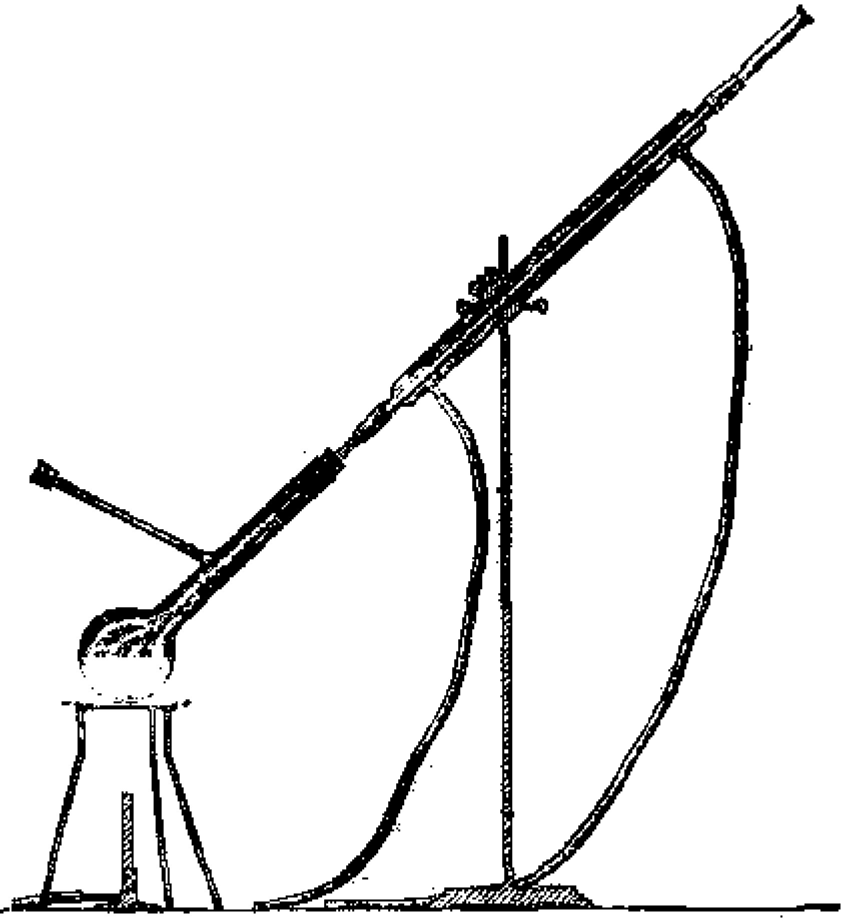


FIG. 16.

If it is desired to distil the product formed directly from the flask, the arrangement represented in Fig. 16 may be used. In this case the side-arm of the distilling flask is covered with a cork into which a hole has been bored half through its length. The side-arm is so placed that the liquid which condenses in it returns to the flask. Heating with a reflux condenser is usually carried out in a round-bottomed flask as shown in Fig. 15. If the contents are apt to boil with bumping the flask is usually heated on a sand-bath; otherwise a free flame and a wire gauze are used. If the liquid boils above 150° an air-condenser is used instead of a condenser provided with a water-jacket.

When it is necessary to heat with a reflux condenser substances which destroy cork and rubber, a simple device can be used which is represented in Fig. 17. A test-tube is selected which fits loosely into a long-necked, round-bottomed flask. The tube is supplied with a rubber stopper and tubes as shown in the drawing. Water is passed through the tube, which is supported in the neck of the flask by means of a clamp. Such an arrangement can be used conveniently instead of that represented in Fig. 15.

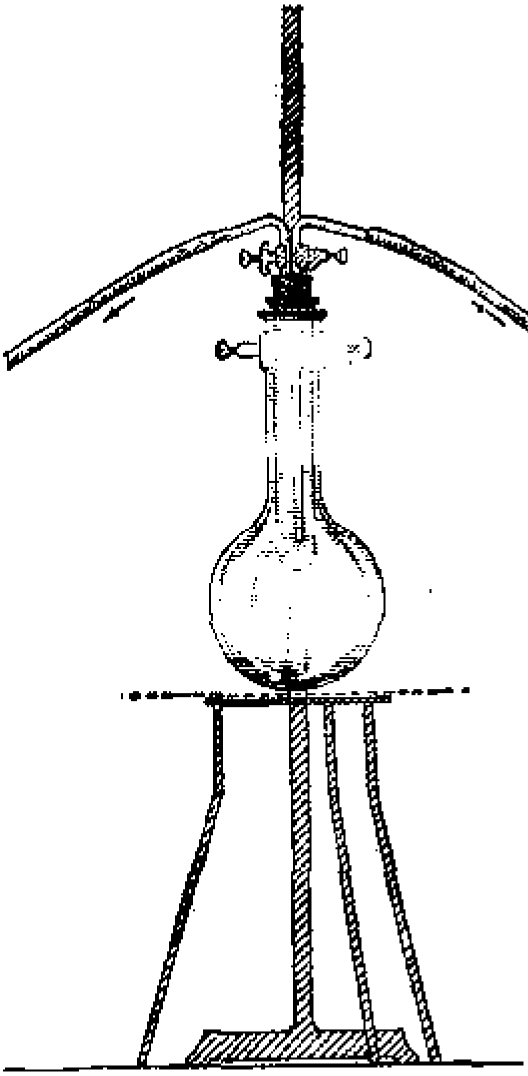


FIG. 17.

A test-tube fitted in this way can be used with a distilling flask, if it is desired to distill from the same flask after refluxing.

In many syntheses hydrogen chloride or bromide is given off. It is inadvisable to let these gases get into the room even when the apparatus is placed under a hood. The top of the condenser should be provided with a tube bent at two right angles. This tube should reach to within about 1 inch of the surface of water contained in a flask supported by a ring-clamp to the stand to which the condenser is attached. If it is necessary to keep the contents of the flask dry during the reaction, a straight drying tube containing calcium chloride should be inserted between the condenser and the flask containing the water.

39. Prevention of Bumping.—When a substance boils irregularly and "bumps," even boiling can often be obtained by placing in the vessel a few pieces broken from a porous plate. The so-called capillary boiling-tubes are also valuable. They can be made by drawing out pieces of glass tubing to stout capillary tubes; these are cut off at such a length that they will reach from the bottom of the flask to well into the neck. They are next put into the flame and melted at such a point that the tube fuses together at about 0.5 cm. from one end. When this end is placed under a liquid the small cavity is filled with air, and as the liquid boils bubbles of vapor are formed at the end of the tube and even boiling results. If the liquid cools below its boiling-point after it has been heated some time, the cavity at the end of the boiling-tube becomes filled with liquid as the result of the condensation of the vapor. In this case the tube must be withdrawn and the drop of liquid shaken from it, or a new tube must be inserted.

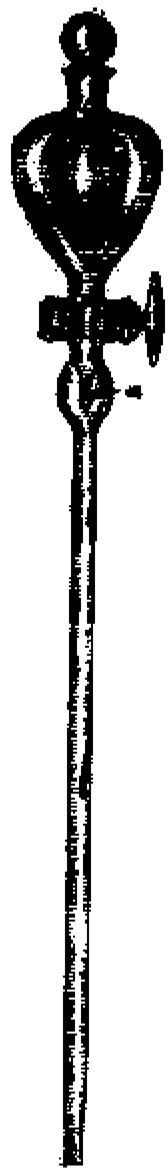


FIG. 18.

40. Dropping Funnels.—A dropping funnel like that shown in Fig. 18 is very useful. With a funnel of this type it is possible to observe at the point marked *a* the number of drops which pass through the funnel. If such a funnel is not available one can be made from an ordinary separatory funnel by attaching to its end a short calcium chloride drying tube as shown in Fig. 19, and connecting the latter by means of a glass tube to the apparatus to be used.

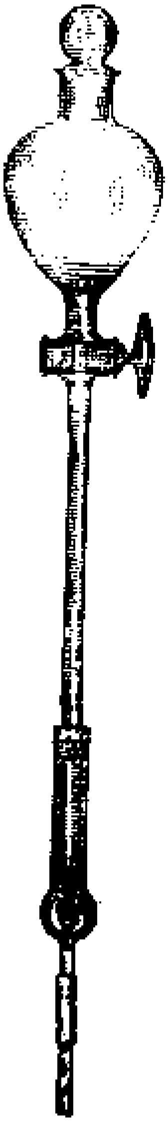


FIG. 19.

41. Manipulation of Sodium.—Sodium is used in the preparation of a large number of organic compounds. As the metal reacts rapidly with oxygen and with water-vapor, it should not be allowed to stay in contact with the air any longer than is necessary. When sodium is to be cut with a knife or pressed into a wire, the coating which covers the metal should be first carefully removed and rejected; and the sodium should be placed immediately under dry ether, if it is not to be used at once. In many preparations in which sodium is used a part of the metal is left unchanged at the end of the experiment. Great care must be exercised in getting rid of the residue. It should not be left in an unlabeled flask or bottle. Under no circumstances should the product be allowed to come into contact with water. Small quantities of alcohol should be added from time to time to the sodium, until enough of the liquid is present to dissolve the residue, or to make with it a thin paste. This mixture should then be poured slowly into water, in order to prevent an accident in case any sodium is enclosed within a mass of inert solid. When sodium is used in a preparation, great care should be taken to prevent water entering the vessel containing the metal, either as the result of using a poorly fitting cork or a defective condenser.

THE MANIPULATION OF SMALL QUANTITIES OF SUBSTANCES

In the identification of organic compounds it is generally necessary to transform them into other compounds, the properties of which are determined as an aid in the identification. It often happens that but a few grams of a substance are available for the purpose. The successful handling of such small quantities requires careful work, and the student should have opportunity to learn the special technique required.

42. Crystallization.—In the purification of small quantities of substances by crystallization a solvent should be selected in which the substance is more or less difficultly soluble, and care should be taken to avoid an excess of the solvent. It is best not to add enough of the solvent to dissolve the substance completely, even at the boiling temperature. The hot solution should be rapidly filtered. This can be done best under diminished pressure. A filter-bottle is selected of such a size that it will hold a 6-inch test-tube and permit a funnel being placed in the neck of the bottle in the usual way. The funnel is fitted with a perforated plate and a circular piece of filter-paper which is cut with a diameter about 8 mm. greater than the plate. The paper is put in place and pressed down so that it covers the joint between the plate and the funnel. A little of the liquid is poured through the funnel and the suction applied. This serves to set the paper firmly in place.

The liquid is poured out of the test-tube, which is then replaced in the bottle. The funnel is put in place and the solution to be filtered is poured into it. Under the diminished pressure, the solution filters rapidly before the compound in solution can crystallize out. The method of filtration described in §10, page 6, is also to be recommended.

43. A filter-bottle provided with a perforated plate and test-tube is used to separate crystals from the mother-liquor containing them. While connected with the suction-pump the mixture of crystals and mother-liquor is poured slowly down a glass rod onto the filter-paper. If a very small amount of crystals is to be separated, care should be taken to collect them in a single spot and not to spread them out over the entire plate. In this way the crystals can be collected in a small mound, a few millimeters in diameter, which can be readily removed from the paper when dry. The crystals should be washed as directed in §12, page 7.

44. Distillation of Small Amounts of Liquids.—The liquid should be distilled from a 5-cc. distilling flask. If this is not available the neck of a broken distilling flask can be converted into a serviceable piece of apparatus for this purpose by sealing it at a point about 5 cm. from the side-tube. In distilling with small flasks an asbestos shield as described in §18, page 10, and a very small flame should always be used; a short thermometer reduces the error arising from stem-exposure.

The boiling-point of 1 cc. of liquid can be determined in this way. In heating the substance, the flame should be applied, at first, in such a way that the vapor condenses in the flask just before it reaches the side-tube. In this way the thermometer is heated up to the temperature of the vapor before the latter is driven over. If the distillation is carried on rapidly the small amount of liquid will have distilled over before the thermometer has been heated up to the temperature of the vapor. For a method of determining the boiling-point of very small quantities of a liquid see Smith and Menzies, *J. Am. Chem. Soc.,* **33**, 897.

45. If it is necessary to distil fractionally a small amount of liquid, a flask should be selected the side-arm of which is as far away from the bulb as possible (see Fig. 4, page 11). Such a flask can be furnished with an efficient fractionating column as follows: Glass beads which pass snugly into the neck of the flask are tied to the end of a cotton thread, or if necessary a fine platinum wire. After the liquid had been introduced, the beads are hung at the bottom of the neck of the flask, which is then filled with more beads, just enough room being left for the thermometer. A column of beads only a few centimeters high is remarkably efficient in bringing about the separation of liquids of different boiling-points through distillation (see Fig. 5, page 11).

46. Extraction of Small Amounts of Substances.—When a small amount of substance is to be extracted the solution is shaken with about an equal volume of ether or other solvent in a test-tube. To separate the two liquids the upper layer is drawn into a pipette. In order to be able to see clearly the position of the end of the pipette, a long rubber tube is connected with it so that the test-tube may be held at the level of the eye while the liquid is being drawn up.

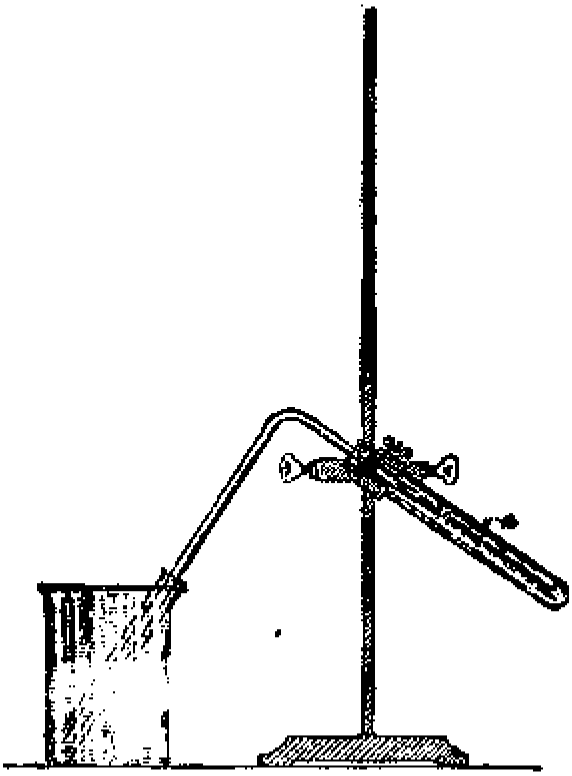


FIG. 20.

If a number of extractions are to be made a simple apparatus which can be made readily is of value. This consists of a test-tube with a side-arm placed at a point slightly above the middle of the tube. The tube is filled with the liquid to be extracted up to the side-arm, which is closed by the end of the forefinger. Ether is added, the tube closed with the thumb, and the mixture shaken. A vessel to hold the ether is placed under the side-arm; when the finger and thumb are removed the ether runs out of the tube.

47. Preparation of Liquids on the Small Scale.—It is often necessary to prepare small amounts of liquids, which are obtained as the result of heating together two or more substances, and subsequent distillation. An example is the preparation of ethyl iodide by heating alcohol and hydriodic acid. A simplified form of apparatus for such work is shown in Fig. 20.

The test-tube *a* is supported by a clamp; the test-tube which serves as a condenser is surrounded by cold water contained in a beaker. It is important that the tube from *a* should extend nearly to the bottom of the condenser, in order that any vapor which passes over may come in contact with the walls of the tube, which are cooled by the water in the beaker. In using an apparatus like this, the distillation should be made very slowly.

DETERMINATION OF PHYSICAL PROPERTIES

48. Calibration of Thermometers.—The thermometers provided for use in determining the physical properties of organic compounds are usually far from accurate. If very exact measurements are to be made, a high-grade thermometer should be calibrated according to the methods described in books dealing with physical measurements. For students' work in organic chemistry, a cheap thermometer may be used provided it is calibrated with reasonable care. A thermometer which is accurate to within 0.5° is satisfactory.

Although most thermometers register correctly at 0° and 100°, it is well to make a calibration at these points. To determine the reading at 0°, a beaker of 100 cc. capacity is filled with finely chopped ice, and water is added until it reaches to within about 2 cm. of the surface of the ice. The thermometer is inserted into the ice and water until the zero point is just above the surface, so it can be seen. The reading on the thermometer is noted when the mercury no longer falls. Care should be taken to have the eye at the height of the top of the mercury column to avoid parallax.

To calibrate the thermometer at higher temperatures it must be heated in such a way that the entire mercury thread is exposed to the vapor of a boiling liquid. This can be conveniently done as follows: Attach to an 8-inch test-tube by means of a closely fitting cork (not a rubber stopper) a short air-condenser. Place in the tube about 10 cc. of water and support the tube and condenser by means of a clamp over a wire gauze. Attach a cotton thread to the thermometer, and lower it through the condenser until the bulb is about 4 inches above the liquid. The thermometer is held in place by tying the upper end of the thread around a small piece of glass rod, which is then placed across the end of the condenser. The water is boiled, and when the entire thermometer is in the vapor, the position of the mercury is noted.

The thermometer should be calibrated at higher temperatures by determining the boiling-points of other liquids in the apparatus described above. The latter should be thoroughly dried and a fresh cork used to avoid the presence of water. The substances which can be used conveniently are aniline, naphthalene, and benzophenone. The boiling-points of these substances at 760 mm. pressure are, respectively, 183.7°, 218.1° and 306.1°. These are the temperatures recorded when the entire thread of mercury in the thermometer is exposed to the vapor of the boiling liquid. The barometric pressure should be noted and a correction made of 0.1° for each 2.7 mm. of pressure; if the observed pressure is less than 760 mm. the correction should be added, and if greater it should be subtracted. The substances used should be pure; the aniline must be redistilled, and the first part of the distillate rejected, in order to free it from the small amount of water that it usually contains. The thermometer should be marked with a number, and the corrections to be applied recorded in the notebook.

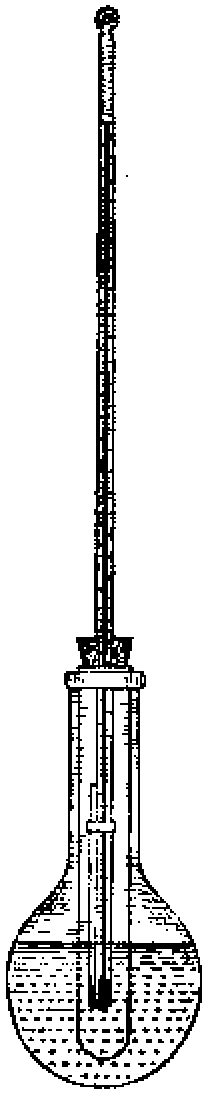


FIG. 21.

49. Determination of Melting-points.—A form of apparatus which can be conveniently used to determine melting-points is represented by Fig. 21. It consists of a 100-cc. round-bottomed flask and a test-tube which fits loosely into the neck of the flask. A thermometer is supported in the test-tube by a cork in which a slit has been cut so that the graduations of the former are visible. The flask and test-tube are filled with pure concentrated sulphuric acid to the heights indicated in the drawing. If the sulphuric acid becomes brown as the result of the introduction of traces of organic matter, a tiny piece of a crystal of potassium nitrate will destroy the color.

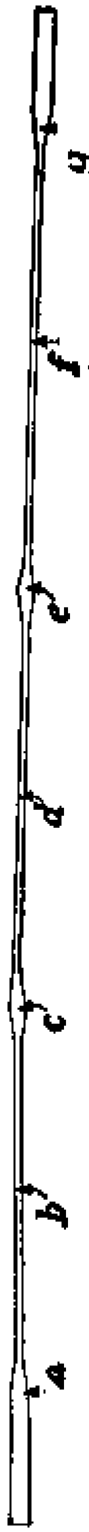


Fig. 22.

The substance, the melting-point of which is to be determined, is dried, usually in the air, and is powdered by rubbing it with a spatula on a clean, porous tile. It is then placed in a small capillary tube which has an internal diameter of about 1 mm.

50. Tubes for the determination of melting-points are conveniently made as follows: A piece of glass tubing of 5 mm. internal diameter is softened by rotating it in a flame; it is removed from the flame and after 2 seconds is slowly drawn out so that the tube is elongated about 10 cm., and the tube formed has at its narrowest point an external diameter of about 1.5 mm. The tube is again heated and drawn out. The process is repeated until the tube is of such a length it can not be conveniently handled. The appearance of the tube so prepared is represented by Fig. 22.

The distance from *a* to *c* should be about 15 cm. The tube is cut at *a*, *c*, *e*, etc. These pieces are then cut in the middle at *b*, *d*, etc., and each piece sealed at these points by holding in a flame. A number of tubes should be prepared at one time. In order to avoid getting dust into the tubes, they should be kept in a test-tube provided with a cork, or should be placed in a small beaker with the open ends downward.

The substance to be melted is placed in a tube. This can be done readily by pressing a little of the substance into the open end of the tube with the aid of a spatula, grasping the tube by the closed end, and drawing a file lightly over it. The vibrations produced in this way cause the powder to fall in the tube. The process is repeated until a layer of the substance from 0.5 to 1 cm. thick has been formed.

The tube is attached to the thermometer by means of a rubber band which is made by cutting off a piece of tubing about 2 mm. in length from a rubber tube of such a diameter that it fits the thermometer snugly when drawn over it. This band should be placed at least 2 cm. above the surface of the acid.

51. In making a preliminary determination of an unknown melting-point, the flask is heated cautiously with a free flame in such a way that the thermometer rises at the rate of about ten degrees per minute. The temperature should be noted at which the substance first shows signs of melting and when it has completely liquefied. As the thermometer is rapidly rising, this result serves only as a guide for the determination of the melting-point. When the apparatus has cooled to a number of degrees below the temperature at which signs of melting were evident, a new tube containing another sample of the substance is introduced into the apparatus and the melting-point redetermined. All melting-point determinations should be made with samples which have not been melted. If the thermometer is at a high temperature when it is removed from the bath, it should not be cooled by placing it in cold water; if this is done the glass is apt to crack. The tube is heated rapidly until the temperature is at least ten degrees below that at which the substance melts. The flame should be removed and the temperature allowed to rise slowly. When the thermometer ceases to rise the flask should be heated cautiously so that when the flame is removed the temperature does not rise more than one degree. In the case of a substance which melts without decomposition, the temperature should be allowed to rise at the rate of about two degrees per minute for the last five degrees. An endeavor should be made to have such control of the bath that the thermometer can be forced up a degree at a time. The heating is continued until the substance completely runs down the tube as a liquid. The point at which this occurs and that at which the substance begins to form in droplets should be recorded as the melting-point of the sample studied. If these are separated by more than one degree, the substance is more or less impure. If the substance shows signs of contracting or softening before it begins to melt, the fact should be noted as it is an indication that it is impure.

The determination of the melting-point should be repeated, and great care taken to allow the temperature to rise very slowly when the substance begins to melt. It may happen that the substance melts within one degree, but that it appears to melt over a considerable range of temperature on account of the fact that the heat has been applied so rapidly that the thermometer rises a number of degrees during the time required to melt the substance.

When a substance appears to be pure and gives a sharp melting-point, a number of determinations should be made. If these give the same result, the melting-point as determined may be considered to be the correct one.

If a substance does not melt sharply it should be recrystallized, and a second determination made. As a result of the purification the melting-point obtained will probably be higher than before. The process is repeated as long as the melting-point rises.

52. The melting-point determined as indicated is below the true melting-point of the substance on account of the fact that only part of the mercury is heated to the temperature of the melting substance. A close approximation of the true melting-point can be found by applying the correction which is found by substituting in the formula $N(t - t')\ 0.000154$, in which N is the number of degrees of mercury not heated directly by the acid in the bath, t the observed temperature and t' the average temperature of the stem outside the bath. The correction, which is added to the observed temperature, is, in the case of a bath like that described, and when the usual form of thermometer which registers up to 360° is used, about 1° at 100°, about 2° at 140°, 3° at 170°, and 6° at 220°.

53. Determination of Boiling-points.—The determination of the boiling-point of a substance is made during the final distillation in its purification. If 20 or more grams are distilled, the boiling-point as determined in the apparatus described above under distillation, may be considered to be correct. Care must be taken, however, not to distil all of the liquid, as when this is done the vapor toward the end of the distillation becomes superheated, and the thermometer does not register the true boiling-point of the liquid.

54. If but a small amount of the substance has been prepared, or the boiling-point of a small sample of an organic compound is desired, the determination is best made in the manner described below, which largely prevents superheating. About 10 cc. of the liquid is placed in a 15-cc. flask provided with a thermometer the bulb of which is placed just below the side-tube. The flask is supported on an asbestos board in which has been carefully cut by means of a sharp cork-borer of brass, a hole about 2 cm. in diameter. The bottom of the flask should fit the hole tightly so that the hot gases from the flame can not come in contact with the upper part of the flask.

On account of the smallness of the flask, a large part of the thermometer is not heated to the temperature of the vapor and a correction should be made for stem exposure as described above under the determination of melting-points. In order to determine the mean temperature of the stem, a second thermometer should be attached by means of rubber bands to the one used to indicate the temperature of the vapors in the flask. The bulb of the second thermometer should be placed at a point half way below the upper end of the first thermometer and the cork.

The condenser to be used is determined by the boiling-point of the liquid (see §20, page 11). The flask should be heated by a free flame of such a size that when it comes in contact with the lower part of the flask it furnishes sufficient heat to keep the liquid boiling at such a rate that about 0.5 cc. distils per minute. The distillation should be stopped when the level of the liquid is just below that of the asbestos-board that supports the flask.

If a very accurate determination of a boiling-point is to be made, the substance should be distilled from a tube of such a length that the thermometer can be heated by the vapor up to the point where the top of the mercury column stands when the substance is boiling. When determined in this way no correction for stem exposure is necessary.

55. As the boiling-point varies with the pressure, in recording accurately determined boiling-points, both the pressure and the temperature are stated. When the determination is made at a pressure within 40 mm. of the normal pressure, 760 mm., a correction can be applied to the observed reading to reduce the boiling-point to that of the substance at the normal pressure. This correction is 0.1° for each 2.7 mm. pressure. If the observed pressure is less than 760 mm., the correction should be added; if greater, it should be subtracted. It is evident that this correction should not be applied if the substance does not boil sharply and if every precaution has not been taken to have a pure substance and to eliminate the errors which commonly are present in a boiling-point determination made in the ordinary way.

56. Determination of Specific Gravity.—The determination of specific gravity is often made in the identification of organic compounds. For this purpose results accurate to two units in the third decimal place are sufficient; these may be obtained by using as little as 1 cc. of a liquid. A convenient form of apparatus for the determination is described by Mulliken.[1] It consists of a 1-cc. pipette and a glass tube, closed at one end, into which the former passes freely (see Fig. 23).

When the apparatus is weighed, it is stood on the pan of an analytical balance and the loop of wire is placed over the hook which supports the scale-pan. The apparatus is calibrated as follows: The pipette and tube are cleaned, dried, and weighed. The pipette is next filled to the mark with distilled water, the temperature of which is noted; any liquid adhering to the outside of the pipette is removed. The pipette is put into the tube and the water allowed to flow out into the latter. The apparatus is weighed again. The increase in weight is the weight of water, at the observed temperature, which fills the pipette. In determining the specific gravity of a substance the pipette is filled with it as before and weighed, and the temperature of the liquid is noted. The specific gravity is obtained by dividing the weight of the substance by the weight of the water. The result obtained is the specific gravity at the temperature at which the substance was weighed, compared with water at the temperature at which it was weighed. As it is customary to refer specific gravities to water at 4°, the volume of the pipette should be calculated for the weight of water which it contains. In the following table are given the weights of 1 cc. of water at temperatures from 14° to 30°.

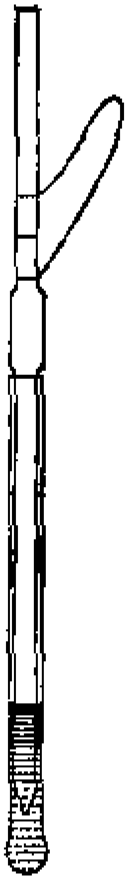


FIG. 23.

Temp.		Temp.		Temp.	
14°	0.9993	20°	0.9982	26°	0.9968
16°	0.9989	22°	0.9977	28°	0.9963
18°	0.9986	24°	0.9973	30°	0.9957

The volume of the pipette may be determined by dividing the weight of the water by the weight of 1 cc. of water at the temperature at which the water was weighed.

In calculating the specific gravity of a substance the weight observed is divided by the volume of the pipette; the result is the specific gravity of the substance at the observed temperature compared with water at 4°. If the number determined in this

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[1] Identification of Pure Organic Compounds, Vol. I.

way for a substance weighed at 18° was found to be 1.365, the result would be expressed as 1.365 18°/4°.

If a number of determinations of specific gravity are to be made, it is advisable to calibrate the pipette to hold 1 cc. If this is done the observed weight of the substance which fills the pipette is its specific gravity referred to water at 4°.

THE QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

57. Test for Metallic Elements.—About 0.1 gram of the substance is heated in a clean, dry, porcelain crucible. If it burns with a flame or leaves a residue of carbon it is probably organic. If the residue is black it should be heated until all the carbon has burned off. If the original substance contained a metal there will be left in the crucible after ignition either a metal, an oxide, or a carbonate. This residue should be identified by the methods of inorganic qualitative analysis. Organic compounds which leave residues on ignition are usually metallic salts of acids.

If it is reasonably certain that the substance does not contain a metal which is readily reduced by carbon, the ignition can be made on a platinum foil.

If there is doubt as to whether the compound is organic, a sample of it can be heated in a hard glass tube with powdered copper oxide, and the evolved gas tested for carbon dioxide. If the substance is volatile it is necessary to place a mixture of it and copper oxide in the bottom of the tube and then add enough of the oxide to make a layer at least 5 cm. thick. The tube is carefully heated, beginning at the point farthest from the bottom of the tube.

58. Test for Non-metallic Elements.—The substance to be analyzed is first decomposed by heating it with metallic sodium, and the resulting mixture, which may contain the following compounds of sodium, is analyzed: chloride, bromide, iodide, phosphide, sulphide, cyanide, and sulphocyanide. The decomposition is accomplished as follows: A clean, dry 6-inch test-tube is supported near the open end in a vertical position by means of a clamp and iron stand. A piece of sodium equal in size to a cube 3 mm. on each edge is cut and wiped free from oil by means of a filter paper. Any deposit on the sodium should be rejected, and the piece selected should have clean freshly cut surfaces on all sides. The test-tube is warmed, and the sodium dropped in. The burner is placed directly under the tube which is heated until a layer of the sodium vapor about 1 cm. thick is formed. The substance to bo analyzed is now dropped into the tube, care being taken to have it fall directly onto the hot sodium without coming into contact with the tube. If the substance is a liquid, about 3 drops should be used. If it is a solid, a little should be taken up on the end of a pen-knife or spatula and dropped into the tube; a second portion should then be added. The flame is removed immediately, and when the tube is cold, the lower end of it should be broken off by tapping the tube with a pestle in a clean, dry mortar. If, during the heating, some of the undecomposed substance has settled on the upper part of the tube, this part should be rejected; only the very end which contained the sodium vapor should be used. About 2 cc. of alcohol is then added to react with any excess of sodium present. When the metal has ceased acting, the contents of the mortar are ground with 20 cc. of distilled water, transferred to a small beaker, heated to boiling, and filtered. If the decomposition has been satisfactorily accomplished a colorless solution is obtained. If this is not the case, a second fusion with sodium should be made, and great care taken to introduce the substance directly into the sodium vapor.

Separate portions of the filtrate are tested for non-metallic elements as follows:

Test for Sulphur.—Add to about 2 cc. of a dilute solution of sodium hydroxide 2 or 3 drops of a solution of lead acetate. To the resulting mixture add about 5 cc. of the filtrate obtained as described above. If sulphur is present, black lead sulphide will be formed. If but a small amount of sulphur is present, a yellow color may be produced without the formation of a precipitate. If this is the case, filter the solution after a few minutes, and examine the paper for a precipitate of lead sulphide.

59. Test for Nitrogen.—Boil for a minute about 2 cc. of the solution from the fusion with 5 drops of a 10 per cent solution of sodium hydroxide and 5 drops of a solution of ferrous sulphate. Cool, and add dilute hydrochloric acid drop by drop, until the solution becomes acid and the precipitate of ferrous hydroxide has dissolved. An excess should be avoided as the inaction which lakes place if nitrogen is present—the formation of ferric ferrocyanide—is more delicate in the absence of an excess of acid. If a large amount of acid appears to be necessary, it is evident that the original fusion did not completely destroy the organic compound.

If a blue or green color does not develop on adding the acid, a drop of ferric chloride should be added to the tube. It often happens that enough ferric ferrocyanide is not formed to produce the characteristic blue precipitate; the formation of a clear green solution is ample proof of the presence of nitrogen. Such a solution usually deposits a blue precipitate on standing.

60. Test for Halogens.—A preliminary test for halogen should be made with some of the original substance. The so-called Beilstein test is made as follows: A piece of stout copper wire is bent around the end of a lead pencil to make a small loop at one end. This end is then heated in a Bunsen flame until it no longer imparts a color to the flame. The wire is allowed to cool, and the clean end is inserted into the substance to be tested if it is a liquid, or a bit of it, if solid, is supported in the loop on the wire. It is then put into the flame. If a halogen is present a green color is imparted to the flame. The test should be repeated a number of times in order to have the conclusion definite. A few nitrogen compounds give a green flame when tested in this way.

If a halogen is found to be present the solution obtained from the decomposition with sodium should be tested.

If sulphur and nitrogen have been found to be absent, about 1 cc. of the solution is acidified with nitric acid, and silver nitrate is added. The color of the precipitate formed is an indication of the halogen present, provided but one is present. If the presence of bromine or iodine is suspected, a second portion of the original solution is acidified, and about 2 cc. of carbon disulphide is added; chlorine water or a solution of sodium hypochlorite is then added, drop by drop. If either sulphur or nitrogen is present, it is necessary to boil the original solution for several minutes with a few drops of dilute sulphuric acid to remove hydrogen sulphide and hydrocyanic acid before the teats for the halogens are applied.

61. Test for Phosphorus.—One cubic centimeter of the original solution from the fusion is boiled for 1 minute with 3 cc. of concentrated nitric acid. This treatment oxidizes the sodium phosphide to sodium phosphate. The presence of the latter is tested for by adding to the cooled solution twice its volume of ammonium molybdate reagent. The tube is heated to such a temperature that it can just be held in the hand, and is then set aside. The formation of a yellow precipitate indicates phosphorus, provided arsenic is not present.

CHAPTER II

GENERAL PROCESSES: HYDROCARBONS OF THE METHANE SERIES

62. Calibration of a Thermometer.—Calibrate a thermometer at 0°, 100°, 183.7°, and 218.1° according to the method described in §48, page 32.

63. Determination of Melting-points.—Determine the melting-point of the substances furnished according to the directions given in §49-52, pages 33-36.

64. Fractional Distillation.—Read the description of fractional distillation in §21-23. Set up an apparatus for distillation like that shown in Fig. 2, page 9. Use a 200-cc. distilling flask and as receivers three 100-cc. flasks which are labeled, respectively, I. 78°-82°; II, 82°-95°; and III, 95°-100°. Place 50 cc. of alcohol and 50 cc. of water in the distilling flask, and heat the latter with a flame of such a size that the liquid distils at the rate of about 1 drop per second. Collect the part which distils up to 82° in the flask numbered I. When this point is reached replace this receiver by flask II, and collect the distillate in this flask until the thermometer registers 95°. At this point use flask III as the receiver. When nearly all the liquid has distilled, pour out the small residue from the distilling flask and dry it, or use a clean dry flask. Measure in a graduated cylinder the volumes of the contents of the three receivers at the end of the first distillation, and record the results in your notebook. (See the tabulation on page 14.) Place in the distilling flask the liquid in receiver I (the first fraction), and distil as before, collecting what boils up to 82° in receiver I. When this point is reached, allow the distilling flask to cool slightly, and then add to it the contents of flask II. Replace the thermometer and distil. Collect what passes over below 82° in flask I, and the part which boils between 82° and 95° in flask II. Remove the flame, and add to the distilling flask the contents of flask III. Replace the thermometer and collect the distillate in the several receivers according to the boiling-point. Measure and record the volumes of the three fractions at the end of this second distillation. Repeat the fractionation a third time and record the volumes of the fractions.

65. Qualitative Analysis of Organic Compounds.—Make analyses of the substances furnished, following the directions given in §58-61, pages 39-42.

66. Preparation of Methane from Sodium Acetate; Properties of Methane (SECTIONS **17, 18**).—(*a*) Grind and mix thoroughly in a mortar 8 grams of fused sodium acetate[1] and 8 grams of soda-lime.[2] Transfer the mixture to an 8-inch test-tube provided with a rubber stopper fitted with a short piece of glass tubing. Connect to the latter by means of a short piece of rubber tubing a delivery-tube arranged to collect a gas over water. Support the test-tube, by means of a clamp, in such a position that the end containing the stopper is slightly lower than the other end; this prevents any water given off during the heating from running back into the hot tube and cracking it. Heat the tube cautiously, keeping the flame in motion, in order to avoid local overheating. (*Eq.*)[3] Collect three 250-cc. bottles of the gas. Prepare a mixture of the gas with air by putting into a fourth 250-cc. bottle 25 cc. of water; cover the bottle with a glass plate, insert it in the pneumatic trough, and pass the gas into the bottle until the water has just been replaced. CAUTION.—Remove the delivery-tube from the water before the heating of the tube is stopped. If during the heating the water begins to go back into the test-tube, the breaking of the latter can be prevented by separating the test-tube from the delivery-tube where they are joined together.

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[1] Commercial fused sodium acetate is generally not anhydrous; it is well to fuse it before use. If the compound is to be prepared from the hydrated salt ($CH_3COONa.3H_20$) proceed as follows: Heat cautiously about 15 grams of the crystalline salt contained in an iron pan over a small flame. Stir continuously with a glass rod. The salt melts at first in its water of crystallization; as the dehydration proceeds it solidifies, and, finally, when anhydrous, melts a second time. Care should be taken to avoid heating the dehydrated salt much above its melting-point, as it undergoes decomposition when strongly heated.

[2] The soda-lime can be replaced by an intimate mixture of 4 grams of powdered sodium hydroxide and 4 grams of quicklime.

[3] The abbreviation (*Eq.*) signifies that an equation for the reaction which takes place should be written.

(b) Inflammability of methane.—Drop a lighted match into one jar of the gas. Is soot produced? Why? (*Eq.*) What is the color of the flame?

(*c*) *Explosive mixture of methane and air.*—Light the mixture of methane and air. Explain the difference between the results obtained in this case and in (*b*). (*Eq.*) Calculate the relation between the volume of methane and the volume of oxygen in the gas exploded. State the volumes which interact according to the equation for the reaction.

(d) Methane and bromine.—Add *one* drop of bromine to a bottle of the gas. This can be done conveniently by placing a pipette, made from a piece of glass tubing drawn down to a small bore at one end, into a bottle of bromine and placing the finger over the end of the pipette, which is then withdrawn. Cover the bottle with a glass plate, and allow it to stand for a few minutes until the bromine has vaporized. Drop a lighted match into the bottle. (*Eq.*) When the reaction is complete breathe sharply across the mouth of the bottle, and test the gases in the bottle with a piece of moist blue litmus paper.

(*e*) *Methane and an oxidizing agent.*—Make a dilute solution of potassium permanganate by dissolving a crystal of the salt in one-half a test-tube full of water. Add the solution to a bottle of methane, replace the cover, and shake. Explain.

NOTES.—(*a*)[1] Soda-lime is preferably used in experiments of this type rather than sodium hydroxide, as the latter rapidly attacks glass at the temperature at which the reaction takes place.

(*b*) The methane prepared in this way is not pure; it contains small amounts of substances (acetone, for example) which impart a yellow color to the flame. The reaction should be brought about at the lowest temperature at which it takes place, in order to reduce the amount of by-products formed. Pure methane burns with a flame that is only slightly luminous.

(*c*) The violence of tho explosion is reduced by the fact that the oxygen which reacts with the hydrocarbon is diluted with nitrogen. A mixture of one volume of methane and two volumes of oxygen explodes with violence when ignited.

(*e*) This test is of value in distinguishing hydrocarbons of the methane series from other hydrocarbons which rapidly reduce an aqueous solution of potassium permanganate. If reduction occurs it is due to the fact that the methane is impure.

[1] The letters used in the notes refer to the paragraphs under these letters in the description of the experiments.

67. Preparation and Properties of Ethane: Grignard Reaction. (*a*) Into a dry 50-cc. Erlenmeyer flask fitted by means of a cork to a return condenser, place 2 grams of magnesium powder and a small crystal of iodine. Add through the condenser 5 cc. of ethyl bromide and 10 cc. of ether dried over sodium. In about 15 minutes when reaction ceases (*Eq.*) replace the condenser by a two-holed stopper carrying a small separatory funnel and a delivery-tube to collect a gas over water. Add water to the flask drop by drop, through the funnel. (*Eq.*) Collect two 250-cc. bottles of the gas.

(*b*) *Inflammability of ethane.*—Drop a lighted match into one bottle of the gas and note the color of the flame.

(*c*) *Ethane and oxidizing agents.*—Test the second bottle of gas to determine whether ethane can be readily oxidized. (See experiment 66*e*, page 45.)

NOTE.—(*a*) A trace of iodine is usually added to the mixture of halide and magnesium in effecting a Grignard synthesis, in order to hasten the reaction. The reaction is similar to that by which methane is formed from methyl iodide and magnesium. (See end of SECTION **17.**)

68. Preparation and Properties of Di-isoamyl: Wurtz Synthesis.—(*a*) To 20 grams of isoamyl bromide contained in a dry 100-cc. round-bottomed flask add 5 grams of sodium cut into about six pieces. Connect the flask with a piece of glass tubing about 3 feet long, to serve as a reflux condenser, and allow it to stand over night. Connect the flask with an air condenser, and distil with a smoky flame which is kept constantly in motion to avoid local overheating. (*Eq.*) Redistil slowly the distillate from a small flask, and save and weigh the fraction which boils at 158°-161°. Isoamyl bromide boils at 118.6° and di-isoamyl at 159°. CAUTION.—Read carefully §41, page 28. The flask contains unused sodium, and water should *not* be put into it. Add portions of 5 cc, of alcohol from time to time until the evolution of hydrogen ceases, and there is enough of the liquid to make a thin paste of it with sodium bromide; then pour the contents of the flask cautiously into an open vessel containing water. Do not pour water into the flask. Great care should be taken in the disposal of sodium residues which should be always treated in the manner just described; serious explosions and accidents frequently happen as the result of a lack of proper precautions.

Calculate the theoretical yield from the isoamyl bromide used and the percentage obtained in the experiment.

(*b*) *Di-isoamyl and bromine.*—Add 2 drops of bromine to about 2 cc. of di-isoamyl. Breathe across the tube. Is there any evidence of substitution? Heat the contents of the tube to boiling and test for hydrobromic acid as before. (*Eq.*)

(*c*) *Di-isoamyl and sulphuric add.*—Add 2 cc. of the hydrocarbon to about 5 cc. of concentrated sulphuric acid, and shake well. Allow the tube to stand a few minutes and observe the contents. Do the two liquids mix?

(*d*) *Di-isoamyl and nitric acid.*—Repeat experiment (*c*) above using concentrated nitric acid instead of sulphuric acid. Record the results obtained.

NOTES.—(*a*) In carrying out the Wurtz synthesis the reaction is often brought about in a solvent; the halide, or mixture of halides, is diluted with about twice its volume of ether which has been dried over sodium. The preparation described above should yield from 7 to 8 grams of the slightly impure hydrocarbon.

(*c* and *d*) Concentrated sulphuric acid and nitric acid are valuable agents for distinguishing between the paraffin hydrocarbons and many other classes of compounds which dissolve in these reagents.

69. Composition of Kerosene (SECTIONS **24** and **28**).—Distil about 25 cc. of kerosene, using a small flask and a condenser. (See Fig. 2, page 9.) CAUTION.—See that all corks fit tightly and that the receiver is not near a flame. Note the temperature at which the liquid begins to drop freely from the condenser and when the last part is distilling over. Compare the boiling-points obtained with those of the paraffin hydrocarbons, and state what. compounds are present in the sample studied.

NOTE.—Crude petroleum is separated into various commercial products according to the specific gravity of the distillates. These products are not carefully fractionated and are mixtures.

70. Properties of Gasoline and Kerosene (SECTIONS **26** to **28**).—(*a*) *Kerosene and acids and alkalies.*—In separate test-tubes shake about 5 cc. of distilled kerosene with 10 cc. each of concentrated nitric acid, concentrated sulphuric acid, and a dilute solution of sodium hydroxide. Note if heat is evolved or if there is a change in color. Record your observations and conclusions. Gasoline behaves in a similar way.

(*b*) *Solubility of kerosene.*—Test the solubility of about 2 cc. of kerosene or 1 gram of paraffin in water, ether, alcohol, and ligroin or petroleum ether. CAUTION.—Volatile inflammable liquids such as ether, alcohol, and petroleum ether should not be heated over a free flame. They can be heated conveniently by immersing the vessel containing them in boiling water.

(*c*) *Flash-point of gasoline.*—Pass a burning match over a few drops of gasoline placed on a watch-glass. What statement can you make in regard to the flash-point of gasoline?

(*d*) *Flash-point of kerosene.*—This experiment should be carried out in a place where there is no draft. Support a plain beaker of 55-cc. capacity in a 100-cc. beaker by means of a triangle made of copper wire, or a piece of pasteboard in which a hole has been cut just large enough to allow the body of the small beaker to pass. Fill the smaller beaker with kerosene and the larger beaker with water. In each case the level of the liquid should be within one-half inch of the top of the beaker. CAUTION.—Have an asbestos-board or a watch-glass at hand with which to smother the flame in case the kerosene takes fire during the experiment. Insert a burning match into the kerosene. What can you say of the flash-point of kerosene? Place the apparatus on a wire gauze, and heat cautiously with a flame, the tip of which should be about 3 inches below the gauze. Insert into the kerosene the bulb of a thermometer, which should be supported by a clamp. The temperature of the oil should rise not faster than 2° per minute. Attach by means of a rubber tube to the gas-cock a blow-pipe or a piece of glass tubing drawn out to a fine opening. The gas should be regulated to produce a flame about one-half inch in length. When the temperature of the kerosene reaches 35°, pass the flame quickly over the surface of the oil, taking care not to touch it. Repeat the test for every degree rise in temperature. Record the temperature at which the vapor of the oil ignites; this is made evident by a slight flash which is more or less difficult to see. As soon as the flash-point has been observed, extinguish the flame under the apparatus. If the kerosene does not flash before 48°, turn out the flame and consult the instructor.

Compare your results with the flash-point of kerosene required by law (SECTION **29**).

NOTE.—(*a*) Owing to the cracking of the paraffin oils in their distillation, samples of the commercial products from petroleum often contain small quantities of hydrocarbons which react with sulphuric acid and with nitric avid. When these impurities have been removed by repeated shaking with concentrated sulphuric acid, the resulting paraffin hydrocarbons show their characteristic inertness.

CHAPTER III

UNSATURATED HYDROCARBONS

71. Preparation and Properties of Ethylene (SECTION **32**).—(*a*) Weigh directly into an 8-inch test-tube 4 grams of phosphorus pentoxide. Connect the test-tube by means of a closely fitting cork with a reflux air-condenser; immerse the tube in cold water, and pour 5 cc. of ethyl alcohol slowly into the condenser. The alcohol should be added cautiously in small portions and the test-tube shaken under water, as much heat is evolved when alcohol comes in contact with phosphorus pentoxide. Support the test-tube at an angle of about 45° with the table by means of a clamp, and connect it with a delivery-tube arranged to collect a gas over water. Heat the tube carefully until the mixture becomes homogenous; then more strongly until a steady stream of gas is evolved. Collect three 250-cc. wide-mouthed bottles of the gas, and prepare an explosive mixture of ethylene and air. This can be done by placing 20 cc. of water in a 250-cc. wide-mouthed bottle, covering the latter with a glass plate, inverting in a pneumatic trough, and displacing the water by ethylene.

(*b*) *Inflammability of ethylene.*—Throw a lighted match into a bottle of ethylene. In order to facilitate the removal of the gas, a stream of water should be poured into the bottle as the gas burns. Note the color of the flame, and compare with results obtained when methane was burned. (Explain.)

(*c*) *Explosive mixture of ethylene and air.*—Throw a lighted match into the bottle containing the mixture of ethylene and air.

(*d*) *Ethylene and bromine.*—HOOD.—Add 2 drops of bromine to a bottle of the gas. (See experiment 66*d*, page 45.) Replace the glass cover and shake. When the color of bromine has disappeared, observe carefully the contents of the bottle. Are there drops of an oil present? (*Eq.*) Test the gas in the bottle with moist blue litmus paper. Compare the results with those obtained with methane.

(*e*) *Ethylene and oxidizing agents.*—Dissolve a small crystal of potassium permanganate in about 20 cc. of water, and add a little of the solution to a bottle of the gas. Replace the cover and shake. Explain the value of the test, and compare the results with those obtained with methane. (See experiment 66*e*, page 45.)

(*f*) *Test for unsaturated compounds in coal gas.*—Collect over water a bottle of illuminating gas. Add a dilute solution of potassium permanganate in portions of 5 cc. to the bottle and shake. What conclusions can be drawn as to the presence of unsaturated hydrocarbons in illuminating gas? What are the chief constituents of coal gas? Of water gas? Of what value are the unsaturated hydrocarbons in these gases?

NOTE.—When sulphuric acid, which is commonly used as a dehydrating agent in the preparation of ethylene, is employed, the reaction takes place at a temperature very near that at which the alcohol chars; as a consequence, carbon often separates, the mixture froths badly, and sulphur dioxide and carbon dioxide are formed. The apparatus for the preparation in this way is described under ethylene bromide (experiment 137, page 108).

72. Preparation of Ethylene from Ethylene Bromide (SECTION **32**).—Into a 6-inch test-tube place about 2 cc. of ethylene bromide, 2 cc. of alcohol, and about 0.5 gram of sheet zinc. Connect the tube with a delivery-tube, warm gently until reaction begins, and collect a test-tube full of the gas over water. (*Eq.*) Burn the gas. (*Eq.*)

73. Preparation of an Amylene (Pentene-2).—Place in a 200-cc. distilling flask 25 cc. of water, add 25 cc. of concentrated sulphuric acid, and cool the mixture in running water. Add next 22 grams of secondary amyl alcohol (see note) and connect the flask with a long condenser through which a rapid stream of cold water is passing. Attach to the condenser by means of a cork an adapter, the open end of which extends as far as possible into a flask. The latter is sunk into ice-water, contained in a beaker. Close the distilling flask with a cork. It is necessary that all corks fit tightly to prevent the loss of amylene which boils at 37°-39°. Heat the flask on a boiling water-bath as long as anything distils. The hydrocarbon is separated and placed in a distilling flask with a little anhydrous calcium chloride. When all evidence of moisture has disappeared it is distilled from a beaker containing water heated to about 60°. The amylene is collected as before in a dry flask surrounded by ice-water. Collect the product boiling from 36°-42°. Calculate the percentage yield and write the equation for the reactions involved. The yield should be from 12 to 15 grams.

NOTE.—The alcohol to be used in this experiment is now made by the Standard Oil Co. of New Jersey and is available commercially. Secondary alcohols, of the general formula R_2CHOH, lose water more readily than primary alcohols, RCH_2OH. For this reason sulphuric acid diluted with water can be used. If the concentrated acid is used the unsaturated hydrocarbon is polymerized to di- and tri-amylenes.

74. Properties of Unsaturated Hydrocarbons (SECTION **38**).—(*a*) *Amylene and bromine.*—Dissolve 1 cc. of amylene in 5 cc. of carbon tetrachloride, and add gradually, as long as an evident reaction takes place, a solution prepared by dissolving 2 cc. of bromine in 50 cc. of carbon tetrachloride. (*Eq.*) Test for evolved hydrobromic acid by breathing across the mouth of the tube.

(*b*) *Amylene and oxidizing agents.*—Shake a few drops of amylene with about 20 cc. of a dilute solution of potassium permanganate prepared by dissolving a crystal of the salt in one-half a test-tube full of water. (*Eq.*)

(*c*) *Test for unsaturated hydrocarbons in gasoline.*—To 10 cc. of gasoline contained in a *dry* test-tube add drop by drop a 5 per cent solution of bromine in carbon tetrachloride. Note if hydrobromic acid is given off, by breathing across the mouth of the tube. Add finally 2 cc. of the solution after it remains colored, and divide the mixture into two portions; place one in your desk the dark and the other in direct sunlight. Examine the tubes in a few minutes. Explain the differences observed.

NOTE.—(*c*) Certain samples of gasoline consist essentially of saturated hydrocarbons. Other samples, which are made from the products formed by cracking crude oils, contain a large percentage of olefines.

75. Preparation and Properties of Acetylene (SECTIONS **41** to **43**).—(*a*) Support a *dry* 200-cc. distilling flask by means of a clamp, and connect the side-arm of the flask with a delivery-tube arranged to collect a gas over water. Fit a dropping funnel into the neck of the flask by means of a cork. Place in the flask about 10 grams of calcium carbide, and let water fall very slowly, drop by drop, from the funnel onto the carbide. (*Eq.*) Fill four 250-cc. bottles with the gas generated, rejecting the first bottle-full collected. Why? Prepare an explosive mixture of acetylene and air by putting 15 cc. of water into a *wide-mouthed* bottle, covering the bottle with a glass plate, inverting the bottle in the pneumatic trough, and displacing the water by acetylene. CAUTION.—Do not let acetylene escape freely into the air; the gas has an unpleasant odor and is poisonous.

(*b*) *Inflammability of acetylene.*—Throw a lighted match into a bottle of the gas. Is much soot deposited? Note the luminosity of the flame and compare your results with those obtained when methane and ethylene burned.

(*c*) *Explosive mixture of acetylene and air.*—Throw a lighted match into a bottle containing the mixture of acetylene and air. How does the explosion compare in intensity with those obtained with methane and ethylene?

(*d*) *Acetylene and oxidizing agents.*—Apply the potassium permanganate test for unsaturation. (See experiment 66*e*, page 45.)

(*e*) *Acetylene and bromine.*—Add to a bottle of the gas about 5 drops of bromine. Replace the cover of the bottle and shake. If the color does not disappear in a minute, add to the bottle a few cubic centimeters of a dilute solution of sodium hydroxide and shake. When the color has disappeared, observe the contents of the bottle carefully. (*Eq.*) Note the odor of the product formed. How could acetylene be obtained from this compound? (*Eq.*)

(*f*) *Test for the triple bond.*—Test a bottle of the gas for a compound containing a triple bond, using an ammoniacal solution of cuprous chloride which can be made as follows: Heat together in a test-tube over a flame, a few pieces of copper oxide and metallic copper with about 10 cc. of dilute hydrochloric acid (sp. gr. 1.1). When the solution becomes colorless, cool, decant off about 5 cc. of the liquid and add ammonia until the solution is alkaline. Add this solution to a bottle of the gas; cover the bottle and shake. (*Eq.*)

NOTES.—(*a*) The acetylene prepared in this way from commercial calcium carbide contains impurities, such as hydrogen sulphide and phosphine. If the gas is to be used to prepare other compounds, it should be purified by passing it through a wash-bottle containing a solution of mercuric chloride in hydrochloric acid.

(*c*) It is easy to obtain an explosive mixture of air and acetylene as the proportion of acetylene in such mixtures may vary between wide limits, namely, from 3 to 82 per cent by volume. In the case of methane and ethylene, the limiting volumes are from 5 to 13 per cent of the former and from 4 to 22 per cent of the latter.

(*f*) This test applies only to compounds containing the $C\equiv CH$ group; the compounds must contain a hydrogen atom linked to a carbon atom which is joined to a second carbon atom by a triple bond.

CHAPTER IV

ALCOHOLS

76. Properties of Methyl Alcohol (SECTION **56**).—(*a*) *Inflammability of methyl alcohol.*—Pour about 1 cc. of methyl alcohol into an evaporating dish and apply a burning match. (*Eq.*) Note the appearance of the flame.

(*b*) *Solubility of methyl alcohol.*—Test the solubility of methyl alcohol in water, ether, ethyl alcohol, petroleum ether, and benzene. Use about 1 cc. of the alcohol in each test.

(*c*) *Methyl alcohol as a solvent.*—Test the solubility of anhydrous calcium chloride and sodium chloride in methyl alcohol.

(*d*) *Methyl alcohol and sodium.*—Add a piece of sodium the size of a small pea to 5 cc. of methyl alcohol. (*Eq.*)

77. Tests for Methyl Alcohol.—*(a) Methyl salicylate.*—Mix together in a test-tube about 0.2 gram of salicylic acid, 1 cc. of concentrated sulphuric acid, and 1 cc. of methyl alcohol, and warm gently. Note and describe the odor. The compound formed is the methyl ester of a salicylic acid, $HO.C_6H_4.COOCH_3$.

(*b*) *Formaldehyde* (SECTION **177**).—Dissolve 5 drops of methyl alcohol in 3 cc. of water. Wind a piece of stout copper wire around a load pencil so that a closely coiled spiral about 2 cm. in length is formed; leave about 20 cm. of the wire to serve as a handle. Heat the spiral in the upper part of a Bunsen flame, and plunge it while red hot into the solution of methyl alcohol. Withdraw the spiral, cool the liquid under running water, and heat again with the hot spiral. In this way the methyl alcohol is oxidized by the hot copper oxide formed on the wire. Note the odor of the liquid while hot. Cool the liquid, add 2 drops of a 0.5 per cent solution of resorcin and pour the resulting mixture, slowly so the two liquids do not mix, down the side of an inclined test-tube containing about 5 cc. of concentrated sulphuric acid.

78. Preparation of Ethyl Alcohol by Fermentation (SECTION **58**).— (*a*) Dissolve 40 grams of commercial anhydrous glucose in 350 cc. of water in a 500-cc. bottle. Add one-fourth of a yeast cake ground to a smooth paste with 50 cc. of water, and about 0.5 gram of Witte's peptone.[1] Close the bottle with a rubber stopper through which passes one end of a glass tube bent in two right angles to form three sides of a rectangle. The other end of the tube passes to the bottom of a test-tube which is held in place by means of cork along the side of which a groove is cut to allow the escape of gas. The test-tube is one-half filled with a solution of barium hydroxide. By using the apparatus arranged in this way, any gas evolved must pass through the solution of barium hydroxide before it escapes. Mark the bottle with your name by means of a label, and set it in a warm place (about 30°). Examine the contents of the bottle at the next laboratory exercise. Has the amount of yeast increased in quantity? What gas has been evolved?

The product obtained is a dilute solution of ethyl alcohol which contains small quantities of other substances. The alcohol should be separated, and the amount formed in the reaction determined as follows: Decant through a folded filter-paper, taking care not to disturb the sediment of yeast, about 250 cc. of the solution. While waiting for the solution to filter, weigh to centigrams a clean dry 100-cc. flask, around the neck of which has been pasted a narrow strip of paper to serve as a reference mark. Fill the flask up to the mark with distilled water, and weigh again. Place exactly 200 cc. of the filtered solution from the fermentation into a 500-cc. distilling flask, neutralize, using litmus paper, with a dilute (10 per cent) solution of sodium hydroxide, and distil into the weighed flask until the liquid fills it exactly to the mark. (For the arrangement of the distilling flask and condenser see Fig. 2, page 9.) Weigh the flask and contents. Save the distillate for a later experiment. Calculate the specific gravity of the distillate, which contains all the alcohol that was present in 200 cc. of the product of fermentation. By reference to a table of the specific gravity of aqueous solutions of alcohol, calculate the weight of alcohol obtained from the 40 grams of glucose used in the experiment. What was the total

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[1] Yeast requires for its growth certain salts which are present in Witte's peptone. If the latter is not available it may be replaced by 20 cc. of a solution made by dissolving 10 grams each of potassium phosphate, magnesium chloride, and calcium nitrate in 1 liter of water.

volume of the solution fermented? Calculate the theoretical amount of alcohol obtainable from 40 grams of glucose and the percentage of this (the yield) obtained in your experiment.

Write an equation for the reaction by which alcohol is formed from glucose. Why is the solution kept in a warm place during fermentation? Why is the solution neutralized before distillation? How could you determine whether an acid volatile with steam was formed during the fermentation?

(*b*) Place the dilute alcohol obtained in (*a*) above in a 200-cc. distilling flask and distil off slowly about 50 cc. Add to this distillate solid anhydrous potassium carbonate as long as the salt dissolves.

(*c*) Test the product obtained in (*a*) or (*b*) by the iodoform test. (Experiment 81*b*, page 59).

NOTES.—(*a*) If very accurate results are desired it is necessary to take into account the temperature of the water in standardizing the contents of the flask, and to note the temperature of the dilute alcohol. The specific gravities of aqueous solutions of alcohol vary with the temperature. In the analysis of beverages for alcohol the specific gravity is usually determined by means of a hydrometer or a Westfall balance.

(*b*) The alcohol obtained in this way still contains water. It may be rendered anhydrous by a second treatment with potassium carbonate and with lime as described in experiment 80 below. The soluble monatomic alcohols can be separated from not too dilute solutions in water by saturating them with potassium carbonate.

79. Properties of Ethyl Alcohol (SECTIONS **60, 64**).—(*a*) *Inflammability of alcohol.*—Touch a lighted match to a few drops of alcohol on a watch-glass.

(*b*) *Solubility of alcohol.*—Test the solubility of alcohol, using about 5 cc. in each experiment, in water, benzene, kerosene, and concentrated sulphuric acid.

(*c*) *Test for water in alcohol.*—Add to 5 cc. of commercial 95 per cent alcohol about 1 gram of anhydrous copper sulphate which can be prepared by cautiously heating the crystalline salt over a free flame in an evaporating dish. Note the change in color. Explain. Repeat the experiment, using absolute alcohol. For what purpose could this reaction be used?

(*d*) Place a crystal of potassium permanganate in about 5 cc. of 95 per cent alcohol. Repeat, using absolute alcohol.

(*e*) *Alcohol and sodium.*—Add to about 5 cc. of absolute alcohol a piece of sodium the size of a pea. Test the evolved gas. (*Eq.*) Evaporate the solution on a water-bath. Dissolve the resulting product in water and test the solution with litmus paper. (*Eq.*)

(*f*) *Alcohol and hydrobromic acid.*—Place 2 cc. of alcohol and 10 cc. of hydrobromic acid (sp. gr. 1.49) in a test-tube supported in a clamp and provided with a delivery-tube. (See Fig. 20, page 31.) Let the second end of the tube pass to within 1 inch of the bottom of a test-tube which is placed in a beaker containing cold water. Heat the solution of alcohol and acid carefully until about 5 cc. of liquid have distilled over. Examine the distillate. (*Eq.*)

(*g*) *Alcohol and acetyl chloride.*—HOOD.—In making the following test take care that the mouth of the test-tube is directed away from you. Add acetyl chloride cautiously, drop by drop, from a pipette to 2 cc. of alcohol in a test-tube, which is kept cool by immersion in water, as long as reaction takes place. Note the gas evolved. (*Eq.*) Pour the contents of the tube cautiously into 5 cc. of cold water, and shake. Note the odor of the product.

(*h*) *Alcohol and acetic anhydride.*—CAUTION.—The reaction which takes place in this experiment is apt to occur with violence. The experiment should be performed under the hood. In a test-tube add 2 cc. of alcohol to 2 cc. of acetic anhydride. Is there any evidence of action? Support the tube in a vertical position by means of a clamp. Place a glass rod into concentrated sulphuric acid, and then rub it against the neck of the bottle to remove the drop that adheres. Put the rod with the trace of acid into the mixture of alcohol and anhydride. Wait until the mixture boils. (*Eq.*) Add the product to 5 cc. of cold water. If the ester does not separate, saturate the aqueous solution with sodium chloride. Note the odor of the product formed.

(*i*) *Oxidation of alcohol.*—Heat together about 1 cc. of alcohol, 5 cc. of a solution of potassium bichromate, and 5 cc. of dilute sulphuric acid. Note the change in color and the production of a characteristic odor. Write the equations for the reaction, including the change which takes place in the potassium bichromate.

NOTE.—(*h*) Sulphuric acid serves as a valuable catalytic agent in bringing about a reaction between alcohols and acid anhydrides.

80. Preparation of Absolute Alcohol (SECTION **60**).—(*a*) In a 500-cc. flask add quicklime broken into small lumps to 200 cc. of 95 per cent alcohol until the pieces just project above the surface of the liquid. Connect the flask with a reflux condenser (§38, page 26), and heat to boiling on a water-bath for 1 hour. Do not place the flask in the boiling water. Remove the bath, and when the alcohol ceases boiling arrange the condenser for distillation (Fig. 2, page 9). Distil from the water-bath and collect the distillate in a filter-bottle, which is attached to the condenser by means of a cork stopper. In order to protect the alcohol, which is hygroscopic, from the moisture in the air, connect to the side-arm of the bottle by means of a piece of rubber tubing a small drying-tube containing calcium chloride. Collect the first 10 cc. in a small dry flask, and then adjust the filter-bottle to receive the rest of the distillate. Keep the absolute alcohol in a stoppered bottle for future use. Why is the first part of the distillate rejected? Give a reason for the fact that absolute alcohol can not be obtained from a mixture with water by fractional distillation. What substance other than quicklime could be used for freeing alcohol from water? Could phosphorus pentoxide, concentrated sulphuric acid, or calcium chloride be used? State a reason for your answer in each case.

(*b*) Test portions of the first distillate, and of the absolute alcohol obtained for water with anhydrous copper sulphate and with potassium permanganate. (See experiment 79*c* and *d,* page 57).

81. Tests for Ethyl Alcohol (SECTIONS **64, 266**).—(*a*) *Ethyl acetate.*—Warm gently together in a test-tube about 1 cc. of alcohol, 1 cc. of glacial acetic acid, and 2 cc. of concentrated sulphuric acid. Note the odor. (*Eq.*)

(*b*) *Iodoform test.*—Add 5 drops of alcohol and about 1 cc. of a dilute solution (10 per cent) of sodium hydroxide to 5 cc. of water in a test-tube. Add to the mixture, drop by drop, a solution of iodine in potassium iodide[1] until a faint yellow color persists after the solution is shaken. Heat the test-tube until it

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[1] This solution is made by dissolving 1 part of iodine and 5 parts of potassium iodide in 15 parts of water.

feels warm to the hand (about 60°). If a precipitate does not separate at once set the tube aside for a few minutes. Note the odor and color of the precipitate.

NOTES.—(*a*) Tests which are based on the recognition of odors are not reliable for the absolute identification of compounds. Whenever possible the compound to be identified is converted into a solid substance, which possesses a definite melting-point. For a test for ethyl alcohol based on this principle see "The Identification of Pure Organic Compounds," by S. P. Mulliken, Vol. I, page 168.

(*b*) A number of substances yield iodoform when treated with iodine and sodium hydroxide. Isopropyl alcohol and acetone give the test immediately in the cold.

82. Preparation and Properties of Allyl Alcohol (SECTIONS **85, 101**).—(*a*) Into a 500-cc. distilling flask, which is connected with a condenser and receiver, place 50 grams of oxalic acid. 200 grams of glycerol and 0.5 gram ammonium chloride. Fit into the neck of the flask by means of a stopper a thermometer so placed that the bulb is near the bottom of the flask. Heat over a wire gauze cautiously. Carbon dioxide is rapidly evolved and the thermometer registers about 130° for some time. As the temperature rises the evolution of gas slackens and finally ceases. When the temperature reaches 195°, the receiver, which contains a dilute aqueous solution of formic acid, is changed. At about 200° carbon dioxide is again evolved, and water and allyl alcohol distil over. When the thermometer registers 260°, the distillation is stopped.

The distillate which contains the allyl alcohol is redistilled slowly from a flask fitted in the usual way with a thermometer. When the temperature reaches 103°, test from time to time about 2 cc. of the distillate for allyl alcohol by saturating it with solid anhydrous potassium carbonate. When an oil no longer separates, stop the distillation. Combine the products and saturate the solution with solid anhydrous potassium carbonate. Separate the layer of oil, and redistil. The allyl alcohol obtained in this way boils at 87°-97° and contains water. Weigh the product obtained and note its odor. The alcohol can be used for the experiments described below. In order to obtain the alcohol in dry condition, it should be placed in a flask and treated with barium oxide until the pieces project from the surface of the liquid. The flask should then be connected with a return condenser and allowed to stand over night. It is necessary to use the condenser, as the heat evolved in the union of the water and oxide often heats the alcohol to boiling. The alcohol obtained directly by distillation from the barium oxide boils at 96°-98°. the yield of alcohol is about 40 per cent of the theoretical.

Allyl alcohol boils at 96.6° and has the specific gravity 0.872 at 0°.

(*b*) Test the solubility of allyl alcohol in water.

(*c*) *Allyl alcohol and bromine.*—HOOD.—To 1 cc. of allyl alcohol add bromine, drop by drop, as long as reaction occurs. (*Eq.*)

(*d*) *Allyl alcohol and acetyl chloride.*—HOOD.—Add acetyl chloride cautiously (see experiment 79*g*, page 58) to 2 cc. of allyl alcohol until reaction ceases. (*Eq.*) Pour the product into 5 cc. of cold water. Shake and note the odor.

(*e*) *Application of the iodoform reaction to allyl alcohol.*—determine whether allyl alcohol gives the iodoform reaction. Carry out the test as in experiment 81*b*, page 59.

(*f*) *Allyl alcohol and oxidizing agents.*—HOOD.—Heat a mixture of 1 drop of the alcohol, 5 cc. of a solution of potassium bichromate, and 5 cc. of dilute sulphuric acid. Note the odor of acrolein (SECTION **190**), which is the aldehyde obtained by the oxidation of allyl alcohol. (*Eq.*) Clean the tube under the hood.

83. Preparation of Secondary Amyl Alcohol from an Amylene (Pentene-2) (SECTION **81**).—Pour 50 cc. of concentrated sulphuric acid into 10 cc. of water, cool the mixture to 25°, and place it in a 250-cc. bottle, the glass stopper of which fits tightly. Moisten the neck of the bottle with a little of the acid so that when the stopper is inserted and rotated, a gas-tight joint will be made. Put in the bottle 25 cc. (16 grams) of pentene-2 (see experiment 73, page 51) and shake vigorously. As soon as there is the slightest indication of a rise in temperature, place the bottle under running water for a few seconds. Continue shaking and cooling in this way until heat is no longer generated (2 to 3 minutes). After the bottle has been shaken 5 minutes set it aside for another 5 minutes. At the end of this time the contents should be somewhat cloudy but should not separate into two distinct layers.

(*Eq.*) Pour the mixture slowly into 400 cc. of cold water and after a few minutes filter it through a moistened filter paper, to remove the insoluble oil, which should have a volume not greater than about 2 cc. Place the aqueous layer, which contains the alcohol formed, in a large flask connected with a condenser. Distil off about 100 cc. of liquid. Dissolve about 10 grams of sodium hydroxide in the distillate, separate the oil, and place it in a small distilling flask. Add 15 grams of sodium hydroxide and attach to the flask by means of a cork a glass tube about 75 cm. long. Place a cork over the side arm of the flask (see Figure 16, page 26) and reflux gently for about 15 minutes. This process serves to remove the water dissolved in the alcohol. Fit the flask with a thermometer, attach it to a condenser, and distil. The alcohol should boil between 115° and 119.5°. If much low-boiling material is obtained the alcohol should be refluxed with more sodium hydroxide to remove dissolved water which lowers the boiling point.

The alcohol obtained is a mixture of pentanol-2 and pentanol-3. (*Eqs.*) The former boils at 118.5°-119.5° and the latter at 116.5°. The yield of mixed alcohols is about 60 per cent of the theoretical.

NOTE.—If concentrated sulphuric acid is used in this preparation, a large part of the amylene is polymerized. If a more dilute acid is used than that recommended, the reaction requires a longer time. Sodium hydroxide is added to the distillate to precipitate the alcohol which is dissolved in the water. Alcohols in general are less soluble in a solution of bases than in water.

84. Properties of Glycerol (SECTIONS **93, 94, 190**).—(*a*) *Solubility of glycerol.*—Test the solubility of glycerol in water, alcohol, ether, petroleum ether, and benzene.

(*b*) *Conversion of glycerol into acrolein.*—Cover the bottom of a test-tube with powdered acid potassium sulphate and then add about 5 drops of glycerol. Heat strongly and note the odor. (*Eq.*)

(*c*) *Test for glycerol with borax bead.*—Prepare a borax bead in the usual way. Place the bead when cold into an aqueous solution of glycerol, and then insert into a Bunsen flame. Note the color of the flame. Glycerol liberates boric acid from borax.

(d) Test for glycerol with a solution of borax.—Make a dilute solution (about 1 per cent) of borax in a test-tube. Add 2 drops

of a phenolphthalein solution. What is the color? Why? Add now a neutral aqueous solution of glycerol slowly until the color is destroyed. Heat the solution to boiling and then cool.

(*e*) *Test for glycerol by the preparation of glyceryl tribenzoate.*—To obtain a solid derivative of glycerol the melting-point of which can be determined proceed as follows: Place in a small flask 3 drops of glycerol, 1 cc. of benzoyl chloride, and 10 cc. of a 10 per cent solution of sodium hydroxide. Cork the flask, and shake vigorously for 10 minutes. At the end of this time the compound formed will adhere to the sides of the flask. Decant off the liquid, and wash with cold water. Pour off as much as possible of the latter, and add 10 cc. of alcohol. Heat on the steam-bath, and filter the hot solution into a small flask. Add 2 cc. of water, stopper the flask, and shake it vigorously under running water. Filter off the crystals by suction, and wash them with a mixture of 5 cc. of alcohol and 2 cc. of water. Let the product, which is the tribenzoate of glycerol, $(C_6H_5COO)_3C_3H_5$, dry in the air, and then determine its melting-point, which is 71°-72°. If the compound does not melt sharply, recrystallize it from alcohol and water as before.

NOTES.—(*b*) If larger quantities of glycerol are used the acid potassium sulphate should be replaced by phosphorus pentoxide; with this reagent frothing is avoided and no sulphur dioxide is formed.

(*d*) Other polyatomic alcohols behave as glycerol does in this test. Ammonium salts cause the disappearance of the color of the phenolphthalein, but the color is not restored in this case by boiling.

(*e*) Alcohols in general are converted into esters of benzoic acid when treated with benzoyl chloride as described in the test. (Baumann and Schotten reaction, SECTION **547.**) It should be noted that glycol gives an ester which melts at 71°; it is evident, therefore, that the test is not applicable in the presence of glycol.

CHAPTER V

ACIDS

85. Formation of Formic Acid by the Oxidation of Methyl Alcohol (SECTION **100**).—Place in a 100-cc. distilling flask, 5 grams of powdered potassium bichromate, 20 cc. of water, and 5 cc. of concentrated sulphuric acid. Cool the flask, and add slowly with shaking 2 cc. of methyl alcohol drop by drop, keeping the flask underwater. Place the flask for about 10 minutes in a beaker containing boiling water. Distil off, using a condenser, about 10 cc. of liquid. Apply to the distillate tests described in experiment 87*b* and *c* below. Write equations for all reactions involved.

86. Preparation of Formic Acid from Oxalic Acid (SECTION **100**).—Into a 250-cc. distilling flask, provided with a condenser and receiver, put 20 grams of anhydrous glycerol and 20 grams of oxalic acid. Close the flask by a cork carrying a thermometer which is so placed that the bulb is below the surface of the glycerol. Heat cautiously with a small flame. Carbon dioxide is given off at about 80°. Maintain the temperature at 105°-110° until the evolution of gas has slackened. Cool the contents of the flask to about 60°, add 20 grams more of oxalic acid, and heat as before. Repeat the addition of oxalic acid until 80 grams in all of the acid have been used. After the last portion of the acid has been added, allow the temperature to rise to 115°. A dilute aqueous solution of formic acid is obtained. (*Eq.*)

87. Properties of Formic Acid (SECTION **100**).—(*a*) *Odor of formic acid.*—Note the odor of the solution obtained in experiment 86 above, and test the solution with blue litmus paper.

(*b*) *Reduction of silver formate.*—Neutralize 2 cc. of the dilute solution of formic acid with ammonia. Add a few drops of a solution of silver nitrate, and warm carefully. (*Eq.*)

(*c*) *Reduction of mercuric formate.*—Shake for about 1 minute 2 cc. of the distillate with 0.2 gram of mercuric oxide. Filter the solution and heat it to boiling. The mercuric formate first formed is reduced to mercurous formate, and finally to mercury. (*Eq.*) This is a valuable test for formic acid.

(*d*) *Reduction of mercuric chloride by formic acid.*—To 5 cc. of the distillate add 2 cc. of a solution of mercuric chloride and heat. The mercuric chloride is reduced to mercurous chloride. (*Eq.*)

(*e*) *Decomposition of formic acid by sulphuric acid.*—To 2 cc. of the distillate add 2 cc. of concentrated sulphuric acid slowly and heat gently. (*Eq.*) Apply a flame to the liberated gas. If an inflammable gas is not obtained, repeat using 0.5 gram of sodium formate.

(*f*) *Oxidation of a formate.*—Neutralize 1 cc. of the distillate with a dilute solution of sodium hydroxide. Add, drop by drop, a dilute (rose-colored) solution of potassium permanganate. (*Eq.*) What is the significance of the result when compared with the action of unsaturated hydrocarbons with potassium permanganate? (See experiment 71*e*, page 51.)

(*g*) *Salts of formic acid.*—Dilute what is left of the distillate with an equal volume of water and divide it in two portions; boil one for about 5 minutes with an excess of lead oxide, and the other with copper oxide. Filter the solutions while still hot and set aside to crystallize.

88. Formation of Acetic Acid from Ethyl Alcohol (SECTION **107**).—To 15 grams of coarsely powdered potassium bichromate contained in a 200-cc. round-bottomed flask, add a mixture of 15 grams of concentrated sulphuric acid and 10 cc. of water. Set the flask on a sand-bath and connect it with a reflux condenser through which a rapid stream of water is passing. Add through the condenser slowly, in portions of 0.5 cc, 3 cc. of alcohol. Shake after each addition and wait until the vigorous reaction which takes place subsides before another addition of alcohol is made. When all the alcohol has been added, heat to boiling for 15 minutes. Change the condenser and distil off about 10 cc. (*Eq.*) Observe the odor of the solution (see note) and test it for acetic acid by experiment 91*a* and *b* below.

NOTE.—There is usually present in the distillate ethyl acetate and aldehyde, both of which have a characteristic odor. A mixture of potassium bichromate and sulphuric acid (chromic acid) is an excellent oxidizing agent to use in the preparation of acetic acid by oxidation, since acetic acid is not readily oxidized by chromic acid.

89. Preparation of Glacial Acetic Acid (SECTION **103**).—Melt cautiously in an iron dish about 50 grams of anhydrous sodium acetate.[1] Grind the salt to a coarse powder in a mortar; weigh 40 grams of the salt and place it in a 200-cc. distilling flask. Add cautiously through a funnel, keeping the flask cold by immersion in water, 25 cc. of concentrated sulphuric acid. Place a thermometer in the flask in order to determine the temperature of the vapor. Connect with a condenser and receiver, and distil off the acetic acid. Weigh the acid obtained. Calculate the theoretical amount which can be obtained from 40 grams of sodium acetate, and the percentage yield of the experiment. CAUTION.—Glacial acetic acid causes painful blisters when left in contact with the skin.

90. Properties of Acetic Acid (SECTION **112**).—(*a*) *Solubility of acetic acid.*—Test the solubility of acetic acid in water, alcohol, ether, and benzene. Place about 10 cc. of the acid obtained in a test-tube surrounded by chipped ice and water. Insert a thermometer into the acid. If crystals do not form, scrape the side of the tube with a glass rod. If the acid freezes, remove the tube, stir with the thermometer, and note the temperature when the acid is about one-fourth melted.[2] Pure acetic acid melts at 16.7° and boils at 119°. One per cent of water lowers the melting-point about 2.1°.

(*b*) *Acetic acid and oxidizing agents.*—Determine whether acetic acid reduces solutions of potassium permanganate, silver nitrate, and mercuric chloride. Compare the results with those obtained with formic acid. (Experiment 87, page 64.)

(*c*) Add a few crystals of chromic acid to a mixture of 5 cc. of glacial acetic acid and 2 cc. of water. Heat to boiling. Is the chromic acid reduced?

(*d*) *Formation of verdigris.*—Stand a piece of copper foil in a small beaker containing acetic acid; a part of the foil should be under the liquid and a part exposed to the air. Examine the foil at the next exercise. What is formed?

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[1] If the anhydrous salt is not available, dehydrate the crystalline salt for this experiment according to the directions given in experiment 66*a*, page 44.

[2] If the acid prepared does not freeze, determine the melting-point, as described above, of a sample of glacial acetic acid.

91. Tests for Acetic Acid (SECTION **114**).—(*a*) *Formation of basic ferric acetate.*—Add a few drops of a solution of ferric chloride to a solution of sodium acetate. Note the color. Heat the solution to boiling. The neutral ferric acetate is converted into a basic acetate. (*Eq.*) In using this test for the free acid it must first be neutralized with sodium hydroxide.

(*b*) *Formation of ethyl acetate.*—Repeat the test involving the formation of ethyl acetate given in experiment 81*a*, page 59.

(*c*) *Conversion of acetic acid into acetanilide.*—Place in a dry test-tube 0.6 gram of anhydrous sodium acetate, 0.25 cc. of concentrated sulphuric acid, 1 cc, of aniline. The substances used should be measured accurately. Close the mouth of the tube with a cork bearing a piece of glass tubing about 2 feet long. Support the tube in a vertical position and heat it so the contents boil gently for about 1 hour. Cool, dissolve the product in 25 cc. of boiling water, filter hot, and set aside to crystallize. Determine the melting-point of the crystals. Acetanilide melts at 116°.

NOTE.—(*c*) The identification of a substance is best accomplished by converting it into a solid which has a definite melting-point and can be readily purified. In the case of acetic acid and its homologues the anilides serve this purpose well (SECTION **497**). They are formed as the result of the elimination of water from the acid and aniline:

$$CH_3COOH + C_6H_5NH_2 = CH_3CONHC_6H_5 + H_2O$$

If the acid to be identified is dissolved in water it is neutralized with sodium hydroxide and the solution evaporated to dryness. The salt is cautiously heated over a free flame to drive out the water of crystallization; it is then heated with aniline and enough concentrated sulphuric acid to set free the organic acid. When salts are used the reaction is as follows:

$$CH_3COONa + C_6H_5NH_2.H_2SO_4 = CH_5CONHC_6H_5 + NaHSO_4 + H_2O$$

92. Preparation and Properties of Soap: Saponification of Fat (SECTION **123**).—(*a*) Weigh 35 grams of lard in a small beaker and add slowly with constant stirring 9 grams of sodium hydroxide dissolved in 9 cc. of water. Rest the beaker in a second beaker containing boiling water and heat the mixture in this way for from 45 to 60 minutes. Stir the mixture occasionally until it hardens. The chief constituents of lard are the glyceryl esters of palmitic, stearic, and oleic acids. Write equations for the reactions which take place when these three substances are heated with sodium hydroxide.

(*b*) *Test for free alkali in soap.*—Determine whether the soap prepared in (*a*) above contains free alkali, as follows: Dissolve a small piece of the soap in cold water and test the solution with a solution of phenolphthalein.

(*c*) *Hydrolysis of soap.*—Shake vigorously a piece of Ivory soap about the size of a large pea with 10 cc. of cold water. Filter and test one-half of the solution with a solution of phenolphthalein. How do you explain the difference between the result of this experiment and that obtained with the soap you prepared? Heat to boiling the other half of the solution of Ivory soap and add phenolphthalein. Explain and write equations for the reaction.

(*d*) *Soft soap.*—Cut the soap you prepared into thin shavings and heat it with 400 cc. of water until it dissolves. Divide the product into four parts. Put aside one of these and allow it to cool. Describe the properties of the soft soap.

(*e*) *Salting out of soap.*—Precipitate one portion of the solution by adding slowly, with stirring, an equal volume of a saturated salt solution. Filter off the precipitate and save the filtrate for another experiment. Wash the precipitate with 50 cc. of saturated salt solution, let it drain thoroughly, and finally spread it on a watch-glass to dry. Test the soap for free alkali as in (*b*) above. From what organic compound has the soap been separated by this treatment?

(*f*) *Solubility of soap.*—Test the solubility of the purified soap in water, in alcohol, and ether. This can be clone most readily by shaking pieces of the soap with about 15 cc. of each of the solvents, filtering, and evaporating the solvents on a water-bath. If there is any residue from the ether, test it to determine whether it is soap, or fat which has not saponified.

(*g*) *Action of hard water and soap.*—To determine the action of hard water on a solution of soap, add to small portions of the solution prepared in (*d*) above, solutions of calcium chloride and magnesium sulphate. (*Eq.*) Test the solubility of the precipitates in water. Explain the difference between the action of sodium chloride and calcium chloride on a soap solution. Did you note any difference in the action of the two salts on a dilute solution of soap? What chemical compounds may be present in natural hard water?

(*h*) *Isolation of fatty acids from soap.*—To the remainder of the solution prepared in *(d)* above, add dilute hydrochloric acid as long as a precipitate is formed. Of what does this precipitate consist? (*Eq.*) Filter and wash with cold water; drain thoroughly and spread the precipitate on a watch-glass to dry. Test the solubility of the precipitate in water, sodium hydroxide (*Eq.*), ether, and alcohol. Place a small piece of the precipitate in a test-tube one-half full of water; heat to boiling and shake. Describe the appearance. Cool and shake. What is the effect of hot water on the acids? On the basis of their solubility, state how you could separate into its constituents a mixture which contained fat, fatty acids, and soap.

(*i*) *Test for unsaturated acids in soap.*—Dissolve about 1 gram of the acids obtained in experiment (*h*) above in 5 cc. of carbon tetrachloride and add, drop by drop, a solution of bromine in carbon tetrachloride. Explain. (*Eq.*)

(*j*) *Identification of glycerol in the product of the hydrolysis of fat.*—The presence of glycerol can be shown as follows: Neutralize with dilute hydrochloric acid about 100 cc. of the solution reserved in experiment *(e)* above; filter, evaporate the filtrate to dryness, and stir the residue of salt and glycerol with about 20 cc. of alcohol. Decant off the liquid through a filter and evaporate on the steam-bath. A sample of impure glycerol will be left. Prove the presence of glycerol by applying two of the tests given in experiment 84, page 62.

NOTES.—(*e*) If one precipitation does not free the soap from alkali, redissolve it and precipitate again.

(*f*) Ether dissolves fat but does not dissolve soap; this solvent can be used, therefore, to determine the presence of unsaponified fat in a sample of soap.

93. Preparation and Properties of Oxalic Acid (SECTIONS **134, 136**).—(*a*) Heat on the steam-bath in an open 500-cc. flask 120 grams of concentrated nitric acid (sp. gr. 1.42) and 20 grams of cane-sugar. As soon as brown fumes begin to be evolved, place the flask in a hood, and let it stand until the rapid evolution of oxides of nitrogen ceases. Evaporate on the steam-bath until the volume of the liquid is reduced to about 30 cc. Set aside to crystallize. Filter off the acid through a funnel provided with a perforated plate, using no filter-paper. Dissolve the crystals in the smallest amount of boiling water possible, and set the solution aside to crystallize. Oxalic acid dissolves in 10.46 parts of water at 14.5c. Weigh the product obtained.

(*b*) *Action of heat on oxalic acid.*—Heat about 1 gram of oxalic acid in a dry test-tube; continue the heating after the water of crystallization has been driven off. Describe the result. Oxalic acid, $(COOH)_2.2H_2O$, melts at 99°; the anhydrous acid sublimes at 150-180°.

(*c*) *Change of a formate to an oxalate.*—Heat in a dry test-tube about 1 gram of sodium formate. (*Eq.*) Apply a flame to the gas evolved. Test the residue for an oxalate according to experiment 94*c* below.

(*d*) *Potassium tetroxalate.*—Dissolve 5 grams of oxalic acid in 30 cc. of hot water. Neutralize exactly one-fourth of this solution carefully with a solution of potassium hydroxide (1:4); combine the solutions and set aside to crystallize. (*Eq.*) When cold, filter off the salt. Dissolve a little of the salt in water, and try its effect on an iron-rust stain, also on a spot made with an iron ink and an ink made from an aniline dye.

(*c*) *Potassium ferric oxalate.*—Add to a solution of ferric chloride a solution of potassium oxalate until a clear green solution is formed. (*Eq.*) Moisten a piece of paper with the solution. Test the paper for a ferrous salt by putting on it a drop of potassium ferricyanide. Expose a piece of the paper to direct sunlight for 1 minute and test again for a ferrous salt.

94. Tests for Oxalic Acid and Oxalates (SECTIONS **134, 136**).—(*a*) *Oxalic acid and sulphuric acid.*—Heat about 2 grams of oxalic acid with about 5 cc. of concentrated sulphuric acid. (*Eq.*) Pour some of the gas formed into a test-tube containing a solution of barium hydroxide, and shake. Ignite the gas which is produced in the reaction. How could you prepare carbon monoxide free from carbon dioxide by making use of this decomposition? What other acid yields carbon monoxide when heated with sulphuric acid?

(*b*) *Silver oxalate.*—In a test-tube neutralize a solution of oxalic acid with ammonia; if a slight excess of ammonia is added, boil the solution until it is neutral to litmus. Cool and add a solution of silver nitrate. A precipitate of silver oxalate is formed. (*Eq.*) Heat to boiling. Compare the results with those obtained with formic acid (experiment 87*b*, page 64).

(*c*) *Precipitation of calcium oxalate.*—To a solution of oxalic acid add ammonia in slight excess, and then a solution of calcium chloride. (*Eq.*) Test the solubility of the precipitate in a solution of acetic acid and in dilute hydrochloric acid. How would calcium carbonate act when treated with acetic acid?

(*d*) *Reducing action of oxalic acid.*—To a solution of oxalic acid or an oxalate add dilute sulphuric acid and a solution of potassium permanganate. (*Eqs.*)

(*e*) Repeat (*d*), using a solution of potassium bichromate in place of one of potassium permanganate. (*Eqs.*)

CHAPTER VI

ETHERS, ESTERS, AND ANHYDRIDES

95. Preparation of Ether from Alcohol (SECTION **143**).—(*a*) CAUTION.—Ether is very inflammable and very volatile; as its vapor readily ignites, vessels containing ether should not be brought near a flame or allowed to stay in a warm place. Place 50 cc. of ethyl alcohol in a 500-cc. distilling flask and add slowly, with constant shaking, 50 cc. of concentrated sulphuric acid. Close the neck of the flask with a two-holed stopper bearing a thermometer and a dropping funnel (Fig. 18, page 28), both of which reach to the bottom of the flask.[1] Place the flask on a sand-bath and connect it by means of a tightly fitting stopper with a long condenser, through which a rapid stream of cold water is passing. Use as a receiver a filter-bottle which is connected with the condenser by a tightly fitting stopper. Attach to the side-arm of the filter-bottle a long rubber tube, which extends almost to the floor. This tube serves to conduct the vapor of the ether, which is very heavy, away from any flames present on the desk. Heat the contents of the flask slowly. When the temperature reaches 140°, and ether distils over, add through the funnel 100 cc. of alcohol, allowing the latter to drop at about the same rate as that at which the ether distils (about 2 drops per second). During the entire time the temperature of the mixture in the flask should be maintained at 140°-145°.

Take the receiver from the immediate vicinity of any flames, and transfer the contents to a separatory funnel. Shake the ether with about one-fourth its volume of a solution of sodium hydroxide Draw off the lower aqueous layer, which should still be alkaline, add to the ether about one-fifth its volume of a cold mixture of equal volumes of concentrated sulphuric acid and water. Shake thoroughly, let the mixture stand until the two layers become clear. Draw off the acid layer and run the ether into a distilling

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[1] If a dropping funnel is not available or if the tube of the funnel is not long enough, arrange the apparatus as described in §40, page 28.

flask. Distil from a water-bath, and collect the distillate in a receiver in the way described above. Record the boiling point and the weight of the product obtained.

Ether boils at 35°. Write equations for the reactions which take place when alcohol is treated with sulphuric acid, and when the product of this reaction is heated with alcohol at about 140°. What would happen if in the experiment the temperature were allowed to rise as high as 180°?

(*b*) *Absolute ether.*—Shake in a separatory funnel 200 cc. of commercial ether with one-fifth its volume of a cold mixture of equal volumes of concentrated sulphuric acid and water. Let the mixture stand until the two layers are clear. Separate the acid layer and distil the ether in the way described in (*a*) above. Place the distillate in a *dry* bottle, add 5 grams of sodium in the form of a wire or thin shavings. Insert a calcium chloride tube in the neck of the bottle and allow it to stand until the evolution of hydrogen ceases. If the sodium becomes covered with a coating of sodium hydroxide, the latter can be removed by pressing upon the metal with a stout glass rod, or fresh pieces of the metal may be added from time to time. For most purposes the ether purified in this way can be used without distillation; it can be carefully decanted from the solid substances present. In order to redistil it, the ether is transferred to a clean dry flask containing about 1 gram of sodium shavings and distilled from a water-bath, taking the precautions described in (*a*) above, and using a carefully dried condenser and receiver. The first few cubic centimeters which distil should be rejected, as they contain the moisture present in the condenser tube and receiver.

NOTE.—(*a*) The ether is shaken with a solution of sodium hydroxide to remove the sulphur dioxide formed as a result of the reduction of the sulphuric acid by the alcohol or by the carbon that separates. The treatment with sulphuric acid removes the alcohol and nearly all the water. The method outlined above can be carried out more rapidly than the one commonly used, namely shaking with a solution of calcium chloride to remove alcohol and then drying first with anhydrous calcium chloride and then with sodium.

96. Properties of Ether (SECTIONS **143-147**).—(*a*) *Volatility of ether.*—Place a few drops of ether in the palm of your hand and breathe sharply across it. Explain the result.

(*b*) *Inflammability of ether.*—Place a few drops of ether on a watch-glass and apply a lighted match.

(*c*) *Explosive mixture of ether and air.*—Hold for about 5 seconds the neck of an open bottle containing ether over an empty wide-mouthed 250-cc. bottle, and then drop a lighted match into the latter.

(*d*) *Solubility of ether in water.*—Test roughly the solubility of ether in water as follows: Into a 100-cc. flask place 5 cc. of ether and add 40 cc. of water. Close the flask with a stopper and shake vigorously. Add water in portions of 5 cc. and shake each time, until the ether has completely dissolved. State the solubility you find as the result of your experiment.

(*e*) *Solubility of water in ether.*—Shake 10 cc. of ether with 10 cc. of water. Decant off the ether through a dry filter-paper into a dry test-tube. Test the filtered ether for water by means of anhydrous copper sulphate. (See experiment 79*c*, page 57.) Is water soluble in ether?

(*f*) *Solubilities of ether.*—Test the solubility of ether in an equal volume of alcohol, benzene, petroleum ether, dilute hydrochloric acid, concentrated hydrochloric acid, and a solution of sodium hydroxide.

(*g*) *Solubility of ether in sulphuric acid.*—Add very cautiously to 2 cc. of ether about 5 cc. of concentrated sulphuric acid. The tube should be shaken under water to keep the mixture cold. Is ether soluble in concentrated sulphuric acid? Pour the mixture slowly into a test-tube containing cracked ice. Are two layers formed? Explain. (See SECTION **145**.)

(*h*) *Reaction between ether and sulphuric acid.*—Repeat experiment (*g*), but warm the mixture gently over a free flame before it is poured onto the ice. Are two layers formed? Explain.

(*i*) *Ether and sodium.*—Add a shaving of sodium to about 5 cc. of absolute ether. If a gas is evolved, wait until the evolution ceases and add a fresh piece of sodium. Explain the result. If anhydrous ether is not available the experiment can be performed with ordinary ether, but a number of additions of sodium will be necessary before the metal does not react with the liquid. Why?

(*j*) *Decomposition of ether by hydriodic acid.*—Mix in a test-tube, kept cold by immersion in water, 1 cc. of ether and 3 cc.

of hydriodic acid (sp. gr. 1.7). lit the tube by means of a cork to a delivery-tube bent at a right angle, (See Fig. 20, page 31.) The end of the tube should extend nearly to the bottom of a test-tube which is placed in cold water. Heat the mixture of acid and ether carefully. When about one-third of the liquid has distilled over, add a little water to the contents of the cold tube and shake. Are there two liquids? Is one heavier than water?

97. Preparation of a Mixed Ether: Isoamyl Ethyl Ether (SECTION **144**).—Place 50 grams of isoamyl alcohol in a 200-cc. round-bottomed flask provided with a reflux condenser. Add slowly through the condenser 6 grams of sodium cut in small pieces. The alcohol may be heated slightly to hasten the reaction. When all the sodium has dissolved, add cautiously through the condenser, as the reaction is apt to be a violent one, 30 grams of ethyl bromide. Heat to boiling for 1 hour. (*Eq.*) Distil directly from the flask, using a water condenser, and collect the distillate in the following fractions: 80°-110°, 110°-114°, 114°-120°, 120°-130°. Fractionate twice. (See §21-23, and experiment 64, page 43.) Redistil the portion boiling at 110°-114°, and collect and weigh the part which distils at 111°-113°. Determine the specific gravity of your product (§56, page 37), and determine whether it dissolves in concentrated sulphuric acid. Calculate the percentage yield of ether obtained from the ethyl bromide used. The yield in the experiment should be about 50 per cent.

Isoamyl ethyl ether boils at 112°, and has the specific gravity 0.764 at 18°.

NOTE.—An excess of alcohol is used in the experiment to facilitate the reaction between it and sodium. Sodium isoamylate is a solid which is soluble in isoamyl alcohol. The sodium and ethyl bromide are used in the proportion of one atomic weight of the former to one molecular weight of the latter.

ACID ANHYDRIDES

98. Preparation and Properties of Acetic Anhydride (SECTIONS **148, 149**).—(*a*) Place 50 grams of freshly fused sodium acetate[1] in a 250-cc. distilling flask. Connect the flask with a condenser

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[1] For the preparation of fused sodium acetate see experiment 60*a*, page 44.

and a receiver, using for the latter a distilling flask which is fitted tightly to the condenser by means of a stopper. Protect the inside of the flask from moisture by connecting a drying tube to the side-arm of the receiver. Insert in the neck of the flask a cork bearing a separatory funnel which contains 40 grams of acetyl chloride. Immerse the flask in cold water and add about one-half of the acetyl chloride very slowly. The liquid should not be allowed to get hot enough to boil. Disconnect the flask from the condenser and shake it cautiously, while it is still in the water. Replace the condenser and add the rest of the chloride. If any liquid distils over during the addition of the acetyl chloride, it should be returned to the distilling flask. Replace the separatory funnel by a cork and distil, keeping the flame in motion to avoid local over-heating. Add about 2 grams of fused sodium acetate to the receiver and distil; note the boiling-point of the liquid, and weigh the product obtained. (*Eq.*) Calculate the theoretical yield, and the percentage of this obtained in the experiment. If the substances from which the anhydride is prepared are not brought together in the proportions represented by the chemical equation, from which substances should the theoretical yield be calculated? In the above experiment which substance is used in excess? Why?

Acetic anhydride boils at 138°. The yield should be from 35 to 40 grams.

(*b*) *Acetic anhydride and water.*—Add about 1 cc. of acetic anhydride to 5 cc. of water. Do the two liquids mix? Shake the test-tube vigorously and finally warm gently. (*Eq.*)

(*c*) *Acetic anhydride and sodium hydroxide.*—Shake 2 cc. of the anhydride with 5 cc. of a solution of sodium hydroxide. (*Eq.*)

(*d*) *Acetic anhydride and alcohol.*—Repeat experiment 79*h*, page 58.

(*e*) *Identification of acetic anhydride.*—Add cautiously 2 cc. of acetic anhydride to 2 cc. of aniline, and heat the mixture to boiling. Pour the product while still hot into about 20 cc. of cold water. Shake vigorously, decant off the water and wash twice with cold water. Dissolve the product in boiling water, avoiding an excess of the solvent. Filter hot through a fluted filter-paper, and cool the solution in running water. Filter off the crystals by suction (§12, page 7), dry them on a porous plate and determine their melting-point. If the compound does not melt sharply, it should be recrystallized from boiling water.

Acetanilide, the product of this reaction, melts at 116°, boils at 304°, and crystallizes from hot water in colorless prisms. (See note below and SECTION **497**.)

NOTES.—*(a)* The first distillate is redistilled from a small amount of sodium acetate in order to convert any unchanged acetyl chloride into anhydride.

(*b*, *c*, and *d)* These reactions apply in general to anhydrides and are useful in their identification. The determination of the physical property of the acids or esters formed is often made in the identification of anhydrides. Sulphuric acid is a valuable catalytic agent in the reaction which takes place between alcohols and anhydrides.

(*e*) The chemical reaction in this test is analogous to that which takes place between an anhydride and ammonia:

$$(CH_3CO)_2O + 2NH_3 = CH_3CO.NH_2 + CH_3COONH_4$$

Aniline is related to ammonia; its formula is $NH_2C_6H_5$. The reaction with acetic anhydride takes place according to the following equation:

$$(CH_3CO)_2O + 2NH_2C_6H_5 = CH_3CO.NHC_6H_5 + CH_3COONH_3C_6H_5$$

In the case of ammonia, acetamide is formed; the product with aniline is acetanilide, The second substance formed is the aniline salt of acetic acid; this is soluble in water and is readily removed when the product of the reaction is crystallized. The preparation of anilides in this way from acid anhydrides is often effected in the identification of anhydrides. The anilides are solids, which can be readily purified; as a consequence, an identification can be accomplished with a very small amount of a substance.

99. Preparation of Succinic Anhydride (SECTION **150**).—HOOD.—Heat to boiling for about one-half hour, in a dry round-bottomed flask provided with a return condenser, a mixture of 10 grams of phosphorus oxychloride and 15 grams of succinic acid. It is advisable to use a return condenser like the one illustrated in Fig. 17, page 27.

When the flask is cold, add 50 cc. of acetone and heat on the steam-bath until the solid has dissolved. Filter hot and set aside to crystallize. Filter off the crystals by suction (§12, page 7), and wash them with a few cubic centimeters of cold acetone. Weigh the product and determine its melting-point. Calculate the percentage yield.

Succinic anhydride melts at 120°; it may be recrystallized from hot chloroform, in which it is difficultly soluble, or from acetone.

NOTE.—Phosphorus oxychloride is used as a dehydrating agent in this preparation. The reaction takes place according to the following equation:

$$2(CH_2COOH)_2 + POCl_3 = 2(CH_2CO)_2O + HPO_3 + 3HCl$$

ESTERS

100. Preparation of Potassium Ethyl Sulphate (SECTION **159**). (*a*) Pour into a small flask 20 cc. of ethyl alcohol, and add slowly with constant shaking 10 cc. of concentrated sulphuric acid. Connect the flask with a reflux condenser and heat on a boiling water-bath for one-hour. Cool the liquid and pour it slowly into 200 cc. of cold water. The solution contains ethyl sulphuric acid, alcohol, and sulphuric acid. The acids are separated by making use of the fact that barium ethyl sulphate is soluble in water and barium sulphate is insoluble. Add to the solution, with constant stirring, small quantities of barium carbonate[1] as long as carbon dioxide is evolved. Filter in a porcelain funnel, and wash the precipitate twice with about 20 cc. of hot water, The filtered solution contains barium ethyl sulphate. Write equations for all the reactions. Test 5 cc. of the solution for barium in the usual way. (*Eq.*) Test the solution for a sulphate. Result? Heat about 5 cc. of the solution with about 1 cc. of dilute hydrochloric acid. (*Eq.*)

(*b*) *Conversion of barium ethyl sulphate into potassium ethyl sulphate.*—Heat the rest of the solution of barium ethyl sulphate to boiling and add a solution of potassium carbonate until the solution is slightly alkaline. (*Eq.*) Filter hot, wash the precipitate twice with a small amount of hot water, and evaporate the filtrate to crystallization (see §9, page 6) on the steam-bath. When cold, filter off the crystals and wash them with a little cold alcohol; dry on a porous tile. The salt can be recrystallized from boiling alcohol.

101. Preparation of Ethyl Acetate from Alcohol and Acetic Acid.—(SECTION **160**).—Mix in a dry 200 cc. distilling flask 50 grams of alcohol, 60 grams of glacial acetic acid, and 4 cc. of

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[1] If barium carbonate is not available, calcium carbonate may be used.

concentrated sulphuric acid. Cover the side-arm of the flask with a cork bored half way through its length. Connect the flask with a reflux condenser, and heat to boiling for 30 minutes. (See Fig. 16, page 26.) At the end of this time, arrange the apparatus for distillation, using a water condenser and having a thermometer to record the temperature of the vapor. Distil into a flask; when the temperature registers 100°, collect separately about 1 cc. of the distillate and add it to about 5 cc. of water. If the mixture does not separate into two layers, stop the distillation. Shake the distillate in the flask with 30 cc. of water, and add solid sodium carbonate until a drop of the ester is neutral to moist litmus paper. Transfer to a separatory funnel, draw off the water, and shake the ester twice with a saturated solution of calcium chloride, using 50 cc. each time. Draw off the ester into a distilling flask, add about one-fourth its volume of anhydrous calcium chloride, close the flask and cover the side-arm with corks, and let stand for at least 1 hour. Distil from a water-bath. Note the boiling-point and the weight of ester obtained, and calculate the percentage yield from the acetic acid used. Why from the acetic acid?

Ethyl acetate boils at 77°, has the specific gravity of 0.9028 18°/4°, and is soluble in 17 parts of water at 17.5°. The yield should be 80 to 85 per cent of the theoretical.

NOTE.—The sulphuric acid used in the preparation serves as a catalytic agent. The amount of alcohol used is that equivalent to the acid (equal molecular proportions) plus that which combines with the sulphuric acid to form ethyl hydrogen sulphate. The ester obtained in the first distillation contains alcohol and acetic acid. The former is removed by shaking with calcium chloride, and the latter by treatment with sodium carbonate.

102. Formation of Ethyl Acetate from Acetyl Chloride and from Acetic Anhydride.—Consult your notes on experiments 79*g* and *h*, page 58. If you have not carried out the experiments, do so now.

103. Properties of Ethyl Acetate (SECTION **162**).—(*a*) *Hydrolysis of ethyl acetate.*—Place 25 cc. of ethyl acetate and a solution of 14 grams of sodium hydroxide in 200 cc. of water in a round-bottomed flask connected by a tightly fitting cork to a reflux condenser. Place the flask in boiling water, and heat until liquid ceases to flow back from the condenser (about threefourths of an hour). Transfer the liquid to a distilling flask, and distil off 50 cc. into a small flask. Reserve for future study the contents of the distilling flask. Add solid potassium carbonate to the distillate in small portions. Close the flask and shake it. Repeat the addition of the salt until a part of it remains undissolved. Pour the two layers into a separatory funnel, run off the lower aqueous solution, and shake again with a small quantity of dry potassium carbonate. Place the alcohol in a small distilling flask, add about one-fourth its volume of anhydrous copper sulphate, and allow the mixture to stand about 15 minutes with occasional shaking. Distil the alcohol on a water-bath directly from the flask, and note its boiling-point. Apply the iodoform test to a few drops of the alcohol (experiment 81*b*, page 59).

Make the original aqueous solution obtained in the hydrolysis strongly acid with dilute sulphuric acid (*Eq.*), and distil over 50 cc. What does the distillate contain? Prove your conclusions by a suitable test. Explain how the procedure used in this experiment serves to separate an acid and an alcohol. Is the process one of general applicability?

(*b*) *Ethyl acetate and concentrated sulphuric acid.*—Add gradually with constant shaking, and keeping the mixture cool by running water, 2 cc. of ethyl acetate to 4 cc. of concentrated sulphuric acid. Pour the solution very slowly, keeping the tube cold, into 10 cc. of cold water. Will this test distinguish an ester from an ether? From a saturated hydrocarbon?

Repeat the experiment, but heat the mixture for a minute at about 100° before adding the solution to water. (*Eq.*)

(*c*) *Ethyl acetate and hydriodic acid.*—Repeat experiment 96*j*, using ethyl acetate in place of ether. For what is the test used? Will alcohol give a positive result?

104. Preparation of Isoamyl Acetate from Sodium Acetate.—Place in a 750-cc. round-bottomed flask, provided with a return condenser, 60 grams of finely powdered anhydrous sodium acetate (see experiment 66*a*), and add through the condenser, very slowly, 70 grams (38 cc.) of concentrated sulphuric acid. Add, next, 65 grams of isoamyl alcohol. Heat on a wire gauze for one-half hour. Connect the flask with a condenser arranged for distillation, and distil as long as liquid passes over. Pour the distillate into a separatory funnel, and wash it twice with an equal volume of water. Separate the ester, and dry it over anhydrous calcium chloride. Pour off the liquid and distil. Collect and weigh the portion which boils at 137°-141°. Calculate the theoretical yield from the sodium acetate used, and the percentage of this obtained. Test the solubility of isoamyl acetate in concentrated sulphuric acid.

Isoamyl acetate boils at 139°. The yield should be about 67 grams.

NOTE.—It is often advisable to prepare esters from salts rather than from the free acids. The salts can be more readily obtained in an anhydrous condition and, being solids, smaller quantities can be handled conveniently. In the preparation of esters from salts, enough sulphuric acid must be added to liberate the organic acid; equal molecular quantities must be used, since acid sulphates are formed. A small excess of sulphuric acid should be present to act as a catalytic agent. Enough of the alcohol is used to interact with both the organic acid and the excess of sulphuric acid.

FATS AND OILS

105. Properties of Fats and Oils (SECTIONS **167-169**).—(*a*) *Solubility of fats and oils.*—Test the solubility of 1 gram of lard and 1 cc. of olive oil in water, ether, alcohol, chloroform, and petroleum ether.

(*b*) *Extraction of fat.*—Partly fill a small evaporating dish with sand; pour 25 cc.of milk, into the dish and evaporate on the steam-bath to dryness. Grind the residue and put it, together with 100 cc. of ether or petroleum ether, into a dry stoppered bottle. At the next exercise filter off the ether into a beaker, and set it aside to evaporate spontaneously. Examine the resulting product. What is it?

(c) Saponification of a fat.—Read your notes on the saponification of lard (experiment 92*a*, page 67). If you have not performed the experiment, do so now.

(*d*) *Saponification of olive oil.*—Warm together on the steam-bath for 10 minutes 5 cc. of olive oil and 1 gram of sodium hydroxide dissolved in 20 cc. of alcohol. Pour the product into water and add dilute sulphuric acid. (*Eq.*)

(*e*) *Saponification of butter.*—Saponify 15 grams of butrat ment with lard (experiment 92*a*, page 67). As soon as the mixture is thick and homogeneous, pour it into 15 cc. of water. Transfer the solution of soap to a distilling flask, acidify with 25 cc. of sulphuric acid (1 part of acid to 4 of water), and distil over about 15 cc. Test the distillate with litmus paper. Are the volatile acids soluble in water? Note the odor of the solution. What causes the odor? Determine whether the oily layer in the distilling flask contains acids. Find out if it is soluble in alkalies. What happens when an acid is added to the alkaline solution so formed?

(*f*) *Test for unsaturated glycerides.*—Dissolve 5 cc. of olive oil or cotton-seed oil in 5 cc. of carbon tetrachloride, and add a solution of bromine in carbon tetrachloride, drop by drop.

(*g*) *Oils and concentrated sulphuric acid.*—Add to 10 cc. of olive oil or cotton-seed oil contained in a small beaker 5 cc. of concentrated sulphuric acid. Stir with a thermometer and note the rise in temperature. Repeat, using kerosene. Is there a difference? Explain.

(*h*) *Emulsification of oils.*—In five test-tubes prepare the following mixtures: (1) 10 cc. of a 0.2 per cent solution of sodium carbonate and 2 drops of neutral olive oil. (2) 10 cc. of a 0.2 per cent solution of sodium carbonate and 2 drops of rancid olive oil. (3) 10 cc. of a warm solution of soap and 2 drops of the neutral oil. (4) 10 cc. of white of egg solution and 2 drops of neutral oil. (5) 10 cc. of water and 2 drops of neutral oil. Shake the tubes very vigorously and let them stand for a few minutes. Record the results in each case. Under what conditions is the oil most perfectly emulsified?

Examine a drop of milk under a microscope.

NOTES.—(*b*) The fat can be extracted from milk in the usual way in a separatory funnel with ether. In the analysis of foods, however, the product is always dried before extraction. Milk can be dried as directed above, or it can be absorbed on filter-paper which is then dried.

(*d*) If saponification is complete there should be no separation of oil when the product is diluted with water.

(*e*) When this reaction is carried out quantitatively and 5 grams of fat or oil are used, the number of cubic centimeters of a tenth normal solution of sodium hydroxide required to neutralize the soluble volatile acids is called the Reichert-Meissl number.

(*g*) The reaction illustrated in this test is the basis of a method used in the analysis of oils. The number of degrees rise in temperature when 50 grams of an oil are treated with 10 cc. of sulphuric acid, in a vessel constructed in such a way as to avoid loss of heat by radiation, is called the Maumené number of the oil.

(*h*) Oils which have become rancid contain free fatty acids. The latter can be detected as follows: Dissolve in about 2 cc. of alcohol a drop of phenolphthalein solution and 1 or 2 drops of a very dilute solution of sodium hydroxide. To the resulting solution, which should have a light pink color, add an alcoholic solution of the fat to be tested for free acid. If the latter is present the color will disappear.

If a sample of rancid olive oil is not available for the experiment, mix together the neutral oil and oleic acid in the proportion of 1 cc. of the former to 1 drop of the latter, and shake 2 drops of the mixture with the solution of sodium carbonate.

The factors which lead to the formation of emulsions are not definitely known. The most permanent emulsions are formed when an insoluble oil is shaken with a solution which contains a substance that interacts with one of the constituents of the oil to produce a colloid. This occurs when an oil containing free fatty acids is shaken with an aqueous solution of an alkali. A layer of soap is formed around the particles of the oil, and it is probable that a layer of oil may surround the colloidal particles of soap. When a solution of egg albumin is shaken with olive oil, a layer of the coagulated protein is formed around the drops of the oil and emulsification takes place.

CHAPTER VII

ALDEHYDES AND KETONES

106. Formation and Properties of Formaldehyde (SECTIONS **176, 177**).—(*a*) Prepare a dilute solution of formaldehyde by oxidizing methyl alcohol as directed in experiment 77*b*, page 55, and make the following tests:

(*b*) Perform experiment 77*b*. Repeat the experiment, using 6 drops of a cold saturated alcoholic solution of gallic acid in place of the solution of resorcin.

(*c*) *Formaldehyde in milk.*—Mix 2 cc. of the formaldehyde solution prepared in (*a*) above with 5 cc. of milk, add 3 drops of a solution of ferric chloride, hold the tube in a slanting position, and pour down it slowly 5 cc. of concentrated sulphuric acid in such a way that the acid forms a layer at the bottom of the tube. Repeat the test with a sample of milk free from formaldehyde, which has been diluted with an equal volume of water.

(*d*) *Reducing action of formaldehyde.*—Clean a test-tube thoroughly by boiling a strong solution of sodium hydroxide in it, and then washing with water. Place in the test-tube about 5 cc. of a dilute solution of silver nitrate, and add a dilute solution of ammonia, drop by drop, until the precipitate first formed is just dissolved. Add about 1 cc. of the dilute solution of formaldehyde and put the tube into warm water.

(*e*) *Formaldehyde and Schiffs reagent.*—Add a few drops of the solution of formaldehyde to 5 cc. of Schiff's reagent.

(*f*) *Formaldehyde and Fehling's solution.*—Add 1 cc. of the dilute solution of the aldehyde to 5 cc. of Fehling's solution and heat to boiling. The preparation of Fehling's solution is described in the Appendix. (See note below and SECTION 188.)

(*g*) *Polymerization of formaldehyde.*—Evaporate on the steam-bath 10 cc. of formalin (a 40 per cent solution of formaldehyde). Heat some of the residue over a free flame and note cautiously the odor.

(*h*) *Formaldehyde and proteins.*—Place in a solution of 1 cc. of formalin and 5 cc. of water a thin piece of gelatin and let it stand for from 10 to 20 minutes. Place the gelatin in water and heat to boiling. Try the action of boiling water on gelatin which has not been in contact with formalin.

NOTES.—(*b*) In these teats very dilute solutions of formaldehyde should be used, since strong solutions give precipitates which obscure the colors that develop.

(*c*) A test similar to that described is made by pouring into the tube containing the milk, so that two layers are formed, concentrated hydrochloric acid containing a small amount of ferric chloride.

(*e*) It should be noted that alkalies or salts which give an alkaline reaction produce a pink color with Schiff's reagent; it also becomes colored when heated. The preparation of the reagent is described in the appendix.

(*f*) Fehling's solution is much used in testing for aldehydes. It consists of a solution prepared by dissolving copper sulphate, sodium hydroxide, and sodium potassium tartrate in water, the tartrate serving to keep in solution the copper hydroxide, which would otherwise precipitate. The aldehyde reduces the cupric compound in the alkaline solution to cuprous oxide.

107. Preparation of Acetaldehyde from Alcohol (SECTION **178**).—A 500-cc. distilling flask containing 80 grams of powdered potassium or sodium bichromate is closed by a cork bearing a separatory funnel, and connected with a long condenser through which a rapid stream of water below 15° passes. The condenser is attached to one end of an adapter the other end of which extends to bottom of a receiver sunk to its neck in ice-water. Drop in slowly through a funnel a cold mixture of 160 cc. of water, 40 grams of alcohol, and 70 cc. of concentrated sulphuric acid. A vigorous reaction takes place; as this subsides the mixture is run in more rapidly. The flask is shaken occasionally to prevent the bichromate from forming a cake at the bottom. When all the mixture has been added, and the action has ceased, replace the funnel by a thermometer and heat the flask very gently; remove the flame as soon as reaction sets up again. Repeat the heating in this way until reaction ceases when the flame is withdrawn. Care should be taken to prevent the rise of the thermometer beyond 65°. Place the distillate in a small distilling flask provided with a long condenser and receiver cooled by ice-water as described above, put the flask in water, and heat the latter slowly up to 50°. Collect the portion which boils between 20° and 35°. Acetaldehyde boils at 21°. The product obtained contains some water, but can be used for the experiments described below.

108. Properties of Acetaldehyde (SECTIONS **179-185**).—(*a*) *Aldehyde and sodium hydrogen sulphite.*—Shake under water 2 cc. of the aldehyde prepared in the experiment just described with 5 cc. of a saturated solution of sodium hydrogen sulphite. (*Eq.*) Note the disappearance of the odor of aldehyde. Add 5 cc. of a strong solution of sodium carbonate and heat, noting the odor. (*Eq.*)

(*b*) *Aldehyde and bromine.*—To 2 cc. of the aldehyde add bromine, drop by drop, as long as the solution is decolorized. The bromine should be added slowly as the reaction at first is delayed. When the reaction is complete add about 10 cc. of water. Does a heavy oil separate? (*Eq.*)

(*c*) *Polymerization of aldehyde.*—Dip a glass rod into concentrated sulphuric acid, and remove as much of the acid as possible by shaking. Dip the rod into 2 cc. of aldehyde. Note the reaction. (*Eq.*) Add 5 cc. of water.

(*d*) *Aldehyde resin.*—Boil a few drops of aldehyde in 5 cc. of water with a few drops of a solution of sodium hydroxide. Note the appearance and odor of the product. Repeat the test using a solution of formaldehyde.

(*e*) *Oxidation of aldehyde.*—Add, in small portions, a dilute solution of potassium permanganate to a solution of 2 cc. of aldehyde in 5 cc. of water. (*Eq.*) Recall the action of an unsaturated hydrocarbon with a solution of potassium permanganate. Is the test with this salt a positive proof that a compound contains a double or triple bond between carbon atoms? How could you distinguish between a solution of an aldehyde and one of ethylene?

(*f*) *Reducing action of aldehyde.*—Warm 5 drops of aldehyde with 5 cc. of Fehling's solution.

(*g*) *Tollen's reagent for aldehydes.*—Test 3 drops of aldehyde with an ammoniacal solution of silver nitrate as described in experiment 106*d*, page 84, or *without* heating with Tollen's reagent.[1] (*Eq.*) Clean the test-tube to be used by boiling it out with a solution of sodium hydroxide.

(*h*) *Schiff's reagent and aldehydes.*—Test a few drops of the aldehyde with about 5 cc. of Schiff's reagent.[1]

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[1] See Appendix.

109. Formation of Acetaldehyde from an Acetate (SECTION **178**).—Mix together 5 grams of sodium formate and 6 grams of anhydrous sodium acetate in an 8-inch test-tube. Place the tube in an inclined position and attach by means of a cork a delivery-tube which dips under water contained in a test-tube. Heat for a few minutes. Test the resulting solution of aldehyde with Schiff's reagent.

KETONES

110. Formation of Acetone from an Acetate (SECTION **193**).—Place in an 8-inch test-tube 7 grams of calcium acetate and 7 grams of anhydrous sodium acetate which have been intimately mixed by grinding together in a mortar. Clamp the tube in a horizontal position and connect it with a condenser. Tap the tube gently so that a channel is formed along its whole length. Heat until the acetates glow, turning the tube from time to time, so that all of the salts can be heated to a high temperature. Redistil the liquid and determine its boiling-point.

Acetone boils at 56°. The yield is from 3 to 4 grams.

NOTE.—Sodium acetate is mixed with calcium acetate in this preparation in order to facilitate the formation of acetone.

111. Properties of Acetone (SECTIONS **194, 200**).—(*a*) *Acetone and Schiff's reagent.*—Add a few drops of acetone to 5 cc. of Schiff's reagent. Examine the solution after it has stood some time.

(*b*) *Acetone and sodium hydrogen sulphite.*—Mix 5 cc. of acetone with 5 cc. of a saturated solution of sodium hydrogen sulphite; shake and cool. *(Eq.)*

(*c*) *Acetone and Tollen's reagent.*—Test a few drops of acetone dissolved in 5 cc. of water with an ammoniacal solution of silver nitrate or with Tollen's reagent.

(*d*) *Conversion of acetone into iodoform.*—Apply the iodoform test to a dilute solution of acetone. (See experiment 81*b*, page 59.)

(*e*) *Acetone and phosphorus pentachloride.*—HOOD.—To 5 cc. of acetone contained in a test-tube placed in cold water add, with constant shaking, small quantities of phosphorus pentachloride as long as any reaction takes place. Pour the contents of the tube slowly into cold water. Does a heavy liquid separate? (*Eq.*)

(*f*) *Identification of acetone.*—Acetone can be converted into a solid compound which is valuable in its identification, especially if the ketone is in a dilute aqueous solution. The substance prepared is formed as the result of the interaction of acetone and benzaldehyde, $C_6H_5.CHO$, in the presence of an alkali; it is called dibenzalacetone. The reaction is as follows:

$$2C_6H_5.CHO + (CH_3)_2CO = (C_6H_5.CH{:}CH)_2CO + 2H_2O$$

Place in a small flask 1 cc. of acetone, 4 cc. of water, 4 cc. of benzaldehyde, 20 cc. of alcohol, and 5 cc. of a 10 per cent solution of sodium hydroxide. Boil gently for 5 minutes. Cool and shake. Filter off the crystals and wash them with 20 cc. of cold alcohol. Recrystallize from 20 cc. of boiling alcohol. Let the solution cool. Filter and wash with 10 cc. of cold alcohol. Dry on a porous plate and determine the melting-point of the crystals. Dibenzalacetone crystallizes in yellow plates and melts at 111°-112°.

CHAPTER VIII

AMINES AND AMIDES

112. Preparation of Methylamine from Acetamide (SECTION **204**).—Place into a 1 liter flask 100 cc. of water and 36 grams of fresh bleaching powder. Add 10 grams of acetamide dissolved in 25 cc. of water in small portions and shake. Add slowly a cold solution of 25 grams of sodium hydroxide in 100 cc. of water. Arrange the apparatus to distil with steam (see Fig. 14, page 20), and connect an adapter by means of a tightly fitting rubber stopper with the end of the condenser. Place the end of the adapter just below the surface of 50 cc. of cold water contained in a beaker, and distil with steam. From time to time remove the adapter, and test the distillate with litmus paper. Stop the distillation when methylamine ceases to distil over. The yield in this preparation, calculated from the methylammonium chloride obtained (see experiment 113*d* below), should be 70 per cent of the theoretical.

NOTE.—In the preparation of methylamine by Hofmann's reaction, bromine and potassium hydroxide are commonly used. The use of bleaching powder, instead of these reagents, which form potassium hypobromite, avoids the handling of large quantities of bromine, and reduces the cost of the preparation. The amount of bleaching powder to be used is determined by the percentage of available chlorine which it contains. The proportions given above are based on a bleaching powder which contains about 35 per cent of available chlorine.

113. Properties of Methylamine (SECTIONS **205-206**).—(*a*) *Basic properties of a solution of methylamine.*—Test the distillate obtained in the experiment just described with pink litmus paper.

(*b*) *Methylamine and solutions of metallic salts.*—Add a little of the distillate, drop by drop, as long as any change occurs, to 1 cc. of dilute solution of copper sulphate. Repeat with a solution of ferric chloride. Add ammonia to solutions of these salts. Write equations for the reactions in the case of ammonia and of methylamine; the reactions in the two cases are analogous.

(*c*) *Carbylamine reaction.*—HOOD.—Warm 1 cc. of the distillate with 2 drops of chloroform and 2 cc. of an alcoholic solution of potassium hydroxide, which may be prepared by heating a little of the solid compound with alcohol and decanting off the solution. (*Eq.*) Note the odor produced. Acidify the contents of the tube before pouring into the sink.

(*d*) *Methylammonium chloride.*—Make the rest of the distillate slightly acidic with hydrochloric acid, and evaporate the solution to dryness on the steam bath. Dissolve the salt in the smallest possible amount of boiling absolute alcohol; a small amount of ammonium chloride may be left as an insoluble residue. To dissolve the salt, add to the beaker on a steam-bath about 25 cc. of the alcohol; cover with a watch-glass, and let the salt digest with the hot alcohol for a few minutes. Filter through a funnel from which the stem has been cut (see Fig. 1, page 6). Continue the addition and digestion as long as the solvent appears to dissolve the salt. About 100 cc. of alcohol will be required. Cool the combined filtrates, and add an equal volume of ether. Filter off the crystals by suction and dry them on a porous plate. Determine the weight and the melting-point of the methylammonium chloride obtained.

(*e*) *Methylammonium chloride and alkalies.*—Heat together in a test-tube a very small amount of the salt with 2 cc. of a solution of sodium hydroxide. (*Eq.*) Note the odor of the gas.

(*f*) *Inflammability of methylamine.*—Place about 0.5 gram of methylammonium chloride and an equal amount of lime in a dry test-tube, and heat. Apply a flame to the gas. Does it burn? Repeat with ammonium chloride. Does ammonia burn in air?

(*g*) *Methylammonium chlorplatinate.*—Dissolve a small amount of methylammonium chloride in a few drops of alcohol, and add, drop by drop, a 10 per cent solution of platinic chloride. Repeat, using a few drops of a strong aqueous solution of ammonium chloride. The reactions in the two cases are analogous. Write the equations for both reactions.

(*h*) *Decomposition of methylammonium nitrite.*—Mix in a test-tube about 0.5 gram of methylammonium chloride with twice its weight of sodium nitrite and about 5 cc. of water. Connect the tube by means of a cork with a delivery-tube arranged to collect a gas over water. Heat the solution gently and collect two test-tubes full of the gas. (*Eq.*) Test the second tube for nitrogen with a glowing splinter. Distil over about 3 cc. from the tube into a second tube, surrounded by cold water. Test the distillate for methyl alcohol (experiment 77*b*, page 55).

114. Isolation of Lecithin from Egg-yolk (SECTION **217**).—Grind the yolk of one hard-boiled egg with 50 cc. of ether. Filter and wash the solid residue twice with 10 cc. of ether. Evaporate off the ether on the steam-bath, or distil it off from a small flask. Extract the residue twice with hot alcohol, using 10 cc. each time. Pour off the alcohol from the heavy oil through a small filter. Evaporate off the alcohol, dissolve the residue in 10 cc. of cold ether, and add 10 cc. of acetone. Stir until the particles of the precipitated lecithin adhere together and form a ball. Place the latter on a filter-paper. Describe its properties. Boil about one-fourth of the lecithin with about 10 cc. of a 10 per cent solution of sodium hydroxide. Note the odor of the gas evolved. What is it? Cool the solution. Is there any evidence of the formation of a soap? Filter, dissolve the precipitate in warm water and add dilute hydrochloric acid to the solution. What is precipitated? Test a part of the lecithin for nitrogen and for phosphorus (§§58, 59, 61, page 39).

NOTE.—Ether dissolves from egg-yolk, in addition to lecithin, some fat and protein. The protein and a part of the fat are removed by extracting the residue from ether with alcohol. The lecithin is finally separated by adding acetone to an etheral solution of the lecithin and fat. The latter is soluble in acetone while the lecithin is insoluble.

AMIDES

115. Preparation of Acetamide from Ethyl Acetate (SECTION **221**).—Mix in a 250-cc. distilling flask 50 grams of ethyl acetate and 100 cc. of a concentrated aqueous solution of ammonia (sp. gr. 0.90). Close the flask with corks and let the mixture stand over night, until the two layers first formed have disappeared. (*Eq.*) Arrange the flask for distillation with a thermometer and water condenser, and use as a receiver a distilling flask or a filter-bottle, the side-arm of which is provided with a tube which dips under water; the latter precaution is taken to absorb the large quantity of ammonia which is given off in the distillation. Distil carefully; collect the first part (about 10 cc.) of the distillate separately and test it for ethyl alcohol When the thermometer registers 160°, replace the water-condenser by an air-condenser, change the receiver, using this time a beaker, and collect what distils at 160°-225°. As the temperature rises the acetamide solidifies in the condenser to a crystalline mass. which can be readily liquefied by warming the condenser cautiously with a free flame. When the distillate is cold pour off from the crystals in the receiver any liquid present, and dry the crystals on a porous plate. Weigh the product obtained and determine its melting-point. Calculate the percentage yield obtained. The slightly impure acetamide may be purified by a second distillation, or by crystallizing it from a mixture of one volume of alcohol and two volumes of ether. If the product obtained in the first distillation does not melt sharply, recrystallize a small portion of it.

Acetamide melts at 82°, and boils at 222°. The yield obtained in the preparation should be about 65 per cent of the theoretical.

NOTE.—The odor of the amide prepared as directed above is due to an impurity which is present in small quantity. By a single recrystallization the compound is obtained in an odorless condition.

116. Properties of Acetamide (SECTION **221**).—(*a*) *Hydrolysis of acetamide.*—Mix about 0.5 gram of acetamide with about 5 cc. of a solution of sodium hydroxide, shake and observe whether the odor of ammonia is present. Heat the solution to boiling. Is ammonia set free? (*Eq.*)

(*b*) Heat to boiling for 1 minute about 0.5 gram of acetamide with 2 cc. of dilute sulphuric acid. Cool, and make alkaline with a solution of sodium hydroxide. Does the solution smell of ammonia? Explain.

(*c*) *Mercury salt of acetamide.*—Add an excess of a solution of sodium hydroxide to 2 cc. of a solution of mercuric chloride. (*Eq.*) Determine whether the precipitate dissolves when a little acetamide is added. (*Eq.*) Test the solution for mercury with hydrogen sulphide.

(*d*) *Acetamide and nitrous acid.*—To an aqueous solution of acetamide add a few crystals of sodium nitrate and a few drops of dilute sulphuric acid. (*Eqs.*)

117. Preparation of Urea from a Cyanate (SECTION **223**).—Dissolve 8 grams of potassium cyanate in 20 cc. of hot water and 13 grams of ammonium sulphate in 20 cc. of hot water. Mix the solutions and evaporate to dryness on the steam-bath. (*Eq.*) Grind the product to a fine powder and dry on the steam-bath for 15 minutes. Place the solid in a dry beaker and add 25 cc. of alcohol. Cover with a watch-glass, and let the mixture digest just below the boiling-point of alcohol for a few minutes. Decant off the liquid through a filter and digest a second time. If the solution is colored, boil the combined filtrates with a little bone-black. Filter and evaporate on the steam-bath to crystallization (see §9, page 6). When the solution is cold, filter off the crystals by suction (see §12, page 7) and dry them on a porous plate. From the filtrate a second crop of crystals may be gotten by evaporation and the addition of an equal column of ether to the cold solution. Weigh the urea obtained and determine its melting-point.

Urea melts at 132°, and can be crystallized from hot amyl alcohol.

NOTE.—The blue substance formed at times in this preparation is probably produced as the result of the following cause: Commercial potassium cyanate may contain potassium ferrocyanide. If this is the case, when a solution of the salt is evaporated in the air with ammonium sulphate containing a trace of iron, Prussian blue is formed.

118. Properties of Urea (SECTIONS **223, 224**).—(*a*) *Nitrate of urea.*—Dissolve a crystal of urea in a drop of water on a microscope slide; place near this solution a drop of concentrated nitric acid, and bring the two together by touching with a glass rod. (*Eq.*) Examine the crystals under the microscope.

(*b*) *Urea and oxalic acid.*—Repeat *(a)* above but use a saturated solution of oxalic acid in place of nitric acid. (*Eq.*)

(*c*) *Hydrolysis of urea.*—Treat about 0.5 gram of urea with 5 cc. of a solution of sodium hydroxide. Note whether ammonia is given off. Explain. Boil the solution for a minute or two and observe if ammonia is given off freely. (*Eq.*) Test the vapor with litmus paper.

(*d*) *Urea and nitrous acid.*—Place in a test-tube 0.1 gram of sodium nitrite and 10 cc. of water; in another tube put 0.1 gram of sodium nitrite, 10 cc. of water and 0.2 gram of urea. Add to each tube 1 cc. of dilute acetic acid. Compare the amount and color of the gas given off in each case. (*Eqs.*)

(*e*) *Urea and sodium hypobromite.*—Prepare an alkaline solution of sodium hypobromite by adding 3 drops of bromine to 5 cc. of a dilute solution (10 per cent) of sodium hydroxide. Add this solution to a dilute solution of urea. (*Eq.*)

(*f*) *Urea and mercuric nitrate.*—To a dilute solution of urea add a 1 per cent solution of mercuric nitrate. A compound of the formula $CO(NH_2)_2.Hg(NO_3)_2.HgO$ is precipitated.

(*g*) *Action of heat on urea: biuret* (SECTION **224**).—Heat cautiously about 0.5 gram of urea in a dry test-tube; continue the heating until a white opaque solid is formed. The residue is a mixture of biuret and cyanuric acid (SECTION **249**). Treat the residue when cold with about 5 cc. of water, shake, pour off the aqueous solution of biuret, and add 5 cc. of a solution of sodium hydroxide and a few drops of a dilute (1 per cent) solution of copper sulphate.

Dissolve the residue insoluble in water in a little ammonia, add a few cubic centimeters of a solution of barium chloride and shake. A precipitate of barium cyanurate is formed.

NOTES.—(*a*) The nitrate of urea is difficultly soluble in cold water and in nitric acid. This fact is made use of in the isolation of urea from urine.

(*c*) Ammonium salts can be distinguished from amides by means of sodium hydroxide; the former yield ammonia in the cold.

(*e*) Ammonium salts give nitrogen when treated with a solution of sodium hypobromite; they must, therefore, be absent when applying the test to urea. This reaction is used in the clinical examination of urine for urea.

(*f*) Many substances related to acid amides, for example the proteins, give precipitates with solutions of mercuric salts.

(*g*) This test for biuret is not characteristic; it is given by many substances in which there is a linking of atoms similar to that in biuret. The test is useful in the study of proteins.

CHAPTER IX

CYANOGEN AND RELATED COMPOUNDS

119. Formation of Cyanogen (SECTION **233**).—(*a*) *From mercuric cyanide.*—CAUTION.—Cyanogen is a poisonous gas. Perform the experiment under a hood. Heat in a small dry test-tube over a free flame about 0.5 gram of mercuric cyanide. Ignite the gas generated. Note the unusual color of the different parts of the flame. (*Eq.*)

(*b*) *From copper sulphate and potassium cyanide.*—CAUTION.—Potassium cyanide is very poisonous. It should not be touched with the fingers; use a spatula or handle small pieces with pincers. HOOD.—Add to 5 cc. of a cold saturated solution of copper sulphate a cold saturated solution of potassium cyanide until the precipitate first formed dissolves. (*Eq.*) Heat to boiling. (*Eq.*) and ignite the gas evolved. Add a solution of potassium iodide to a solution of copper sulphate. (*Eq.*) Determine by an appropriate test if iodine is liberated.

120. Formation of Potassium Cyanide from Potassium Ferrocyanide (SECTION **238**).—Heat to a high temperature in a porcelain crucible about 1 gram of potassium ferrocyanide. *(Eq.)* *When* cold add water, and heat to boiling. Pour off the solution and test for a cyanide according to the next experiment.

121. Test for a Soluble Cyanide (SECTION **240**).—To 1 cc. of a dilute solution of potassium cyanide add 5 drops of a solution of sodium hydroxide and 5 drops of a solution of ferrous sulphate; heat to boiling, cool, and add dilute hydrochloric acid, drop by drop, until the solution shows an acid reaction. If no color develops add 3 drops of a solution of ferric chloride. Potassium ferrocyanide is formed from the potassium cyanide and ferrous sulphate; the ferrocyanide and the ferric salt then form Prussian blue. **(***Eqs.***)**

NOTE.—It is usually not necessary to add ferric chloride, since the ferrous sulphate contains enough ferric salt to give the reaction. An excess of hydrochloric acid should be avoided since it interferes with the formation of the ferric ferrocyanide.

122. Action of Cyanides on the Soluble Salts of Heavy Metals (SECTION **238**).—(*a*) Add a few drops of a solution of potassium cyanide to a solution of ferric chloride. (*Eq.*) Next add an excess of potassium cyanide (*Eq.*), acidify, and then add a solution of ferrous sulphate. (*Eq.*)

(*b*) Add a few drops of a solution of potassium cyanide to a solution of silver nitrate (*Eq.*); add an excess of the cyanide. (*Eq.*) Determine if silver chloride is soluble in potassium cyanide. Precipitate some silver cyanide and determine its solubility in nitric acid and in ammonia. How could you distinguish silver chloride from silver cyanide?

123. Properties of Potassium Ferrocyanide (SECTION **240**).—(*a*) *Conversion into hydroferrocyanic acid.*—Add concentrated hydrochloric acid to about 10 cc. of a saturated solution of potassium ferrocyanide as long as a precipitate is formed, (*Eq.*) Pour off the liquid and place a part of the crystals on a porous plate. They turn blue due to oxidation.

(*b*) *Decomposition with strong sulphuric acid.*—In a test-tube moisten with 5 drops of water about 1 gram of powdered potassium ferrocyanide and add 5 cc. of concentrated sulphuric acid. Heat and apply a flame to the gas evolved, (*Eq.*)

(*c*) *Ferrocyanides of heavy metals.*—Add a solution of potassium ferrocyanide to solutions of salts of ferric iron, silver, copper, and mercury. (*Eqs.*)

124. Preparation of Potassium Ferricyanide from Potassium Ferrocyanide (SECTION **241**).—Dissolve 25 grams of potassium ferrocyanide in 50 cc. of warm water and add bromine-water to the solution until it no longer gives a blue color when a drop is placed on paper treated with a solution of ferric chloride (*Eq.*) About 175 cc. will be required. Evaporate to dryness in an evaporating dish on a steam-bath. Grind the solid in a mortar. add 10 cc. of cold water and grind again. Transfer the solid to a suction-filter and remove the liquid. Disconnect the filter-flask from the pump and add to the solid 10 cc. of cold water. After 2 or 3 minutes draw off the liquid. This procedure serves to remove most of the potassium bromide formed in the reaction between the ferrocyanide and bromine,

Transfer the solid to a small beaker, add 50 cc. of water, heat to boiling, and filter. Evaporate the filtrate on the steam-bath until the surface of the liquid is just covered by a solid crust. Set aside over night. Filter off and save the crystals, and let the mother-liquor evaporate spontaneously to recover the salt in solution.

125. Properties of Potassium Ferricyanide (SECTION **241**).—

(*a*) *Ferricyanides of heavy metals.*—Add a solution of potassium ferricyanide to solutions of salts of ferric iron, ferrous iron, silver, copper, and mercury. (*Eq.*)

(*b*) *Potassium ferricyanide as an oxidizing agent.*—In a small beaker dissolve 2 grams of lead nitrate in about 10 cc. of boiling water, and add a solution of sodium hydroxide until the precipitate first formed has dissolved. Next add a strong aqueous solution of 4 grams of potassium ferricyanide, and heat to boiling. (*Eq.*) Filter off the precipitate, test the filtrate for a ferrocyanide and determine if the precipitate is lead dioxide, PbO_2. Add hydrochloric acid to a little of the substance and heat. (*Eq.*)

NOTE.—(*b*) An alkaline solution of potassium ferricyanide is a valuable mild oxidizing agent, which is frequently used in the oxidation of organic compounds. The oxidizing power is equivalent to that represented in the following equation:

$$2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + O$$

ALKYL CYANIDES

126. Preparation of Methyl Cyanide (SECTION **244**).—Weigh directly into a dry 100-cc. distilling flask 20 grams of phosphorus pentoxide and add 20 grams of powdered acetamide; stir the mixture and shake it. Close the flask with a cork bearing a thermometer, connect with a condenser, and use a 25-cc. distilling flask as a receiver. Heat cautiously with a small flame, kept constantly in motion, as long as any liquid distils. Add to the distillate about 2 grams of phosphorus pentoxide, and redistill, collecting the portion which boils at 80°-82°. Weigh the distillate and calculate the percentage yield obtained.

Methyl cyanide (acetonitrile) boils at 81.6°. The yield obtained in the above experiment should be 50-60 per cent of the theoretical.

127. Hydrolysis of Methyl Cyanide (SECTION **244**).—(*a*) Heat about 1 cc. of methyl cyanide with a dilute solution of sodium hydroxide, and note the odor of the gas evolved. (*Eq.*)

(*b*) In a small round-bottomed flask mix 3 cc. of water and 6 cc. of concentrated sulphuric acid; cool the mixture and add 5 grams of methyl cyanide. Connect the flask with a return condenser and boil gently for 15 minutes. (*Eq.*) Dilute with about 5 cc. of water and distil off about 5 cc. Test the distillate for acetic acid. (See experiment 91, page 67.) Make a part of the contents of the flask strongly alkaline with sodium hydroxide and note the odor.

128. Formation of an Isocyanide (SECTION **246**).—Repeat the carbylamine test for primary amines (experiment 113*c*, page 90), in which an isocyanide is formed, or apply the test to aniline, $C_6H_5NH_2$, which is a primary amine containing the phenyl radical, C_6H_5; phenyl isocyanide, C_6H_5NC, is formed. Proceed as follows: HOOD.—Warm together 2 drops of aniline, 3 drops of chloroform, and 2 cc. of an alcoholic solution of potassium hydroxide. (*Eq.*) CAUTION.—As phenyl isocyanide has a very disagreeable odor and is poisonous, the tube containing it should be washed thoroughly under the hood.

CHAPTER X

HALOGEN COMPOUNDS

129. Preparation of Methyl Iodide from Methyl Alcohol and Phosphorus Iodide (SECTIONS **55, 252**).—In a 200-cc. round-bottomed flask place 15 grams of methyl alcohol and 3.2 grams of red phosphorus. Have ready a reflux condenser with cork attached. Place the flask in cold water and add in small portions at a time 38 grams of iodine; the addition should take about 10 minutes. If the contents of the flask begin to boil, attach it to the reflux condenser; when reaction ceases add more iodine. Finally attach the flask to the condenser and let it stand for at least 4 hours (preferably over night). Distil through a condenser from a water-bath, as long as any liquid passes over. The receiver should be placed in cold water as methyl iodide is very volatile. Wash the distillate by decantation with a dilute aqueous solution of sodium hydroxide until the lower layer is colorless, and then once with water. Separate the methyl iodide carefully from the water using a separatory funnel, and transfer it to a small distilling flask. Add about 10 grams of anhydrous calcium chloride. Stopper the flask, place a cork over the end of the side-arm, and set aside until the liquid is quite clear. Place a thermometer in the flask, connect the latter with a condenser, and distil from a water-bath. Note the boiling-point and weight of the methyl iodide. Calculate the theoretical yield from the iodine used (why iodine?), and the percentage of this obtained.

Methyl iodide boils at 44°, and has the specific gravity 2.27 at 15°. The yield in the experiment should be about 80 per cent of the theory.

NOTE.—An excess of the alcohol is usually taken in preparing alkyl halides by the method illustrated above. The phosphorus and iodine are used in the proportions necessary to form phosphorus tri-iodide, PI_3. The chief reaction which takes place is represented by the following equation:

$$3CH_3OH + P + 3I = 3CH_3I + P(OH)_3$$

The hydriodic acid which is evolved is produced as the result of side-reactions, which are described in the case of phosphorus trichloride in SECTION **65**.

130. Properties of Methyl Iodide (SECTION **254**).—(*a*) *Action of light on methyl iodide.*—Place in each of two small test-tubes 2 cc. of methyl iodide and close the tubes tightly with corks. Put one tube in the desk in the dark, and allow the other to stand in direct sunlight. At the end of an hour or two, examine the two tubes. To remove the iodine set free, add a drop of mercury or some copper wire and shake. The alkyl iodides should be kept in well-stoppered bottles of brown glass.

(*b*) *Methyl iodide and silver nitrate.*—To a few drops of colorless methyl iodide suspended in water add a solution of silver nitrate and shake. Repeat, using a solution of methyl iodide in alcohol and of silver nitrate in alcohol. (*Eq.*)

(*c*) *Methyl iodide and sodium hydroxide.*—Shake occasionally during half an hour a mixture of 1 cc. methyl iodide and 5 cc. of a dilute solution of sodium hydroxide. At the end of this time neutralize with dilute nitric acid, filter, and test a part of the filtrate for methyl alcohol according to experiment 77*b*, page 55, and a part for an iodide. For other reactions of alkyl halides, see the experiments with ethyl bromide below.

NOTE.—(*a, b,* and *c*) Methyl iodide is much more reactive than the other alkyl iodides. Reactions analogous to those illustrated in the above experiments take place with the higher iodides, but much more slowly. The bromides are less reactive than the iodides; the chlorides are, in most cases, very stable. Tertiary halides are much more reactive than the halides derived from secondary and primary alcohols.

131. Preparation of Ethyl Bromide from Alcohol, Potassium Bromide, and Sulphuric Acid (SECTION **252**).—Add to a mixture of 60 grams of alcohol and 50 cc. of water, contained in a 1-liter flask, 100 cc. of concentrated sulphuric acid. Cool thoroughly in running water, and add 100 grams of finely powdered potassium bromide. Connect the flask by means of a bent glass tube and a *rubber* stopper with a long condenser through which a rapid stream of water is passing, and fit an adapter by means of a cork to the end of the condenser. Use a 300-cc. Erlenmeyer flask as a receiver, and place it in a beaker about one-half full of cold water. Fill the receiver half full of water and adjust the condenser so that the end of the adapter is below the surface of the water. These precautions are taken because ethyl bromide is a very volatile liquid (boiling-point 39°). Place a sand-bath under the flask containing the reaction mixture, heat with a large flame, and distil as rapidly as possible. As distillation proceeds, the ethyl bromide drops to the bottom of the receiver, and the aqueous part of the distillate finally overflows into the beaker. Distil until drops of the insoluble bromide cease to appear, About one hour is required for the distillation if it is carried on rapidly.

Decant off most of the water from the ethyl bromide into a beaker, add a dilute solution of sodium hydroxide, shake, and decant. Wash again with water, and transfer to a separatory funnel; run off the lower layer into a small dry distilling flask, add anhydrous calcium chloride (about one-fourth the volume of the bromide), and close the flask tightly with corks. Set aside until the liquid is quite clear and no drops of water are visible; if the calcium chloride appears moist, add more and set aside again. Connect the flask with a long condenser and use as a receiver a dry flask surrounded by ice-water. Distil from a water-bath and collect the portion which boils at 35°-40°. Calculate the theoretical yield from the potassium bromide used (why from the bromide?) and the percentage yield obtained. Write equations for all reactions. Why does the solution turn red during the heating? (*Eq.*)

Ethyl bromide boils at 38.4° and has the specific gravity 1.47 at 13°. The yield in this preparation should be about 80 per cent of the theoretical.

NOTE.—The ethyl bromide prepared in this way contains a small amount of ether, from which it cannot be separated readily by distillation, since ether boils at 35° and ethyl bromide at 38.4°. In separating the two substances advantage is taken of the fact that ether is soluble in cold concentrated sulphuric acid, while ethyl bromide is not soluble. The bromide prepared by the method given above can be purified by adding it slowly with constant shaking, to an equal volume of concentrated sulphuric acid kept cold by immersion in ice-water. After this treatment the liquids are separated and the ethyl bromide shaken with water, dried, and distilled.

132. Properties of Ethyl Bromide (SECTIONS **254**, **255**).—(*a*) *Solubilities of ethyl bromide.*—Using about 1 cc. in each test, determine whether ethyl bromide dissolves in the following liquids: water, alcohol, ether, petroleum ether, and cold concentrated sulphuric acid.

(*b*) *Test for bromine in ethyl bromide.*—Test ethyl bromide for halogen with a copper wire (§60 page 41).

(*c*) *Ethyl bromide and silver nitrate.*—Shake about 2 cc. of ethyl bromide with 5 cc. of water to remove any free hydrobromic acid which may be present. Separate the bromide by means of a pipette and dissolve it in 5 cc. of an alcoholic solution of silver nitrate. Is silver bromide precipitated? Stopper the test-tube, and allow it to stand until the next laboratory exercise. Is silver bromide precipitated? Compare the result with that obtained with methyl iodide.

(*d*) *Ethyl bromide and alcoholic potassium hydroxide.*—Shake a small piece of potassium hydroxide with 10 cc. of *absolute* alcohol. Filter off the liquid and dissolve in it 2 cc. of ethyl bromide. Boil for 1 minute. (*Eq.*) Dilute with water, acidify with a dilute solution of pure nitric acid, and add a solution of silver nitrate.

(*e*) *Ethyl bromide and magnesium.*—Just cover the bottom of a test-tube with magnesium powder. Add 2 cc. of ethyl bromide, 2 cc. of ether, and a very small piece of iodine; place the tube in warm water for 1 minute. Cool and add a little water. (*Eq.*)

(*f*) *Ethyl bromide and sodium.*—To 5 cc. of ethyl bromide in a dry test-tube add a piece of sodium the size of a pea. Close the tube with a cork carrying a small drying-tube containing calcium chloride, and set aside. Examine in an hour. (*Eq.*)

NOTES.—(*a*) Some tertiary halides are decomposed when treated with concentrated sulphuric acid.

(*d*) This reaction is useful as a test to distinguish alkyl halides from certain halogen derivatives of benzene and other hydrocarbons, which are not decomposed readily by alcoholic potassium hydroxide. It is necessary to use a solution of potassium or sodium hydroxide free from halogen compounds. Since the alkalies usually contain chlorides, the solution is prepared by using absolute alcohol in which sodium chloride and potassium chloride are insoluble.

133. Preparation of Ethyl Iodide from Ethyl Alcohol and **Hydriodic Acid.**—Place 60 grams of a strong solution of hydriodic acid and water (the constant-boiling mixture, which contains 57 per cent hydrogen iodide, and has the specific gravity 1.7) in a

200-cc. distilling flask connected with a condenser through which a rapid stream of cold water is passing. Connect an adapter to the condenser and use as a receiver a flask surrounded by water. Close the distilling flask with a stopper bearing a dropping funnel (see Fig. 18, page 28), the end of which reaches to the bottom of the flask. Heat the hydriodic acid to boiling, and drop in through the funnel 10 grams of alcohol at about the same rate as that at which the iodide distils over (about 1 drop per second). Add water to the receiver, shake, and decant off the water into a beaker. Separate the iodide by means of a separatory funnel, place it in a small distilling flask, and add about one-fourth its volume of anhydrous calcium chloride. Cover the side-arm of the flask with a cork, and place one in the neck of the flask. Let the iodide stand until it is quite clear, and distil from a water-bath. Calculate the percentage yield obtained.

Ethyl iodide boils at 72.3°, and has the specific gravity 1.944 (14°). The yield in this preparation is about 90 per cent of the theory, calculated from alcohol; a slight excess of the hydriodic acid is used.

134. Preparation of Isoamyl Bromide from Isoamyl Alcohol and Hydrobromic Acid.—Distil slowly from a 250-cc. distilling flask, provided with a thermometer and connected with a water condenser, a mixture of 30 grams of isoamyl alcohol and 115 grams of the constant-boiling mixture of hydrobromic acid and water, which contains 48 per cent of hydrogen bromide and has the specific gravity 1.49. Distil until the thermometer registers 124°. Add 100 cc. of water to the distillate, place the mixture in a separatory funnel, and return to the distilling flask the oil, which is a mixture of isoamyl bromide and unchanged alcohol. Distil as long as an oil passes over. Put the liquid in the flask in the bottle reserved for hydrobromic acid residues.

Separate the oil and shake it with an equal volume of concentrated sulphuric acid, which dissolves from the mixture the unchanged alcohol and the isoamyl ether formed in a secondary reaction. Separate the oil, wash it with water, and after drying with calcium chloride pour it through a funnel containing a bit of cotton-wool into a small distilling flask. Distil. Record the boiling-point and the weight of the product, and calculate the percentage yield from the weight of alcohol used.

Isoamyl bromide boils at 118°, and has the specific gravity 1.219 at 15°. The yield is about 66 per cent of the theoretical calculated from the alcohol used.

NOTE.—It is frequently advantageous to prepare the alkyl bromides and iodides from the alcohols and aqueous solutions of the halogen acids (the so-called constant-boiling mixtures with water). This is particularly the case when a very pure product is sought, or when an expensive synthetic alcohol is used. In the latter case it is well, in order to increase the yield, to use a large excess—two or three times the theoretical amount—of the acid; the latter can be recovered readily. In making the lower alkyl halides, a good yield can be obtained by using slightly more than the theoretical amount of the halogen acid; in the case of the higher alcohols a large excess is necessary. The alkyl halides prepared in this way are contaminated in certain cases with a trace of an unsaturated hydrocarbon; this can be removed by shaking them with a dilute solution of potassium permanganate.

135. Preparation of Normal Butyl Chloride (SECTION **252**).—In a 500-cc. flask dissolve in 95 grams of concentrated hydrochloric acid 135 grams of anhydrous zinc chloride, keeping the mixture cold to avoid loss of hydrogen chloride. Add next 37 grams of normal butyl alcohol and connect the flask to a reflux condenser or preferably use the form of apparatus represented in Fig. 17, page 27. Boil the mixture gently for one hour. Separate the upper layer, and place it with about an equal volume of concentrated sulphuric acid in a distilling flask. The side-arm of the latter is closed by a cork and the neck connected with a return condenser (see Fig. 16, page 26). The mixture is cautiously heated so that the chloride boils gently. At the end of one-half hour distil off the chloride using a water-condenser. Wash the distillate with a dilute solution of sodium hydroxide, separate it, and place it in a small distilling flask with a little anhydrous calcium chloride. Set aside for a while and distil collecting the portion boiling at 76°-78°. Weigh the chloride and calculate the percentage yield, which should be about 66 per cent of the theoretical based on the weight of alcohol used.

Normal butyl chloride boils at 78° and has the specific gravity 0.907 at 0°.

NOTE.—It has been shown recently that alkyl chlorides can be prepared from alcohols and hydrochloric acid in the presence of water, provided zinc chloride is present. The metallic chloride probably acts as a catalytic agent and not as a dehydrating agent, as has been assumed in the past. During the reaction a part of the alcohol is converted into polymerization-products which are removed with difficulty from the chloride by distillation. These products are destroyed by hot concentrated sulphuric acid.

136. Preparation and Properties of Chloroform (SECTION **264**). (*a*) Place in a liter flask 150 grams of fresh bleaching powder and 400 cc. of water. Shake vigorously in order to break up the lumps of bleaching powder, and connect the flask with a reflux condenser. Through the condenser add, drop by drop, from a separatory funnel a mixture of 12 grams of acetone and 50 cc. of water. Arrange the flask for distillation with steam (see §28, page 19) and distil as long as the chloroform comes over. Wash the chloroform by decantation twice with water, separate, and place it in a small dry distilling flask with anhydrous calcium chloride. When the liquid is quite clear and no drops of water are visible, distil from a water-bath, using a condenser. Weigh the product, determine its specific gravity (§56, page 37), and calculate the percentage yield obtained.

Chloroform boils at 61° and has the specific gravity 1.498 at 15°. The yield should be about 20 grams.

(*b*) *Odor and solubility of chloroform.*—Note the odor of chloroform and determine whether it is soluble in water, ether, alcohol, benzene, petroleum ether, and concentrated sulphuric acid.

(*c*) *Chloroform as a solvent.*—Determine if the following substances are soluble in chloroform: iodine, butter, vaseline, olive oil, a bit of black rubber tubing. In the latter case, let the liquid stay in contact with the rubber for some time; then pour off the liquid onto a watch-glass, and let it evaporate.

(*d*) *Inflammability of chloroform.*—Try to ignite some chloroform. Light a match and pour on the flame the vapor from some chloroform which has been heated to boiling.

(*e*) *Test for chlorine in chloroform.*—Apply the test for halogen with a copper wire (§60, page 41). Shake some chloroform with a little water and test the aqueous solution with silver nitrate. If silver chloride is formed wash the chloroform until the wash-water no longer reacts with silver nitrate. Separate the chloroform with a pipette, dissolve it in alcohol and add an alcoholic solution of silver nitrate.

Decomposition of chloroform in sunlight.—Place some chloroform which contains no free hydrochloric acid in a test-tube, close the tube with a stopper, and allow it to stand several days in a place where it will be in a strong light. Note the odor, shake with water, and test the aqueous solution with silver nitrate.

(*g*) *Chloroform and sodium hydroxide.*—Heat a few drops of chloroform for 1 minute with about 5 cc. of a very dilute solution of sodium hydroxide free from chlorides. (*Eq.*) Test half of the solution for chloride. Neutralize carefully the rest of the solution with hydrochloric acid, add 5 drops of a dilute solution of mercuric chloride and heat. (See note below and experiment 87*d*, page 65.)

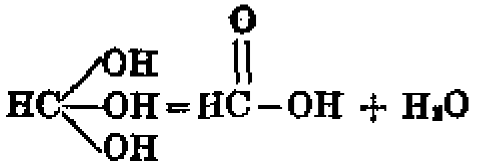
(*h*) *Carbylamine reaction* (SECTION **206**).—HOOD.—Warm together 1 drop of aniline, which is a primary amine and has the formula $C_6H_5NH_2$, 1 drop of chloroform, and 1 cc. of an alcoholic solution of potassium hydroxide. (*Eq.*) On account of the very disagreeable odor produced, the test-tube should be washed in the hood with concentrated hydrochloric acid.

(*i*) *Oxidation of chloroform.*—Heat together a few drops of chloroform, a small crystal of potassium bichromate, and 2 cc. of concentrated sulphuric acid. (*Eq.*) Cautiously note the odor of the gas formed.

NOTE.—(*a*) The yield of chloroform is affected greatly by the quality of the bleaching powder used. The acetone is added slowly as the reaction is a vigorous one, and frothing is apt to occur if the flask becomes hot.

(*g*) The reaction between chloroform and sodium hydroxide is analogous to that between the alkali and other halogen compounds. In this case the three chlorine atoms are replaced by hydroxyl groups; the resulting compound loses water and formic acid is produced:

$$CHCl_3 + 3NaOH = CH(OH)_3 + 3NaCl$$



$$HC(OH)_3 = HC(=O)-OH + H_2O$$

$$HCOOH + NaOH = HCOONa + H_2O.$$

137. Preparation of Ethylene Bromide (SECTION **32, 269**).—(*a*) *With phosphorus pentoxide as dehydrating agent.*—Weigh directly into a 200-cc. distilling flask 40 grams of phosphorus pentoxide; close the side-arm of the flask with a stopper and connect the flask with a reflux condenser (see Fig. 16, page 26). Place the flask in cold water, and with constant shaking add slowly through the condenser 30 grams of alcohol. Heat the flask carefully with a free flame until the phosphorus pentoxide has dissolved. Remove the condenser, place the flask on a wire gauze at such a height that it can be heated with a burner, close with a stopper, and connect with the absorption apparatus which is arranged as follows: Fit three 8-inch test-tubes with *tightly fitting* stoppers each containing two holes. The stoppers should be covered with paraffin. This can be done by inserting them into paraffin melted in an evaporating dish. As the apparatus must be tight it is advisable to use stoppers of rubber. Prepare three tubes bent at a right angle of such a length that when passed through the holes in the stoppers they will extend the bottom of the test-tubes; also three shorter right-angle tubes which just pass through the stopper. Put one long and one short tube into each stopper, and connect the tubes in such a way that a gas passing through the train when the test-tubes are in place, will pass to the bottom of each test-tube through the long tube. Put 10 cc. (30 grams) of bromine in each of two of the test-tubes, and cover with a layer of water about 2 cm. high, which largely prevents the volatilization of the bromine as the gas passes through. The three test-tubes are now placed in beakers containing cold water, and connected with the distilling-flask, the empty tube which serves to condense any liquid which distils over, being placed next to the flask. In order to prevent bromine from getting into the air, connect a drying tube containing soda-lime with the tube farthest removed from the distilling flask. Test the apparatus to see if all joints are tight.

Heat the flask cautiously at first and then to such a temperature that ethylene is given off freely. After the gas begins to come off the apparatus needs little attention if it is so placed that the flame is not in a draught; if this is the case, use a chimney so that a steady heat may be obtained. Heat as long as ethylene is formed; from one-half hour to an hour is usually sufficient. If the bromine has not been used up when the ethylene ceases to be evolved, remove the tubes containing ethylene bromide, and under the hood transfer the liquids to a flask. Wash by decantation with a dilute solution of sodium hydroxide until the heavy oil is colorless, and then once with water. Separate the bromide, and dry it with calcium chloride. After standing an hour or more, until the liquid is clear and no water is visible, filter through a funnel, containing a bit of cotton wool, into a small distilling flask. Distil, using a thermometer and water condenser, and collect the fraction which boils at 130°-132°. Calculate the percentage yield both from the alcohol and bromine used.

Ethylene bromide melts at 8.4° and boils at 132°, and has the specific gravity of 2.189 at 15°. The yield in this preparation is about 55 grams.

(*b*) *With sulphuric acid as dehydrating agent.*—Mix cautiously in a 1-liter, round-bottomed flask 90 cc. of alcohol and 135 cc. of concentrated sulphuric acid; then add about 50 grams of coarse sand and about 5 grams of aluminium sulphate. Place the flask on a wire gauze and connect it by means of a tightly fitting stopper, preferably one of rubber, with an absorbing train of test-tubes like that described in (*a*) above. In this case use four test-tubes which contain, respectively, beginning with the one nearest the flask, 20 cc. of a dilute solution of sodium hydroxide, 20 cc. of concentrated sulphuric acid, 10 cc. of bromine covered with water, and 10 cc. of bromine covered with water. Attach a drying tube containing soda-lime to the last tube. Place all of the tubes in cold water. Make a test to determine if all joints in the apparatus are tight.

Heat the flask at the lowest temperature at which ethylene is freely evolved. It is very essential to avoid over-heating, which results in frothing and the liberation of carbon. If this occurs, the contents of the flask should be poured out and ethylene should be prepared from a new mixture. When the bromine is decolorized, treat the product as directed in (*a*) above.

The yield is about 55 grams.

NOTE.—Sand is added to the flask to distribute the heat more evenly and, thus, to assist in preventing frothing. In the presence of aluminium sulphate, the decomposition of alcohol into ethylene takes place at about 140°, whereas in the absence of the sulphate a temperature of about 180° is required. At the lower temperature carbonization is not apt to occur.

ACYL CHLORIDES

138. Preparation of Acetyl Chloride (SECTION **274**).—Connect a 200-cc. dry distilling flask with a separatory funnel and a condenser; for use as a receiver, attach to the latter, by means of a tightly fitting cork, a 200-cc. distilling flask or filter-bottle. Connect to the side-arm of the receiver a drying tube containing calcium chloride, which serves to protect the distillate from moisture. As a large quantity of hydrochloric acid is set free during the reaction between acetic acid and phosphorus trichloride, the drying tube should be fitted with a glass tube which reaches to just *above* the surface of some water contained in a flask. When the apparatus is arranged, place a water-bath containing cold water in such a position that the bulb of the distilling flask is covered with water. Put 50 grams of *glacial* acetic acid in the flask, and run in slowly through the funnel 40 grams of phosphorus trichloride. The latter should be weighed and transferred to the funnel in the hood. When the phosphorus trichloride has been added, heat the water in the bath to 40°-50°, until the evolution of hydrochloric acid slackens and the liquid has separated into two layers; then heat the water to boiling as long as any distillate comes over. Redistil the distillate, using a thermometer, a condenser, and a receiver protected from the air as directed above. Collect the fraction which boils at 50°-55°. Weigh the product, and calculate the theoretical yield and the percentage of this obtained.

Acetyl chloride boils at 51°. The experiment should yield about 40 grams.

139. Properties of Acetyl Chloride (SECTION **275**).—(*a*) *Acetyl chloride and water.*—Cautiously add about 0.5 cc. of acetyl chloride to 2 cc. of ice-water. Observe if two layers form, and then shake carefully. (*Eq.*)

(*b*) *Acetyl chloride and alcohol.*—Cautiously add acetyl chloride, drop by drop, to 2 cc. of alcohol as long as reaction takes place. Is hydrogen chloride given off? Pour the product into 5 cc. of water, shake and note the odor. (*Eq.*)

(*c*) *Acetyl chloride and an amine.*—Add to 5 drops of aniline, $C_6H_5NH_2$, acetyl chloride, drop by drop, until reaction ceases. (*Eq.*) Add to the tube 10 cc. of water, heat to boiling, and filter hot. Set the tube aside to cool.

CHAPTER XI

COMPOUNDS CONTAINING TWO UNLIKE SUBSTITUENTS

140. Preparation and Properties of Trichloroacetic Acid (SECTION **290**).—(*a*) HOOD.—In a 250-cc. flask place 25 grams of chloral hydrate and add 15 cc. of fuming nitric acid (sp. gr. 1.5). Heat the flask over a small flame until reaction begins; then remove the flame. When the reaction has apparently ceased, heat gently until the liquid becomes almost colorless. (*Eq.*) Transfer the liquid to a small distilling flask and distil very slowly, using an air-condenser. When the temperature reaches 150°, change the receiver, using this time a small distilling flask, and collect what comes over up to 200°. Redistil slowly and collect the fraction boiling at 193°-195°. Weigh the product and calculate the percentage yield.

Trichloroacetic acid melts at 55° and boils at 195°. The amount obtained in this preparation should be about 10 to 12 grams.

(*b*) Dissolve in a test-tube about 1 gram of the acid in water, and add 5 cc. of a dilute solution of sodium hydroxide. Attach to the tube by means of a cork a piece of glass tubing about 3 feet long, clamp the tube over a wire gauze, and heat gently so that the solution just boils. At the end of 5 minutes cool the tube, examine the contents and note the odor. (*Eq.*)

141. Preparation and Properties of Lactic Acid (SECTION **298**).—(*a*) In a 750-cc. flask dissolve 50 grams of cane-sugar or anhydrous glucose in 500 cc. of water; add 20 cc. of sour milk and 20 grams of precipitated calcium carbonate. Set the flask in a warm place (temperature about 40°) and allow the fermentation to proceed for one week. The flask should be taken at least twice a day. At the end of the time add a small amount of calcium carbonate, heat to boiling, filter, pour the solution into a flat dish, and let it evaporate spontaneously. Filter off the solid by suction, dissolve it in a small amount of boiling water, filter if necessary, and set the solution aside to crystallize. Separate the crystals as before and let them dry on a porous plate. The yield is about 35 grams.

(*b*) *Lactic acid and ferric chloride: test for an α-hydroxy acid.*—The solution of lactic acid required for this and the following experiments can be made from lactic acid, or prepared from the calcium lactate obtained in (*a*) above, as follows: Dissolve about 2 grams of the salt in 20 cc. of boiling water and add a dilute solution of sulphuric acid, drop by drop, as long as a precipitate is formed. If it is difficult to determine when the correct amount of acid has been added, filter onto a watch-glass a few drops of the solution and add to the filtrate a drop of sulphuric acid. If an excess of sulphuric acid has been used, add to the original solution a little of a solution of calcium lactate. When all the calcium has been precipitated, warm the solution and filter. In a small evaporating dish add to 5 cc. of the solution 1 drop of a 10 per cent aqueous solution of ferric chloride. Repeat the test, using 5 cc. of water instead of the solution of the acid. Compare the color in the two cases.

(*c*) *Solubility of lactic acid.*—Determine whether lactic acid can be extracted from water by ether. Describe fully how you made the test.

(*d*) *Application of the iodoform reaction to lactic acid.*—Determine whether lactic acid gives the iodoform reaction (experiment 81*b*, page 59).

NOTE.—(*a*) The sour milk used in the preparation contains the lactic acid bacteria. The milk should be used before the curd has separated. The latter is needed for the development of the bacteria during fermentation. Calcium carbonate is added to neutralize the lactic acid as it is formed, since the fermentation stops if the acid accumulates. Toward the end of the fermentation butyric acid is usually formed. The odor produced is due to this cause. When the sugar has been fermented the calcium carbonate passes into solution. If there is a large residue at the end of a week the milk was not satisfactory. The zinc salt of lactic acid is characteristic. It can be prepared by digesting a strong solution of the acid with zinc carbonate, filtering hot, and evaporating to crystallization.

142. Properties of Tartaric Acid and Tartrates (SECTIONS **310-314**).—(*a*) *Behavior of tartaric acid and tartrates on heating.* Heat a little tartaric acid in a test-tube. Note the change in appearance and the odor produced. What products are formed? Repeat, using Rochelle salt.

(*b*) *Tartaric acid and ferric chloride.*—Apply the test for an α-hydroxy acid as follows: Dissolve about 0.1 gram of tartaric acid in 100 cc. of water. To 20 cc. of this solution add 1 drop of a 10 per cent aqueous solution of ferric chloride. Compare the color with that produced by adding 1 drop of ferric chloride to 20 cc. of water, and in a second tube to 20 cc. of water containing 1 drop of acetic acid. The depth of color can be more readily observed by looking down the tubes placed on white paper.

(*c*) *Potassium salts of tartaric acid.*—Make a cold saturated solution of tartaric acid by shaking an excess of the acid with 5 cc. of water. Decant off the liquid and acid, drop by drop, a 10 per cent solution of potassium hydroxide, until a crystalline precipitate forms (*Eq.*); then add an excess of the solution of potassium hydroxide. (*Eq.*)

(*d*) *Calcium tartrate: test for tartrates.*—Neutralize a solution of tartaric acid or of cream of tartar with ammonia, and add to the solution 1 cc. of a solution of calcium chloride. (*Eq.*) If a precipitate of calcium tartrate does not appear, rub a glass rod against the side of the tube under the surface of the liquid. Filter off the precipitate, and pour 5 cc. of a solution of sodium hydroxide through the filter into a clean test-tube. Heat the filtrate to boiling. This behavior of tartaric acid is characteristic, and is used in the identification of the acid and its soluble salts.

(*e*) *Reducing action of tartrates.*—To a dilute solution of Rochelle salt or sodium tartrate contained in a test-tube, which has been cleaned by boiling in a solution of sodium hydroxide and washing with water, add 1 cc. of a solution of silver nitrate. Dissolve the precipitate by adding ammonia, drop by drop, avoiding excess, and place the tube in hot water. Compare the results with those obtained with formaldehyde (experiment 106*d*). Is the formation of a silver mirror a positive test for an aldehyde?

(*f*) *Fehling's solution.*—Add to 1 cc. of a solution of copper sulphate 5 cc. of a solution of sodium hydroxide (*Eq.*); then add a solution of Rochelle salt or of sodium tartrate until the precipitate dissolves. (*Eq.*) Repeat, using glycerine in place of Rochelle salt. It is necessary to have a large excess of sodium hydroxide. What organic compounds other than acids dissolve copper hydroxide? Determine if Rochelle salt will dissolve the hydroxides of iron and aluminium.

NOTES.—(*b*) This test for α-hydroxy acids must be made in the cold, as a solution of ferric chloride alone develops a decided yellow tint on being heated. In applying the test to an unknown substance a very dilute solution should be used, and the color developed should be compared with that formed in a solution of equal concentration of an α-hydroxy acid (tartaric acid). Many solutions of hydroxyl compounds when sufficiently concentrated give a yellow color with ferric chloride. The colors given by polybasic and ketonic acids are usually more intense or of a different shade from those given by α-hydroxy acids.

(*d*) In making this test the calcium tartrate is usually filtered off before solution in sodium hydroxide, since the carbonate that the alkali contains produces a precipitate of calcium carbonate, which is insoluble. The presence of ammonium salts should be avoided in making the test, as they interfere with the precipitation of calcium tartrate.

143. Properties of Citric Acid and Citrates (SECTION **318**).—(*a*) *Decomposition of citric acid by heat.*—Heat a little citric acid in a dry test-tube. Note the odor. What acids are present among the products of decomposition when citric acid is heated? (See SECTION **141**.)

(*b*) *Calcium citrate: test for citric acid.*—Dissolve about 1 gram of citric acid in about 50 cc. of water. Neutralize 5 cc. of the solution with ammonia, avoiding an excess of the latter. If too much has been added, add a little of the solution of the acid until the reaction is neutral or slightly acidic. To the solution of ammonium citrate add about 2 cc. of a 10 per cent solution of calcium chloride. Is a precipitate formed? Compare the behavior of tartrates. Heat the solution to boiling and set aside. Examine in a few minutes. A precipitate of tricalcium citrate is formed. Is the precipitate of tricalcium citrate crystalline? Wash the salt by decantation three times with water, and determine its solubility in a solution of sodium hydroxide. Compare the result with that obtained with tartrates. Preserve the solution of citric acid for experiments (*d*) and (*e*) below.

(*c*) *Presence of citric acid in lemon juice.*—Test 5 cc. of lemon juice or pineapple juice for citric acid as described above. Add ammonia to the filtered juice but have it slightly acid when making the test.

(*d*) *Reducing power of citrates.*—Neutralize 5 cc. of the solution of citric acid prepared in *(b)* above with sodium hydroxide, add 1 cc. of a solution of silver nitrate, and then ammonia drop by drop, until the precipitate is dissolved. Place the tube in boiling water for two minutes. Is a mirror of silver formed? (Compare with tartrates.) Heat the solution to boiling for two minutes. Set aside and examine later.

(*e*) *Reduction of ferric citrate by light.*—Add to 5 cc. of a solution of ferric chloride, until a clear green color is formed, a solution of ammonium citrate, prepared by neutralizing a solution of citric acid with ammonia. Moisten a piece of paper with the solution, dry the paper in the dark in your desk and then expose it to sunlight under a piece of thick paper in which a design has been cut. At the end of 10 minutes place the paper in a dilute solution of potassium ferricyanide. Write the formulas for all the substances involved in the reactions, starting with ferric chloride.

NOTE.—(*b*) In the presence of a large excess of sodium hydroxide, calcium chloride gives a precipitate in the cold with solutions of alkali citrates. Calcium citrate is soluble in acetic acid (calcium oxalate is insoluble).

144. Preparation of Acetoacetic Ester (SECTION **324**).—(*a*) The ethyl acetate to be used in this preparation must be dried and distilled just before use. Place 250 cc. of ethyl acetate, which should be neutral, in a 500-cc. flask, and add anhydrous calcium chloride (about one-fourth of the volume of the ester). Let the mixture stand over night or longer. Distil directly on a water-bath from the calcium chloride, and collect the distillate in a dry receiver which is protected from the moisture of the air. Provide a reflux condenser for a 500-cc. flask, which has been carefully dried, and set the flask in cold water. Add 200 grams of the dried ethyl acetate and 20 grams of sodium in the form of wire or very thin shavings (see §41, page 28). Connect the condenser with the flask. When the evolution of hydrogen ceases, heat the flask on a water-bath at such a temperature that the contents boil gently. When all the sodium has dissolved, about 3 hours being required, cool the flask, and add slowly a mixture of 1 part of concentrated hydrochloric acid and 4 parts of water, until the solution shows an acid reaction after having been shaken thoroughly. Add an equal volume of a saturated solution of sodium chloride, transfer to a separatory funnel, and separate the ester as carefully as possible from water. Shake the ester with a little anhydrous calcium chloride until it becomes clear and no water can be seen, pour off from the drying agent, and distil the liquid slowly from a flask provided with a small Hempel tube (see Fig. 5, page 11). Discard the distillate which boils up to 160°; collect the following fractions: 160°-175°, 175°-185°, 185°-200°. The fraction boiling at 175°-185° is nearly pure acetoacetic ester. By redistilling the other fractions a further quantity can be obtained, but as acetoacetic ester decomposes slowly on boiling at atmospheric pressure, it is not advisable to carry out an extended fractionation. If a better yield is desired, the product of the reaction may be distilled under diminished pressure.

Acetoacetic ester boils at 182° at 760 mm., 74° at 14 mm., and 88° at 29 mm. It has the specific gravity of 1.03 at 15°. The yield in this preparation should be 35-40 grams.

(*b*) Compare the solubility of acetoacetic ester in water and in a solution of sodium hydroxide. Explain.

(*c*) Dissolve a few drops of acetoacetic ester in 1 cc. of alcohol and add a few drops of a solution of ferric chloride. What does the result indicate?

145. Acetoacetic Ester Synthesis (SECTION **325).**—(a) *Preparation of ethylacetoacetic ester.*—Into a 500-cc. flask place 60 cc. of absolute alcohol. Weigh 4.6 grams of sodium and cut it into five or six pieces. Hold the flask under running water and add one piece of the metal. At the end of about a minute, when the violent reaction ceases, add the rest of the sodium and connect the flask by means of a tightly fitting cork or rubber stopper with a long reflux condenser through which a rapid stream of water is passing. When the metal has dissolved add *slowly* through the condenser 26 grams of acetoacetic ester, and then 24 grams of ethyl bromide. Heat slowly to boiling on a water-bath until a drop of the solution when mixed with a drop of water does not show an alkaline reaction. Avoid too rapid heating at first, as the reaction may become violent and ethyl bromide be lost. The time required is about 2 hours. When the reaction is complete, distil off the excess of alcohol on the water-bath, add 50 cc. of water to the residue, and shake until the salt has dissolved.

Separate the oil in a small separatory funnel, dry over calcium chloride and distil. Collect the portion which boils at 192°-200°. Calculate the percentage yield. Write equations for all the reactions involved.

Ethylacetoacetic ester boils at 198°. The yield should be about 22 grams.

(*b*) *Hydrolysis.of ethylacetoacetic ester* (SECTION **326**).—*Ketone hydrolysis.*—In a 500-cc. flask dissolve 10 grams of sodium hydroxide in 100 cc. of water, add 15 grams of ethylacetoacetic ester, and connect with a reflux condenser. Place the flask *in* a bath containing boiling water for 2 hours. Cool, place the contents of the flask in a small separatory funnel, separate the oil, and dry over calcium chloride. Pour off the oil from the drying agent after a few hours and distil it. Collect what boils at 198°-103°.

Methyl propyl ketone, the product of the reaction, boils at 102°, The yield obtained is about 60 per cent of the theoretical.

Acid hydrolysis.—In a small flask dissolve 5 grams of sodium hydroxide in 15 cc. of water and add 5 grams of ethylacetoacetic ester. Shake vigorously and connect the flask with a reflux condenser. Place the flask in boiling water for 2 hours. At the end of this time distil with steam (§28, page 19) until about 100 cc. of water have passed over. (What else passes over?) Cool the flask through which steam has been passed, make the contents acid to litmus with dilute sulphuric acid, and then add about 50 cc. of the acid in excess to liberate the organic acids formed in the hydrolysis. Distil again with steam into a clean receiver until about 300 cc. of water have passed over. Note the odor of this second distillate. Neutralize the latter with sodium hydroxide and evaporate to dryness. The residue is a mixture of sodium acetate and sodium butyrate. Put a little of the solid on a watch-glass and add a few drops of concentrated sulphuric acid. Note the odor. Add to this a few drops of alcohol, and after warming gently note the odor.

The presence of butyric acid in this mixture can be shown in another way as follows: Dissolve about 0.5 gram of the salt in 5 cc. of water. Acidify with dilute sulphuric acid, warm to liberate any carbon dioxide present. Neutralize with ammonia, and add a solution of calcium chloride. If a precipitate is formed, it is calcium butyrate. Filter this off and heat the filtrate to boiling. Since calcium butyrate is slightly less soluble in hot water than in cold, the cold saturated solution deposits a precipitate when heated to boiling. Write equations for all reactions involved in the experiment.

NOTE.—(*a*) If the solution of sodium acetoacetate and ethyl bromide does not become neutral on boiling, it is evident that some of the latter has been lost. This may result from too active boiling at first or there may have been a leak in the stopper connecting the flask with the condenser. If this occurs add more of the bromide and heat again.

146. Properties of Chloral (SECTIONS **329, 331**).—(*a*) *Preparation from chloral hydrate.*—Shake in a small test-tube about 3 grams of chloral hydrate and 3 cc. of concentrated sulphuric acid. (*Eq.*) Separate by means of a pipette the oil which floats on the sulphuric acid, and add it to one-half its volume of water. (*Eq.*)

(*b*) *Test for the aldehyde group.*—Determine whether chloral hydrate forms a silver mirror with ammoniacal silver nitrate (experiment 106*d*, page 84), and whether it produces a color with Schiff's reagent.

(*c*) *Decomposition of chloral hydrate by alkalies.*—Dissolve about 1 gram of chloral hydrate in water and add a solution of sodium hydroxide. (*Eq.*) Test for chloroform.

CHAPTER XII

CARBOHYDRATES

147. Properties of Dextrose (SECTIONS **349-361**).—(*a*) *Taste and solubility of dextrose.*—Taste equal amounts of dextrose and cane-sugar. Determine whether dextrose is soluble in the following liquids: water, alcohol, and ether.

(*b*) *Presence of alcoholic hydroxyl groups in dextrose.*—In a 100-cc. bottle shake 10 cc. of a 10 per cent solution of dextrose with 2 cc. of benzoyl chloride and 25 cc. of a 10 per cent solution of sodium hydroxide. Shake vigorously until the odor of the benzoyl chloride disappears. Write the structural formula of the compound formed.

(*c*) *Dextrose and copper hydroxide.*—Precipitate copper hydroxide by adding 5 cc. of a solution of sodium hydroxide to 1 cc. of a solution of copper sulphate, and then add 5 cc. of a strong solution of dextrose (about 20 per cent) and shake. It is necessary to have a large excess of the alkali present. Compare with experiment 142*f*, page 112. Heat the solution nearly to boiling.

(*d*) *Dextrose and alkalies.*—Boil 10 cc. of a 10 per cent solution of dextrose with 5 cc. of a solution of sodium hydroxide. Compare the result with that obtained with aldehyde and sodium hydroxide (experiment 108*d*, page 86).

(*e*) *Dextrose and Schiff's reagent.*—Determine whether dextrose produces a color with Schiff's reagent (experiment 108*h*, page 86).

(*f*) *Reducing action of dextrose: silver mirror.*—Test a dilute solution of glucose with an ammoniacal solution of silver nitrate or with Tollen's reagent (experiment 106*d*, page 84).

(*g*) *Reducing action of dextrose: Fehling's solution.*—Test a dilute solution of dextrose with Fehling's solution.

(*h*) *Preparation of dextrosazone.*—Dissolve 1 gram of dextrose in 20 cc. of water and add 2 grams of phenylhydrazine hydrochloride, which should be colorless (see note), and 3 grams of hydrated sodium acetate. Heat the solution by placing the flask in boiling water for 10 minutes. Cool under running water, filter by suction, and wash the crystals with cold water. Redissolve the crystals in the smallest possible amount (about 20 cc.) of boiling 50 per cent alcohol. Filter the hot solution, cool in running water, filter off the crystals, and dry them on a porous plate, and finally at 100°. Determine the melting-point of the crystals in a bath, the temperature of which is rising rapidly, as dextrosazone decomposes slowly when heated. The melting-point of dextrosazone is 204°-205°.

NOTES.—(*b*) The insoluble compound formed is a pentabenzoate of dextrose which is produced as the result of the replacement of the hydrogen atoms of the hydroxyl groups in dextrose by the benzoyl radical present in benzoyl chloride, C_6H_5COCl. The test is an application of the Baumann-Schotten reaction (see SECTION **547**).

(*c*) Polyhydroxy alcohols and compounds related to them, such as the sugars, dissolve the hydroxides of certain heavy metals, Compounds similar to that present in Fehling's solution (SECTION **311**) are formed. The sugars also form soluble compounds with calcium and barium hydroxides.

(*e*) Although many of the carbohydrates contain the aldehyde group, they do not produce a color with Schiff's reagent.

(*h*) Phenylhydrazine and its salts decompose rapidly when exposed to air and to light. Pure compounds must be used in the preparation of osazones. The phenylhydrazine can be dissolved in an excess of acetic acid, just before use, or the hydrochloride and sodium acetate may bo used. The pure hydrochloride can be prepared as follows: Redistil the phenylhydrazine if it is colored. Dissolve the compound in 12 times its volume of alcohol, and add pure concentrated hydrochloric acid as long as a precipitate is formed. Filter off the precipitate by suction, and wash it with alcohol until it is colorless. Wash twice with ether. If the salt is not to be used immediately, dry it in the air for half an hour, and then for 1 hour at 100°. Place the salt in a tightly stoppered bottle of brown glass.

MONOSACCHARIDES AND DISACCHARIDES

148. General Reactions and Properties of the Sugars.—All the experiments given in this section should be performed in each case with samples of dextrose, levulose, maltose, lactose, and sucrose.

(*a*) *Molisch reaction for carbohydrates* (SECTION **386**).—Place a piece of the carbohydrate about the size of a mustard seed in

10 drops of water, and add 2 drops of a 10 per cent solution of α-naphthol in chloroform. Allow 1 cc. of pure concentrated sulphuric acid to flow, from a pipette, down the side of the inclined tube so that two layers are formed. A pipette for this purpose may be made by drawing out a piece of glass tubing to a fine opening at one end. Observe what happens in a few seconds. Shake and allow the mixture to stand 2 minutes; note the color, Dilute with water, note the change, add an excess of ammonia, and note the color.

(*b*) *Solubility of sugars.*—Determine whether the carbohydrates are soluble in water, in alcohol, and in ether. Dry test-tubes should be used when the solubilities in alcohol and ether are studied.

(*c*) *Reduction of silver salts.*—Determine whether dilute solutions of the carbohydrates give a mirror with an ammoniacal solution of silver nitrate or with Tollen's reagent. (See experiments 106*d*, page 84, and 108*g*, page 86.)

(*d*) *Reduction of Fehling's solutions.*—Dissolve about 0.1 gram of the carbohydrate in 5 cc. of water, and add 3 cc. of each of the solutions which combined make Fehling's solution. (See Appendix for the composition of this solution.) Heat to boiling.

(*e*) *Fermentation of carbohydrates.*—Fill fermentation-tubes with 10 per cent solutions of the carbohydrates. Add to each 2 cc. of a mixture made by rubbing one-quarter of a yeast-cake with 10 cc. of water. Label the tubes, and place them in a thermostat at 30°-35° until the next exercise. Test the gas formed. Which of the sugars are fermentated by common yeast?

(*f*) *Formation of osazones.*—Place in separate test-tubes 5 cc. of 2 per cent aqueous solutions of the five carbohydrates; label the tubes. Mix intimately 1.3 grams of colorless phenylhydrazine hydrochloride and 2 grams of crystallized sodium acetate. Divide the mixture into 5 equal parts and put one of the parts into each of the five tubes. Note the time, and place the tubes in a beaker containing boiling water and heat for one-half hour. Shake the tubes when the salts have dissolved in order to mix the solution. Examine the tubes frequently and note the order in which the precipitates first appear. At the end of one-half hour place the tubes in a rack and see if any osazones crystallize out on cooling slowly. Make a full record of the results of the experiment. Examine all the osazones under a high-power microscope, and sketch the crystals.

(*g*) *Summary of results.*—Prepare a table in which are tabulated the results of experiments *a, b, c, d, e*, and *f* above. State how you could distinguish each one of the five sugars from the others.

149. Properties of Sucrose (SECTIONS **366, 368**).—(*a*) *Preparation of caramel.*—Place about 2 grams of sucrose in a test-tube and heat it for 15 minutes in an oil-bath at 210°. Taste the product and determine if it is soluble in water.

(*b*) *Sucrose and sulphuric acid.*—Add to about 2 grams of sugar 2 cc. of water and then 5 cc. of concentrated sulphuric acid. If no marked change occurs heat gently. Repeat using dextrose instead of sucrose.

(*c*) *Sucrose and alkalies.*—Heat 5 cc. of a solution (about 10 per cent) of sucrose with a solution of sodium hydroxide. Is the solution highly colored? Compare with the results obtained with dextrose. What conclusion can be drawn from the experiment? What other tests lead to the same conclusion? (See experiment 148*c*, *d*, *f*, page 120.)

(*d*) *Formation of tricalcium saccharate.*—Shake 10 cc. of a 20 per cent solution of sucrose with an excess of milk of lime, which can be prepared by slaking a little quicklime and grinding the calcium hydroxide with enough water to make a thin paste. Filter the solution and heat it to boiling. (*Eq.*)

(*e*) *Inversion of sucrose.*—Boil for 5 minutes a solution of about 0.2 gram of sucrose in 10 cc. of water to which has been added 1 cc. of dilute hydrochloric acid. Neutralize the solution with sodium hydroxide, and test for a reducing sugar with Fehling's solution.

150. Isolation of Lactose from Milk (SECTION **371**).—In a beaker heat 200 cc. of milk to about 50°, and add a dilute solution of acetic acid as long as a precipitate is formed (about 5 cc. of a 10 per cent solution of the acid). Stir until the casein collects into a ball; remove this and neutralize the solution with a dilute solution of sodium hydroxide. Make the solution weakly acidic by adding 2 or 3 drops of very dilute acetic acid. Heat the solution to boiling and add about 1 gram of precipitated calcium carbonate. Stir thoroughly and filter hot. Evaporate the solution to about 40 cc, cool, add 3 volumes of alcohol, and filter. Set aside the solution in a shallow dish until the next exercise. Filter off the crystals of lactose by suction and wash them with alcohol. Dry the crystals in the air. Taste the sugar.

NOTE.—The procedure adopted in this experiment is designed to bring about the precipitation of the proteins the milk contains. The solution is heated with calcium carbonate before evaporation in order to neutralise the free acid present, and thus largely prevent the hydrolysis of lactose which takes place when the sugar is heated with water in the presence of acids.

151. Oxidation of Lactose (see galactose, SECTIONS **359** and **319**).—Heat 10 grams of lactose on the water-bath with about four times its weight of concentrated nitric acid (28 cc.) until the brown oxide of nitrogen is formed. Keep the mixture at 70°-80° until the evolution of gas ceases. Dilute the solution with one-half its bulk of water and let it stand until cold. mucic and oxalic acids crystallize out. Filter, save the filtrate, and wash the crystals with warm alcohol to dissolve the oxalic acid, and then twice with a small amount of cold water. Recrystallize the residue, mucic acid, from a small amount of boiling water.

Neutralize the filtrate obtained above with solid potassium carbonate, strongly acidify with glacial acetic acid, and let stand until crystals of potassium hydrogen saccharate are formed. Filter these off and recrystallize them from the smallest possible amount of boiling water.

Dissolve a few crystals of mucic acid in a few drops of a solution of potassium hydroxide on a microscope slide. When the solution has evaporated examine the crystals under the microscope. The form of the crystals of potassium mucate is characteristic. Describe their appearance.

When the ammonium salt of saccharic acid or of mucic acid is heated, pyrrole is formed (SECTION **658**). The latter imparts a carmine-red coloration to a pine-wood shaving which has been moistened with hydrochloric acid. Test the mucic acid obtained in this way as follows: Mix 0.1 gram of the acid with 2 cc. of ammonia and evaporate to dryness. Heat the residue strongly in a test-tube; during the heating suspend in the tube a soft pine splinter which has been soaked in concentrated hydrochloric acid for a minute or two.

POLYSACCHARIDES

152. Properties of Starches (SECTIONS **375, 376**).—(*a*) *The form of starch grains.*—Examine under the microscope and sketch the following starches: potato, arrowroot, corn, rice, and wheat.

(*b*) *Application of the Molisch test for carbohydrates.*—Test a bit of starch, filter-paper, and gum arabic as described in experiment 148*a*, page 119.

(*c*) *Colloidal solutions: dialysis.*—Select a piece of parchment-paper, about 10 inches square, which contains no small holes. Wet the paper thoroughly and form it into a bag of about 100 cc. capacity; insert the neck of a small funnel into the mouth of the bag and fix it in place by tying a string around it. Fill the bag with water, dry it carefully on the outside, and hang it up for a few minutes. If the bag leaks it must be discarded and a new one made.

Prepare a starch solution as follows: Grind about 2 grams of starch with 10 cc. of cold water, pour the mixture into 300 cc. of boiling water, and set aside to cool. Pour the water out of the parchment bag and fill it half full with the starch solution. Take care not to spill any of the solution on the outside of the bag. Suspend the bag in a beaker containing about 100 cc. of water. The beaker should be of such a size that the water in it and that in the solution in the bags are at approximately the same level. Set aside until the next exercise and test the water outside the bag for starch according to experiment (*f*) below.

Prepare a second bag and carry out a similar experiment, using a 10 per cent solution of glucose. In this case test the water outside the bag for glucose by Fehling's solution. Explain dialysis and state why, by means of it, it is possible to separate the polysaccharides from the sugars.

(*d*) *Starch and Fehling's solution.*—Wash about 2 grams of starch by decantation twice. Shake up the residue with a little water, and pour it into 200 cc. of boiling water. Test about 1 cc. of this solution with Fehling's solution.

(*e*) *Starch and alkalies.*—Warm 5 cc. of the solution prepared in (*c*) with 5 cc. of a solution of sodium hydroxide. Compare the results with those obtained in the case of a monose (experiment 147*d*, page 118).

(*f*) *Starch and iodine.*—Add to 5 cc. of the solution of starch 1 drop of a solution of iodine in potassium iodide. Heat the solution to boiling, and then cool.

Shake up a little starch with cold water, filter and add a few drops of iodine solution to the filtrate.

Test solutions of dextrose, sucrose, lactose, and dextrin with a *very* dilute solution of iodine (light straw-yellow in color).

(*g*) *Hydrolysis of starch: with an acid.*—Boil in an Erlenmeyer flask about 150 cc. of the starch solution prepared in (*c*) above with 10 cc. of concentrated hydrochloric acid. Every 5 minutes pour out about 2 cc. of the solution, cool, and test with a very dilute iodine solution. Describe the colors produced as the hydrolysis progresses. When iodine produces no color in the solution, neutralize about 5 cc. of it and test with Fehling's solution.

(*h*) *Hydrolysis of starch: with saliva.*—A free flow of saliva is easily obtained by chewing some insoluble substance such as paraffin. Collect about 40 cc. in this way. Filter the saliva through a wet filter. Test a portion of the saliva by allowing a piece of red and of blue litmus paper to stay in contact with it for 5 minutes.

Prepare 600 cc. of starch paste, using 25 grams of arrowroot starch. (Do this in the usual way, by rubbing the starch with a little cold water and pouring the suspension into boiling water. Boil for 2 or 3 minutes.) Save one-third of the paste for subsequent experiments. When the paste has cooled to 40°, mix two-thirds of it with 25 cc. of the filtered saliva and watch carefully for changes in consistency and opalescence of the mixture. At 2-minute intervals remove a few drops to a porcelain plate, and test with a very dilute iodine solution. Record the time required for the solution to clear and to reach the point where it no longer produces a color with iodine. Compare your figures with those of your neighbors. Are the salivas equally active?

Evaporate the solution in a casserole to about 100 cc. on the steam-bath. (If this point is not reached at the end of the exercise, leave the labeled casserole on the steam-bath in the care of the instructor.) Filter out the small precipitate of carbonate and cellulose. Pour the solution into 3 volumes of alcohol to precipitate dextrins. Is the amount large? Filter. Evaporate the alcohol and water on the steam-bath to a volume of about 50 cc. What is the consistency of the residue? Try the reducing power and make an osazone. What is the final product of salivary digestion?

163. Conditions Influencing Salivary Digestion.—For the following experiments dilute the filtered saliva with 5 volumes of water and dilute the starch paste with an equal volume of water.

(*a*) *Temperature.*—In each of four test-tubes put 5 cc. of starch paste. Keep two tubes at room temperature, chill the third in ice-water, and warm the fourth in a 40° water-bath. When the tubes have reached the temperature indicated, add to the second, third, and fourth in quick succession 1 cc. each of diluted saliva, and to the first 1 cc. of boiled, diluted saliva. Maintain the tubes at their respective temperatures. Note the time required for each to clear. Apply the iodine test at once and at intervals of 5 minutes. After half an hour put the first and third tubes in the 40° bath and continue the observations. Compare the effect of high and low temperature on the enzyme.

(*b*) *Acid and alkali.*—Neutralize to litmus 5 cc. of filtered saliva, using 0.4 per cent hydrochloric acid, and dilute with 5 volumes of water. Prepare a series of eight tubes containing 5 cc. each of hydrochloric acid of various percentage strengths: 0.2, 0.1, 0.05, 0.025, etc. To obtain these dilutions, measure 10 cc. of 0.2 per cent acid in a graduate, pour half into the first tube, fill the graduate to the 10-cc. mark with water, mix, pour half into the second tube, and so on. To each tube add 5 cc. of starch paste, mix thoroughly, and add to each in quick succession 1 cc. of the neutralized saliva. Apply the same tests of digestion as were used in previous experiments. What concentration of acid is inhibitory? Compare your results with those of your neighbors. Test each tube with litmus, and with congo paper.

Plan and carry out a similar experiment to determine the effect of alkali on ptyalin. Use 1 per cent sodium carbonate for the highest concentration of alkali.

(*c*) *Condition of starch.*—Test the digestibility of raw starch, Continue the experiment, using a little toluene for antiseptic.

till the following exercise. What do you infer as to the desirability of cooking starchy foods thoroughly?

(*d*) *Specificity.*—Try the action of saliva on cane-sugar and Irish moss. What criterion of digestion will you use?

154. Preparation and Properties of Dextrin (SECTION **377**).—Heat about 5 grams of starch for one-half hour at 220°-225° in an oil-bath or air-bath. Pour the product into a mortar, add 2 cc. of water, and notice the adhesive quality of the mixture. Add 25 cc. of water and grind with a pestle. If there is a residue of starch which has not been converted into dextrin, filter through a folded filter. Use 2 cc. of the solution to determine whether the product reduces Fehling's solution. Test 2 cc. of the solution with a drop of iodine solution and note the color.

Add to the rest of the solution three times its volume of alcohol. Filter off the precipitated dextrin and wash twice with alcohol. Dissolve a little of the precipitate and test its reducing power with Fehling's solution. Determine the color produced by iodine solution. How does the color compare with that obtained during the intermediate stages of the hydrolysis of starch by acid (experiment 152*g*, page 124).

155. Properties of Cellulose (SECTIONS **380-382**).—(*a*) *Solubility in Schweitzer's reagent.*—This reagent is a saturated solution of copper hydroxide in a concentrated solution of ammonium hydroxide. It can be prepared as follows: Dissolve 5 grams of copper sulphate in about 100 cc. of water, and add a solution of sodium hydroxide as long as a precipitate is formed. Wash the precipitate three times by decantation with 500 cc. of water, and then filter through cotton; wash until the wash water is free from sulphates. Press out as much water as possible from the precipitate. Add to 10 cc. of concentrated ammonia (sp. gr. 0.90) the copper hydroxide as long as it dissolves. Add pieces of filter paper to the reagent as long as they dissolve, and filter through glass wool. Pour the solution into dilute hydrochloric acid.

(*b*) *Preparation of parchment-paper.*—Pour slowly with stirring 50 cc. of concentrated sulphuric acid into 30 cc. of water. Cool the solution to 15° to 20° and immerse in it strips of dry filter-paper. At the end of 15 to 20 seconds remove the paper, and wash it rapidly in running water; immerse the paper in a dilute solution of ammonia, and wash again with water. Test the toughness of the paper and of a piece of wet filter-paper. Put drop of a dilute solution of iodine in potassium iodide on the paper. Hang up a piece of the paper to dry and examine it at the next exercise.

(*c*) *Hydrolysis of cellulose.*—Grind in a mortar a pinch of cotton-wool or a filter-paper with a few drops of concentrated sulphuric acid until a sticky mass is obtained; add 50 cc. of water cautiously, and boil the resulting solution for 15 minutes. Neutralize the solution with sodium hydroxide, and test for a reducing sugar with Fehling's solution.

(*d*) *Preparation of cellulose acetate* (SECTION **381**).—In a small flask place 20 cc. of glacial acetic acid, 3 cc. of acetic anhydride, 4 drops of pure concentrated sulphuric acid, and 0.5 gram of cotton-wool. Press the cotton into the solution, and after a few minutes stir it so that most of the air bubbles are removed. Close the flask with a cork and let it stand over night or longer. (*Eq.*) Pour the solution in a thin stream, and with stirring, into 500 cc. of water. Filter, using a large funnel. Wrap the cellulose acetate in a piece of cotton cloth (a towel), and squeeze out as much water as possible; then set it aside until dry. Put about one-half the dry product in a small beaker or test-tube and add 10 cc. of chloroform. After standing some time the acetate should pass into solution. Pour the solution onto a watch-glass and let it evaporate slowly. When the chloroform has evaporated, put some water into the watch-glass and allow it to stand for a minute or two. Lift the edge of the film and remove it slowly from the glass. Dry the film and reserve it for a future test. Test the solubility of the rest of the acetate in glacial acetic acid, in alcohol, and in ether.

(*e*) *Preparation of cellulose nitrate.*—Pour 10 cc. of concentrated sulphuric acid into 10 cc. of concentrated nitric acid. To the hot mixture add 0.5 gram of cotton-wool. At the end of 3 minutes withdraw the nitrated cotton, and remove most of the acid adhering to it by pressing it with a glass rod against the side of the beaker. Put the cotton into a large amount of cold water. Wash for a minute in running water. squeezing out the water from time to time, and set aside to dry spontaneously. Hold a small bit of the dry nitrate with tongs, and place it in a flame. Test the solubility of a small amount of the product in alcohol.

Repeat using ether. In a test-tube cover some of the nitrate with a mixture made of equal volumes of alcohol and ether. At the end of a few minutes pour off the liquid onto a glass plate or watch-glass and let the solution evaporate slowly. Remove the film as in (*d*) above and dry. Place the edge of the film in a flame and as soon as it begins to burn remove it. Note the rate at which the film burns. Repeat using the film made from cellulose acetate. Do you observe any difference?

156. Properties of Pentosans (SECTIONS **365, 382, 656**).—(*a*) *Tests for lignin.*—Dissolve a few drops of aniline in a few drops of dilute hydrochloric acid, and dilute with 5 cc. of water. Pour one-half of the solution onto a piece of paper made from wood-pulp (newspaper) and one-half onto a paper made from linen. Repeat the tests using a solution of phloroglucinol in dilute hydrochloric acid.

(*b*) *Hydrolysis of pentosans.*—Boil a little gum arabic or wheat bran with 10 cc. dilute hydrochloric acid, and hold over the tube a piece of paper which has been dipped into a dilute solution of aniline in acetic acid.

CHAPTER XIII

COMPOUNDS CONTAINING SULPHUR

157. Formation of Mercaptan (SECTION **391**).—HOOD.—Warm together about 1 gram of potassium ethyl sulphate, 1 gram of sodium sulphide, and 2 cc. of water. (*Eq.*) Note the odor.

158. Preparation of Potassium and Mercuric Thiocyanates (SECTION **401**).—CAUTION.—Potassium cyanide is poisonous and should not be handled with the fingers. Boil together 13 grams of potassium cyanide, 6 grams of flowers of sulphur and 50 cc. of water, until the sulphur has dissolved. (*Eq.*) Filter the solution and evaporate to crystallization (§9, page 6). Cool, filter off the crystals, dry them, and evaporate the mother-liquor again to crystallization. Collect the crystals as before. Weigh the product obtained.

Dissolve a few of the crystals in water, and add the solution to a solution of ferric chloride.

Add a saturated solution of potassium thiocyanate to a saturated solution of mercuric chloride; filter off the precipitate, and press it into cones about 0.5 inch high and set aside to dry. Apply a lighted match to the top of a dried cone.

159. Formation of Potassium Xanthate (SECTION **402**).—Make a saturated solution of potassium hydroxide in alcohol by warming an excess of the alkali with 15 cc. of alcohol. Cool the solution, decant off the clear liquid, and add 3 cc. of carbon disulphide. (*Eq.*) Allow the solution to cool. Filter off the crystals, wash them with a mixture of 5 cc. of alcohol and 5 cc. of ether and dry them. Dissolve a little of the compound in water, and add a few drops of a solution of copper sulphate. The brownish-black precipitate of cupric xanthate changes immediately to yellow cuprous xanthate.

CHAPTER XIV

URIC ACID AND RELATED COMPOUNDS

160. Isolation of Uric Acid from Urine (SECTION **410**).—Add 50 cc. of concentrated hydrochloric acid to 500 cc. of urine and set aside in a cool place for 24 hours. Pour off the liquid from the crystals of uric acid which adhere to the side of the vessel. Collect the crystals, dissolve them in the smallest possible amount of boiling water, boil with a little bone-black, and filter the solution hot. On cooling, colorless crystals of uric acid are obtained. Examine them under the microscope and sketch the crystals.

161. Properties of Uric Acid (SECTION **410**).—(*a*) *Solubility of uric acid and its salts.*—Shake up about 0.01 gram of uric acid with about 5 cc. of water. Does the acid dissolve? Add a dilute solution of sodium hydroxide, drop by drop, and shake. When all the acid has dissolved add a slight excess of dilute hydrochloric acid, heat to boiling, filter and set aside.

(*b*) To a dilute solution of uric acid in sodium hydroxide add a little ammonia, some magnesia mixture, and ammoniacal silver nitrate. The gelatinous precipitate formed is silver magnesium urate. The insolubility of this salt is utilized in the separation of uric acid from urine. The purine bases in urine give similar insoluble salts.

(*c*) *Reduction of silver nitrate by uric acid.*—Dissolve a trace of uric acid in a few drops of a solution of sodium carbonate, and pour the solution upon a piece of paper moistened with silver nitrate solution. The silver salt is reduced to metallic silver. This reaction is known as Schiff's test for uric acid.

(*d*) *Murexide test for uric acid.*—On a small watch-glass moisten a few crystals of uric acid with 2 or 3 drops of dilute nitric acid. Evaporate to dryness on the steam-bath. Cool and add from a glass rod a drop of ammonia. A similar color test is given by other purines.

Repeat the test using bromine-water instead of nitric acid.

162. Isolation of Caffeine from Tea (SECTION **418**).—Boil gently 10 grams of tea with 500 cc. of water for 15 minutes. Filter through a folded filter, and precipitate the tannin by adding) drop by drop, to the hot filtrate a 10 per cent solution of lead acetate. When a precipitate is no longer formed, filter the solution again, and evaporate it to about 75 cc. If a precipitate has separated during the evaporation, filter again. Cool the solution, and extract it with 30 cc. of chloroform. Separate the chloroform and filter it through a dry paper. Set the solution aside to evaporate spontaneously. Observe the appearance of the crystals. Apply the murexide test to a few of the crystals. Use in one experiment nitric acid, and in another bromine-water. (See experiment 161*d* above.) Sublime the rest in watch-glasses. (See §35, page 24.) Taste a little of the sublimed caffeine.

CHAPTER XV

AROMATIC HYDROCARBONS

163. Preparation of Benzene from Benzoic Acid (SECTION **427**).—In a 6-inch evaporating dish place 10 grams of sodium hydroxide and 25 cc. of water. Heat over a free flame and stir until the sodium hydroxide dissolves; then stir in gradually 12 grams of benzoic acid. Evaporate to dryness over a free flame, which is kept constantly in motion; this will take about 10 minutes. Grind the mixture of sodium benzoate and sodium hydroxide in a mortar, and transfer it to an 8-inch test-tube. Clamp the test-tube in an inclined position so that the mouth of the tube is slightly lower than the other end; this will prevent any water given off during the heating from running back into the tube and cracking it. Connect the tube with a condenser and receiver, and heat with a free flame kept constantly moving, until no more liquid distils over. Measure the volume of the benzene and calculate the number of grams and the percentage yield obtained. Separate the benzene from the water, dry it with calcium chloride, and distil, noting the temperature.

Benzene melts at 5.4°, boils at 80.4°, and has the specific gravity 0.8736 (20°/4°). The yield should be about 6 grams.

NOTE.—By converting the benzoic acid into sodium benzoate in the presence of an excess of sodium hydroxide, an intimate mixture of the two substances is obtained. In this condition the compounds enter into reaction more readily and at a lower temperature than does a mixture of the acid and soda-lime; such mixtures are commonly used in the preparation of hydrocarbons from acids.

The benzene prepared in this way contains a small amount of diphenyl, which may be isolated from the residue left after the distillation of the hydrocarbon. The residue on crystallization from alcohol yields crystals of diphenyl, which after two sublimations melt at 71°.

164. Properties of Benzene (SECTION **430**).—(*a*) *Test for thiophene in commercial benzene* (SECTION **653**).—To a few drops of sulphuric acid add a crystal of isatin, about 5 cc. of crude benzene, and shake.

Test for carbon disulphide in benzene.—Add to about 10 cc. of crude benzene 2 drops of phenylhydrazine and set aside for some time. If carbon disulphide is present, a crystalline pre-----ate of the formula $(C_6H_5NH.NH_2)_2.CS_2$ will separate. If crude benzene is not available add 1 drop of carbon disulphide to 10 cc. of benzene, and test this mixture.

(*c*) *Melting-point of benzene* (SECTION 7).—Place about 50 cc. of benzene in a flask, insert a thermometer so that the bulb is covered, and place in a freezing mixture of ice and salt. When the benzene has become solid, remove the flask, and allow the mixture to melt partly. Note the temperature when about one-fourth of the benzene is liquid. Pour off the liquid, melt the benzene, and place the flask again in the freezing mixture, and let it stay until the benzene is solid. Remove the flask and determine the melting-point as before. Repeat until the melting-point remains constant. Pure benzene melts at 5.4°.

(*d*) *Inflammability of benzene.*—Burn a few drops of benzene in an evaporating dish. Is much soot formed?

(*e*) *Benzene and sulphuric acid.*—Shake 2 cc. of benzene with about 5 cc. of pure concentrated sulphuric acid. Is the hydrocarbon soluble? If the benzene is pure it will not markedly color the acid.

Shake together about 2 cc. of benzene and 5 cc. of fuming sulphuric acid (sp. gr. 1.89 at 20°) as long as heat is developed. Does the hydrocarbon dissolve? (*Eq.*) Pour the mixture slowly into a test-tube two-thirds full of ice. Does any insoluble substance separate?

In order to compare the behavior of aromatic hydrocarbons with that of the paraffins, repeat the above experiment using petroleum ether or gasoline in place of benzene.

(*f*) *Benzene and nitric acid.*—CAUTION.—As the reaction may become violent the mouth of the tube should be held away from the experimenter. Repeat experiment (*e*) above with both benzene and petroleum ether or gasoline, using fuming nitric acid (sp. gr. 1.48) in place of fuming sulphuric acid. When this test is applied to unknown substances, very small quantities should be used at first, since fuming nitric acid reacts with certain substances with explosive violence.

(*g*) *Test for a double bond in benzene.*—Apply the test with a solution of potassium permanganate. (See experiment 71*e*, page 51.)

(*h*) *Benzene and bromine.*—Add to about 10 cc. of benzene 1 cc. of a solution of bromine in carbon tetrachloride. Divide the solution into two parts; place one in direct sunlight and the other in the dark in your desk. Observe the two tubes after a few minutes. Compare the results with those obtained with gasoline (experiment 74*c*, page 52) and with amylene (experiment 74*a*, page 52).

HOOD.—Mix 5 cc. of benzene with 2 cc. of bromine. Add a small tack or clean piece of iron filings to the mixture. From time to time shake the mixture and breathe across the mouth of the tube. (*Eq.*) Let the mixture stand under the hood until the next exercise and then pour it into water. Is the liquid heavier than water? Explain.

NOTES.—(*d*) When aromatic compounds burn they produce a large amount of soot. Soot is also formed when unsaturated compounds and paraffin derivatives which contain alkyl radicals with four or more carbon atoms are burned. The simpler paraffin derivatives do not produce soot on burning. The behavior of an unknown substance on ignition is frequently determined as a preliminary test in its identification. The test is best made by putting some of the liquid or solid on a small roll of copper gauze, to which a piece of wire is attached to serve as a handle.

(*e* and *f*) The determination of the behavior of substances with sulphuric acid and with nitric acid is a valuable aid in their identification. Aromatic compounds yield, in general, soluble sulphonic acids with fuming sulphuric acid, and insoluble or difficultly soluble nitro-compounds with fuming nitric acid.

(*g*) The unsaturation of benzene and other aromatic hydrocarbons is of quite a different kind from that of ethylene. Aromatic hydrocarbons do not readily react with potassium permanganate in the cold.

165. Preparation of Ethylbenzene: Fittig Synthesis (SECTION **424**).—(*a*) In a round-bottomed one-half liter flask, which is placed in a vessel containing cold water, put 200 cc. of ether dried over sodium (see experiment 95*b*, page 73) and 27 grams of sodium in the form of a wire or thin shavings. Connect the flask by means of a *tightly fitting* stopper with a reflux condenser through which water is passing. In order to guard against any water entering the flask, wrap the stopper and the neck of the flask with a towel. CAUTION.—Read §41, page 28, carefully. When hydrogen is no longer evolved, add through the condenser a mixture of 60 grams of bromobenzene and 60 grams of ethyl bromide. At the end of about an hour turn off the water from the condenser, and let the reaction proceed for at least over night. Connect the flask with a condenser and receiver, and distil off the ether on a water-bath. Distil the residue directly with a large smoky flame, which is kept constantly in motion, as long as any liquid passes over. Fractionate (see §23, page 13) the product twice, and keep the fraction boiling at 133°-137°. Calculate the percentage yield obtained from the bromobenzene used. Add about 50 cc. of alcohol to the flask containing the excess of sodium, and let the mixture stand at least one-half hour.

Ethylbenzene boils at 135°, and has the specific gravity 0.883 at 0°. The yield in the preparation should be 25 to 28 grams.

(*b*) Ethylbenzene may be considered as a substitution-product of ethane and of benzene. Determine whether the hydrocarbon shows the characteristic properties of a paraffin or an aromatic hydrocarbon. State in your notes what tests were applied and the results in each case.

NOTE.—(*a*) In the preparation of hydrocarbons by the Fittig synthesis the halides used are often diluted with ether in order to moderate the reaction; the volume of ether used ordinarily is twice that of the halogen compounds. Benzene and petroleum ether are also used as diluents, especially in the ease of very active substances, when it is desired to have the reaction take place very slowly. When reaction takes place sluggishly, the mixture without diluents can be heated on a water-bath or in an oil-bath. The reaction between halides and sodium is catalyzed by a few drops of ethyl acetate or methyl cyanide.

The rates at which the halides react with sodium are different, and, consequently, an excess of the more reactive halide is used when a hydrocarbon containing two radicals is prepared. In the preparation of ethylbenzene the quantity of ethyl bromide required theoretically for 60 grams of bromobenzene is 41 grams; it has been found that a better yield is obtained if 60 grams of ethyl bromide are used. An excess of sodium is also used, as the metal becomes coated with sodium bromide, and thus is prevented from further action. The amount of sodium equivalent to 60 grams of bromobenzene and 60 grams of ethyl bromide is 21.5 grams; 27 grams of the metal are used.

If all the substances used have not been carefully dried, the hydrogen formed as the result of the reaction between sodium and water reduces a part of the halides to hydrocarbons.

In the preparation of hydrocarbons containing two different radicals, the product obtained is usually a mixture; in addition to ethylbenzene, some diphenyl and butane are formed in the preparation described above.

166. Preparation of Diphenylmethane (SECTION **435**).—As a large amount of hydrochloric acid is formed in the preparation the apparatus should be set up under a hood. In a 500-cc. flask provided with a reflux condenser, place 120 grams of benzene and an aluminium-mercury couple which is prepared as follows: Cut up 2 grams of aluminium foil into strips about 1 inch by 0.5 inch and allow them to stay in a solution of mercuric chloride, made by dissolving 1 gram of the salt in 200 cc. of water, for 8 to 10 minutes; a film of mercury is deposited on the aluminium. Wash the couple thoroughly with water, then with alcohol, ether, and finally with benzene. Into the upper end of the condenser place a separatory funnel containing 60 grams of benzyl chloride; allow the chloride to drop very slowly into the flask. At the end of an hour heat the flask on a water-bath for about 15 minutes. Pour the contents of the flask into an equal volume of water, which contains a little sodium hydroxide, shake, separate the benzene solution, and extract the aqueous layer once with a little benzene. Combine the benzene solutions, and dry them with calcium chloride. Pour off the solution into a distilling flask, and distil, using a condenser, until the temperature of the vapor reaches 150°. Remove the condenser, attach a short air condenser, distil, and collect the fraction which boils at 250°-300°. Redistil and collect the portion boiling at 255°-265°. Record the weight obtained, and calculate the percentage yield from the benzyl chloride. The yield should be about 35 grams.

Diphenylmethane melts at 26° and boils at 262°.

NOTE.—In the preparation of certain compounds by condensation as the result of the elimination of chlorine and hydrogen, an aluminium-mercury couple gives better results than aluminium chloride. It is probable that a little aluminium chloride is first formed by the action of the metal on the organic halogen compound; the presence of mercury makes the aluminium more active.

167. Oxidation of Diphenylmethane to Benzophenone (SECTIONS **435, 487, 572**).—In the identification of organic substances they are frequently oxidized and the products isolated. The following procedure is an example of one commonly used. Dissolve 5 grams of diphenylmethane in 10 cc. of glacial acetic acid and add a solution of crystalline chromic anhydride prepared by dissolving 4.5 grams of the anhydride in 5 cc. of water, and adding 30 cc. of glacial acetic acid. Let the mixture stand for half an hour, and then warm for an hour on the steam-bath. Pour the product into 100 cc. of water, filter off the oil through a moist filter paper, dissolve it in 20 cc. of hot alcohol, and add cold water until the solution clouds. Set aside to crystallize.

If an oil separates, rub it against the side of the beaker with a glass rod. A form of benzophenone which crystallizes with difficulty, is produced as the result of the oxidation of diphenylmethane. If a sample of benzophenone is available a trace can be used to seed the oil if it does not crystallize when rubbed sharply against the beaker. Determine the melting-point of the crystals. Benzophenone melts at 48°.

NOTE.—In oxidizing compounds with chromic anhydride, a slight excess is used over that required for the oxidation. Two molecules of the anhydride furnish three atoms of oxygen. If the compound which is insoluble in water is to be oxidized, acetic acid is often used as a solvent. As chromic anhydride is difficultly soluble in glacial acetic acid, it is first dissolved in a little water and acetic acid added to the solution. Oxidation takes place more readily in the presence of a small amount of sulphuric acid, which is often used as a catalytic agent.

168. Formation of Hexaphenylethane (SECTION **439**).—In a test-tube put about 20 cc. of ethyl acetate or ether, 1 gram of triphenylchloromethane and 5 grams of finely granulated zinc. Close the tube with a *tightly fitting* cork, and shake frequently during 10 minutes. Dissolve a little iodine in ethyl acetate. Filter off the solution from the zinc rapidly through a fluted filler-paper into two test-tubes; to one add the iodine solution drop by drop. (*Eq.*) Shake the other solution in contact with air, (*Eq.*) set the tube aside, and examine it in a few minutes.

169. Properties of Naphthalene (SECTIONS **446-448**).—(*a*) *Solubility of naphthalene.*—Test the solubility of naphthalene in hot and in cold water, alcohol, and ether.

(*b*) *Naphthalene and bromine.*—Add bromine, drop by drop, to a few crystals of naphthalene. Compare the ease of substitution in the case of this hydrocarbon with that of benzene.

(*c*) *Compound of naphthalene and picric acid.*—CAUTION.—Picric acid stains the hands; it should be handled carefully. Dissolve 0.1 gram of the hydrocarbon and 0.2 gram of picric acid in 5 cc. of boiling alcohol. Allow the solution to cool spontaneously, and collect the yellow needles on a filter by suction (see §42, page 29) and wash them three times with cold alcohol, using 1 cc. of alcohol each time. Dry the crystals on a porous tile for half an hour in the air, and then determine their melting-point. The compound of naphthalene and picric acid has the formula $C_{10}H_8.C_6H_2(NO_2)_3OH$; it melts at 150.5°.

NOTE.—(*b*) Naphthalene and bromine react readily without the presence of a halogen carrier. The reaction can be used to prepare anhydrous hydrogen bromide.

(*c*) Picric acid, which is trinitrophenol, forms crystalline addition-products with a number of organic compounds; these are frequently made as an aid in the identification of certain hydrocarbons. (See anthracene, SECTION **449**.)

CHAPTER XVI

NITRO COMPOUNDS AND SULPHONIC ACIDS

170. Preparation of Nitrobenzene (SECTIONS **460, 462**).—To 80 cc. of concentrated sulphuric acid, contained in a one-half liter flask, add 70 cc. of concentrated nitric acid cautiously with shaking. Keep the mixture cool by placing the flask in cold water. To the cold mixture of acids add slowly and with vigorous shaking 50 grams of benzene from a small flask in portions of about 2 cc. The addition should take about one-half hour. From time to time test the temperature of the mixture which should be kept warm (40°-50°). If the temperature rises above 50°, place the flask in cold water. When all the benzene has been added, connect the flask with a reflux air-condenser and place it *in* a water-bath the temperature of which is about 60°. Shake the flask vigorously about every 5 minutes. At the end of an hour cool the flask in running water, pour the contents into a separatory funnel, and separate the upper layer of nitrobenzene from the acids. Wash with about 100 cc. of water. As nitrobenzene is heavier than water the lower layer is separated this time and shaken vigorously with a dilute solution of sodium hydroxide until the aqueous layer shows an alkaline reaction. The nitrobenzene is finally washed again with water, tested for free acid, which should not be present, separated, and warmed on the steam-bath with about 10 grams of anhydrous calcium chloride until the turbid liquid has become clear and no drops of water are visible. Decant or filter the liquid into a distilling flask, and distil using an air condenser. Reject the first part of the distillate which contains benzene and is apt to be cloudy due to the presence of a trace of water, and collect what distils at 204°-208°. Calculate the percentage yield obtained from the benzene.

Nitrobenzene boils at 207° (uncorrected), melts at 3°, and has the specific gravity 1.204 at 20°/4°. The yield should be about 60-70 grams.

NOTE.—A low yield of nitrobenzene may be the result of one of the following causes: Either the nitration was effected at too low a temperature and a quantity of benzene is recovered in the final distillation, or the temperature of the mixture reaches too high a point and a large amount of dinitrobenzene is formed. In the latter case there will be an appreciable residue in the flask when the temperature reaches 207° in the final distillation. This result is apt to occur if the benzene is added too rapidly at first, and the mixture of acid kept at too low a temperature; little nitration occurs, and when the mixture is heated in the water-bath, the reaction takes place rapidly, and the heat generated causes the temperature to rise above 60°, with the result that dinitrobenzene is formed. The effect on the result of the temperature at which nitration is carried out is marked, as can be seen by comparing with the above preparation that of dinitrobenzene described below.

It is necessary to wash the nitrobenzene free from nitric acid. If this is not done, the acid which remains dissolved in the nitrobenzene will react further with it when the product is distilled. Brown vapors of oxides of nitrogen will be given off, dinitrobenzene will be formed, and an explosion may occur. The residue of dinitrobenzene should not be distilled; it is apt to decompose violently when the flask is nearly empty. It may be dissolved out of the flask and crystallized from alcohol.

171. Properties of Nitrobenzene (SECTIONS **461, 469**).—(*a*) *Solubility of nitrobenzene.*—Describe the odor of nitrobenzene. Determine whether nitrobenzene is soluble in alcohol, ether, benzene, dilute hydrochloric acid, and a solution of sodium hydroxide. Mix about 2 cc. of nitrobenzene with 5 cc. of concentrated sulphuric acid and pour the mixture into water. How could you most readily separate into its constituents a mixture of benzene and nitrobenzene?

(*b*) *Reduction of nitrobenzene to aniline.*—Place 2 cc. of nitrobenzene and about 3 grams of granulated tin in an 8-inch test-tube, and add with constant shaking, in portions of 1 cc., 5 cc. of concentrated hydrochloric acid. The acid should be added at such a rate that the tube becomes hot, but care should be taken to avoid a violent reaction. Do not add the next portion of acid until the solution begins to cool. Finally, boil the solution for about 3 minutes, shaking the tube constantly. Cool under running water and add a strong solution of sodium hydroxide (1:2) until the precipitate first formed has largely dissolved (about 20 cc.). Remove with a pipette a few of the oily drops which separate. Put 1 drop of the oil on a watch-glass and place near it a drop of concentrated hydrochloric acid; bring the drops together by touching them with a glass rod. (*Eq.*)

Aniline hydrochloride, $C_6H_5NH_2.HCl$, is formed as a crystalline solid. Shake up a few drops of the aniline with 2 cc. of water and add a few drops of bromine-water. Tribromoaniline, $Br_3C_6H_2NH_2$, is precipitated.

(*c*) *Reduction of nitrobenzene to phenylhydroxylamine* (SECTION **506**).—Dissolve 3 drops of nitrobenzene in 2 cc. of water and 2 cc. of alcohol, and add about 6 drops of a 10 per cent solution of calcium chloride and a pinch of zinc dust. Heat to boiling for one-half minute and filter. Add to the filtrate a strongly ammoniacal solution of silver nitrate. The phenylhydroxylamine, C_6H_5NHOH, formed as the result of the reaction reduces the silver salt to metallic silver.

NOTES.—(*a*) Many nitro compounds are insoluble in sodium hydroxide but impart a marked color to the solution of the alkali. Concentrated sulphuric acid is a valuable reagent to separate many nitro compounds from substances which are insoluble in the acid. The change in appearance of the nitrobenzene after solution and precipitation is due to the fact that when a solution of an oil insoluble in water is poured into water, the oil separates in minute globules which cause a milky appearance.

(*b*) The reduction of nitro compounds to amines, which are soluble in dilute acids, is a reaction of importance in their identification. It should be noticed, however, that substances other than nitro compounds can be reduced to amines. Among these are hydroxylamines, and azo, hydrazo and azoxy compounds (SECTIONS **509, 510**). The test is, nevertheless, of value in the identification of nitro compounds.

(*c*) Nitro compounds are reduced in neutral solution to hydroxylamine derivatives; the reaction takes place more readily *in* the presence of a little calcium chloride. The hydroxylamines reduce an ammoniacal solution of silver nitrate. Nitroso, azo, and azoxy compounds behave in a similar manner.

172. Preparation of m-Dinitrobenzene (SECTION **463**).—To 5 grams of benzene contained in a 100-cc. flask, fitted with a cork and a piece of glass tubing about 2 feet long to serve as a reflux condenser, add slowly in small portions, shaking the flask constantly, a cooled mixture of 18 cc. of concentrated nitric acid and 30 cc. of concentrated sulphuric acid. The acid should be added at first in portions of about 1 cc; about 10 minutes are required for the addition of the mixture. After the main reaction has ceased, remove the condenser and boil the mixture *gently* over a free flame for 5 minutes. Cool the contents of the flask to about 80° and pour the product slowly with stirring into about

200 cc. of water. Filter by suction, and wash twice with water. Dissolve the dinitrobenzene in 40 cc. of hot alcohol and set aside to crystallize. Filter off the crystals by suction and wash with 10 cc. of cold alcohol. Dry the crystals on a porous plate, and determine their melting-point. By adding 10 cc. of water to the filtrate a small additional amount of dinitrobenzene can be obtained. Calculate the percentage yield.

m-Dinitrobenzene crystallizes in colorless, odorless needles, which melt at 90°, and boil at 297°. It is readily soluble in hot alcohol; it dissolves in about 28 parts of alcohol at 20°. The yield in the preparation should be about 9 grams.

NOTE.—Small quantities of benzene and other hydrocarbons can be readily identified by converting them into solid nitro derivatives the melting-points of which can be determined. As little as 2 or 3 drops of benzene is sufficient for the identification of the hydrocarbon in this way. In working with such a small quantity proceed as follows: Mix 3 drops of benzene and 1 cc. each of concentrated sulphuric acid and concentrated nitric acid. Boil the mixture for one-half minute. Cool, and pour slowly into 10 cc. of water. Shake, filter by suction (§42, page 29), and wash with water. Dissolve in a boiling mixture of 4 cc. of water and 4 cc. of alcohol. Set aside to crystallize, filter, wash with 5 cc. of cold 50 per cent alcohol, and dry on a porous plate. The compound prepared in this way melts at 89°-89.5°.

SULPHONIC ACIDS

173. Preparation of Sodium Benzenesulphonate (SECTION **470**).—In a 250-cc. flask place 50 grams of fuming sulphuric acid which contains 8 to 10 per cent of sulphur trioxide (sp. gr. 1.90), connect the flask with a reflux condenser, and add, drop by drop, from a separatory funnel suspended in the condenser, 20 grams of benzene. During the addition of the benzene, which should take from 10 to 15 minutes, the flask should be shaken vigorously every minute or two. If all the benzene does not dissolve after continuous shaking for a few minutes, heat the mixture on a water-bath until solution is complete.

The sulphonic acid formed can be separated in the form of a salt by either of the methods described below. In the first method (*a*), which in the case of benzenesulphonic acid is simpler, advantage is taken of the fact that sodium benzenesulphonate is insoluble in a solution of sodium chloride. The second method (*b*) is the one commonly used to isolate sulphonic acids. It is based on the fact that the calcium salts of sulphonic acids are soluble in water, whereas calcium sulphate is very difficultly soluble. In certain cases it is advisable to prepare the barium salts.

(*a*) Dissolve 65 grams of sodium chloride in 250 cc. of water, and filter the solution if necessary. Measure off 200 cc. of the solution, and reserve the rest for washing the crystals of sodium benzenesulphonate. Pour into 200 cc. of the salt solution, slowly and with stirring, the mixture of benzenesulphonic acid and sulphuric acid. Filter off from the warm solution the diphenylsulphone, $(C_6H_5)_2SO_2$, which separates, and cool the filtrate in cold water, using ice if necessary. If crystals do not separate, scratch the side of the vessel containing the solution with a glass rod. Let the crystals stand with the mother-liquor for about 15 minutes to insure the complete separation of the salt. Filter by suction, and drain off as much of the liquid as possible by pressing the solid down firmly with a spatula. Disconnect the filter-flask from the pump, and cover the salt with a part of the sodium chloride solution which was reserved for this purpose. When the liquid has penetrated into the solid, remove it by the aid of the pump; repeat the washing with more of the salt solution. Draw off as much of the liquid as possible, and transfer the sodium benzenesulphonate to a porous plate to dry. The compound prepared in this way contains about 0.5 per cent of sodium chloride. Weigh the product and calculate the yield. About 30 grams of sodium benzenesulphonate should be obtained.

(*b*) Pour the mixture of sulphuric acid and benzenesulphonic acid into 500 cc. of water in a large evaporating dish, and heat it to boiling. Add precipitated calcium carbonate, which has been rubbed to a thick paste with water, until the solution no longer shows an acid reaction. Filter through a cotton cloth filter to separate most of the calcium sulphate, and wash the precipitate with hot water. If a small amount of solid passes through the filter the solution need not be refiltered, as the precipitate will be removed in a later filtration. Evaporate the solution to about one-half its volume, and add just enough of a solution of potassium carbonate to precipitate the calcium and convert the salt into potassium benzenesulphonate. If it is difficult to determine when the calcium has just been precipitated, filter off a few cubic centimeters of the solution from time to time, and add to the filtrate a drop of the solution of potassium carbonate. An excess of potassium carbonate should be avoided, for a sample of pure potassium benzenesulphonate is desired. Filter off the calcium carbonate, wash it with a little hot water, evaporate the solution to crystallization, and let it cool. Filter off the crystals and dry them on a porous plate. The filtrate on evaporation will yield a further quantity of the salt. Calculate the percentage yield obtained.

Potassium benzenesulphonate crystallizes in lustrous plates, which effloresce in the air. The salt is very soluble in water, and melts above 300° with decomposition.

NOTE.—(*b*) The free sulphonic acid can be obtained from the calcium salt by adding to its solution just enough sulphuric acid to precipitate the calcium as sulphate, evaporating the solution to a small volume, and placing it in a desiccator to evaporate over sulphuric acid. In the preparation of free sulphonic acids in this way it is better to prepare the barium salt, as barium sulphate is less soluble in water than calcium sulphate, and the free acid is not contaminated with a small amount of sulphate.

174. Identification of a Sulphonic Acid by Conversion into a Phenol (SECTION **477**).—Melt about 1 gram of sodium hydroxide in a small iron or porcelain crucible, and add to the fused mass about 0.5 gram of sodium benzenesulphonate. Keep the mixture just above its melting-point, and do not let it char. Stir occasionally during 5 minutes. Cool, dissolve in water, acidify with dilute hydrochloric acid, and note the odor produced. Filter and add bromine water, drop by drop. Write equations for all the reactions involved in the test.

175. Preparation of Benzenesulphonyl Chloride (SECTION **473**).—Convert all of the salt of benzenesulphonic acid obtained in experiment 173 above into benzenesulphonyl chloride as follows: HOOD. Place the dry salt in a flask and add phosphorus pentachloride, which should be weighed in the hood, in the proportion of 3 parts by weight of the salt to 4 parts by weight of the chloride. Heat the mixture on the steam-bath, with occasional shaking, for half an hour. Cool, and add to the liquid about ten times its volume of ice-water. Shake about every 10 minutes in order to facilitate the reaction of the phosphorus oxychloride present with water. At the end of an hour pour off the water and wash the oil twice with water by decantation. Separate the benzenesulphonyl chloride and calculate the percentage yield.

The chloride can be used without further purification for the experiments given below. If it is desired to preserve the chloride for future use (see experiment 186, page 157), it should be taken up in ether, dried over calcium chloride and distilled under reduced pressure (§24, page 15) after the ether has been removed.

Benzenesulphonyl chloride is a colorless liquid which distils at 246°-247° with decomposition, and undecomposed at 120° under a pressure of 10 mm. It melts at 14.5°.

176. Preparation of Benzenesulphonamide (SECTION **474**).—Put into a test-tube about 1 cc. of benzenesulphonyl chloride and add about 5 cc. of strong ammonia. Shake until a solid is formed and the odor of the chloride has disappeared. Pour off the liquid and wash twice with water by decantation. Add about 20 cc. of water; heat to boiling until the substance has dissolved. Filter, if necessary, and set the solution aside to crystallize. When cold, filter by suction, wash with cold water, and dry the amide for half an hour on a porous place. Determine the melting-point of the amide. If the crystals do not melt sharply, recrystallize them from hot water.

Benzenesulphonamide crystallizes from hot water in needles, which melt at 156°.

NOTE.—Sulphonamides are frequently made in the identification of sulphonic acids or their salts. The preparation can be carried out with small quantities in a few minutes. Proceed as follows: Warm together in a test-tube on a steam-bath about 0.5 gram of the salt with an equal volume of phosphorus pentachloride, until the mixture liquefies. Cool, pour 5 cc. of water into the tube, warm gently, and shake for about 1 minute. Pour off the liquid and wash twice by decantation with 5 cc. of cold water. Add 6 cc. of ammonia and proceed as described in the experiment above.

177. Preparation of p-Toluenesulphonic Acid (SECTION **476**).—To 25 grams of toluene in a 200-cc. flask add 25 cc. of pure concentrated sulphuric acid, and place on the steam-bath. Allow the mixture to stand until the toluene has dissolved. This will require about 2 hours if the flask is shaken once in a while. Let the solution cool; before it solidifies pour it, with stirring, into 100 cc, of pure concentrated hydrochloric acid. Heat the mixture on the steam-bath until the solid dissolves. Set aside to crystallize. Filter by suction, and wash the crystals with concentrated hydrochloric acid. Press the crystals to remove as much of the mother-liquor as possible and dry them on a porous plate. Weigh the toluenesulphonic acid and calculate the percentage yield from the toluene used.

p-Toluenesulphonic acid crystallizes from water, in which it is very soluble, in long colorless needles. It is less soluble in concentrated hydrochloric acid. It melts at 104°-105°. The yield should be about 25 grams. The amide can be prepared by the method described in experiment 176; it melts at 136°-137°.

CHAPTER XVII

HALOGEN DERIVATIVES OF AROMATIC HYDROCARBONS

178. Preparation of Bromobenzene (SECTION **481**).—To 50 grams of benzene in a 200-cc. flask add 35 cc. (105 grams) of bromine. Fit the flask with a cork stopper through which passes a glass tube, bent twice at right angles. The longer arm of the tube which passes through the cork should be about 2 feet long. Place below the end of the shorter arm a flask containing 100 cc. of water to absorb the hydrobromic acid formed in the reaction; the end of the tube should be just above the surface of the water. Put the flask containing the benzene and bromine in a pail or large beaker containing ice-water, and add to the flask two clean iron tacks or nails. Allow the reaction to proceed until the next laboratory exercise. Wash the product with water, and with a little sodium hydroxide if necessary, until any excess of bromine has been removed. Place the liquid in a separatory funnel, separate it, and dry it with anhydrous calcium chloride. Fractionate three times, collecting the following fractions: up to 120°, 120-150°, 150°-160°, 160°-200°. The fraction boiling at 150°-160° is practically pure bromobenzene. Calculate the molecular proportions in which the reacting substances were used in the preparation and the percentage yield obtained. Determine the specific gravity of the bromobenzene (§56, page 37).

The residue boiling above 200° contains *p*-dibromobenzene. It may be poured while still hot onto a watch-glass, and crystallized from alcohol. (See directions under the preparation of dibromobenzene.)

Put the hydrobromic acid collected as a by-product in the reaction into the bottle provided for hydrobromic acid residues. This preparation yields a large amount of hydrobromic acid, as one-half of the bromine used is converted into the acid. On distillation the aqueous solution yields an acid than can be used conveniently for the preparation of alkyl halides.

Bromobenzene boils at 156°, and has the specific gravity 1.491 at 20°. The yield in this experiment should be from 60 to 65 grams.

NOTE.—In order to obtain a good yield of bromobenzene, it is advisable to keep the mixture of benzene and bromine cold during the reaction. The product obtained consists of a mixture of benzene, bromobenzene, and dibromobenzene. The effect of the temperature on the reaction is clearly seen by comparing the method used in this preparation with that employed to prepare dibromobenzene. See the experiment below.

179. Preparation of p-Dibromobenzene (SECTION 482).—HOOD. To 5 grams of benzene in a small round-bottomed flask add 10 cc. of bromine. Close the flask with a cork through which passes a piece of glass tubing about 3 feet long to serve as a reflux condenser. Place the flask in the hood, drop into it a tack or piece of clean iron filing, and allow the reaction to proceed spontaneously to completion; this usually takes about 30 minutes. Then heat the flask cautiously over a free flame for 2 minutes to expel most of the excess of bromine. Add about 50 cc. of water and heat to boiling, shaking vigorously. Cool until the dibromobenzene solidifies, and decant off the liquid. Repeat the washing with hot water twice, adding to the liquid the last time about 50 cc. of a solution of sodium hydroxide. Cool and wash the crystals once more with cold water, decant off the water, add 75 cc. of alcohol and a little bone-black, and heat to boiling. Filter the hot solution, and add 20 cc. of water. Set aside to crystallize. Separate the crystals and determine their melting-point. Calculate the percentage yield obtained.

p-Dibromobenzene crystallizes in colorless leaflets, which melt at 89° and boil at 219°. The yield should be about 13 to 14 grams.

180. Properties of Aromatic Halogen Compounds (SECTION **479**).-(*a*) *Solubility of halogen compounds.*—Determine whether bromobenzene is soluble in the following: Water, alcohol, ether, concentrated sulphuric acid, dilute hydrochloric acid, and a solution of sodium hydroxide.

(*b*) *Inflammability of halogen compounds.*—Wrap a strip of copper gauze about 1 cm. wide around a piece of wire to serve as handle, so that a roll about as thick as a lead pencil is formed.

Pour a few drops of the liquid or place a few crystals on the gauze and place it for an instant in a flame. Remove the gauze and note whether soot is formed by holding the burning substance in front of a piece of white paper. Determine whether the following substances burn, and whether soot is produced: Benzene, bromobenzene, dibromobenzene, benzyl chloride, ethyl bromide, chloroform, carbon tetrachloride. What conclusions can be drawn from the experiment? (See the note to experiment 164*d*, page 134.)

(*c*) *Comparison of the behavior of compounds containing the halogen joined directly to the benzene ring with those containing the halogen in a side-chain.*—Read carefully SECTIONS **479, 480**. Compounds of the two classes behave differently with an alcoholic solution of potassium hydroxide. In order that conclusive results may be drawn from the test, it is necessary to have a solution of the alkali which is free from halogen. As all samples of commercial potassium hydroxide contain potassium chloride, prepare a solution by dissolving about 1 gram of the hydroxide in 20 cc. of *absolute* alcohol; filter from the undissolved carbonate and chloride and use the clear filtrate for the tests.[1] Test a part of the solution so prepared for a halide as follows: Dilute with water, acidify with nitric acid, and add silver nitrate. Add 3 drops of benzyl chloride to 5 cc. of the alcoholic potassium hydroxide solution, and boil gently for 2 minutes. Dilute with water, acidify with pure dilute nitric acid, and add a few drops of a solution of silver nitrate. Repeat the experiment, using bromobenzene. In order not to confuse with silver bromide the cloudiness produced when the bromobenzene is precipitated from the alcoholic solution by the addition of water, add 3 drops of bromobenzene to 5 cc. of alcohol and dilute with the amount of water used in the test. Compare the appearance of the solution with the one which was heated. If the unchanged precipitated organic halogen compound interferes with the observation of the silver halide, it can be removed by shaking the solution with ether, and adding the silver nitrate to the clear aqueous solution.

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[1] A solution which can also be used for the test may be prepared by dissolving about 0.5 gram of clean sodium, free from any crust, in 20 cc. of alcohol and adding a few drops of water.

NOTE.—(*c*) In applying this test it is necessary to determine first whether the compound contains any free halogen acid, which has been produced as the result of decomposition on standing. Shake a little of the substance with water, and test the aqueous solution with silver nitrate. If a precipitate is formed, the halide must be washed with water until the latter gives no test for halides.

181. Preparation and Properties of Triphenylchloromethane (SECTION **488**).—(*a*) Attach to a 500-cc. flask by means of a stopper a small drying tube containing anhydrous calcium chloride. Provide a beaker containing cold water into which the flask can be sunk up to the neck and held in place by a wire. Add to the flask 31 grams of carbon tetrachloride, 78 grams of benzene, and 28 grams of anhydrous aluminium chloride in the form of lumps.

Let the flask stand in the hood for at least 24 hours. In a beaker place 100 grams of shaved ice or snow and add 100 cc. of concentrated hydrochloric acid. Pour the mixture into the flask, add 50 cc. of benzene, and shake the flask under running water until two distinct layers are formed. Separate the upper layer with the aid of a separatory funnel, and add to it about 5 grams of anhydrous calcium chloride. Shake the flask to bring the drying agent in contact with any water present. In about 5 minutes filter the solution into a flask and distil on a boiling water-bath as long as any liquid passes over. Pour the contents of the flask into a beaker, add to the flask 100 cc. of petroleum ether, and pour the latter into the beaker.

The next day filter off the crystals by suction. Disconnect the flask from the pump, add 25 cc. of petroleum ether and in a few minutes draw off the liquid adhering to the crystals. Repeat the washing with another 25 cc. portion of petroleum ether. Spread the crystals on a paper to dry and weigh them.

Triphenylchloromethane melts at 109°-111°. It can be crystallized from boiling ligroin, in which it is readily soluble hot and difficultly soluble cold. Since triphenylchloromethane is decomposed when heated with water, anhydrous solvents should be used. The compound can be obtained in a very pure condition by recrystallizing it from the boiling acetyl chloride. The yield of the material obtained is 60 per cent of the theoretical. By distilling off the solvent from the first crystallization, and adding to the residue 50 cc. of petroleum ether, an additional quantity of triphenylchloromethane can be recovered which increases the yield to 75 per cent.

NOTE.—If the dark red oil which separates at first in the reaction is decomposed at once by water, benzophenone chloride, $(C_6H_5)_2CCl_2$, is obtained. This red oil, which is a molecular compound of benzophenone chloride and aluminium chloride, reacts on standing with more benzene and is converted into a substance of the composition $(C_6H_5)_2CCl.AlCl_3$, which is a crystalline solid. Water decomposes this addition-product into its constituents.

(*b*) *Reaction with water.*—Powder about 0.1 gram of triphenylchloromethane and shake it in a test-tube with water. Let the mixture stand a few minutes and then test the aqueous solution for hydrochloric acid with litmus paper and with silver nitrate.

(*c*) *Reaction with sulphuric acid.*—In a small beaker treat about 2 grams of triphenylchloromethane with 5 cc. of concentrated sulphuric acid, and shake until solution is complete. Is hydrogen chloride given off? Compare the results with those obtained with ethyl bromide (experiment 132*a*, page 101). Pour the solution into 50 cc. of water, filter off by suction the precipitate of triphenylcarbinol, wash with water, and dry it. Add a small amount of the carbinol to a little concentrated sulphuric acid on a watch-glass. Grind thoroughly some of the carbinol in a mortar with a little concentrated hydrochloric acid for about 1 minute. Remove the product with a spatula to a porous plate and let it dry. Add the compound to a little concentrated sulphuric acid. Write equations for all reactions which take place.

(*d*) *Reaction with silver nitrate.*—Dissolve a bit of triphenylchloromethane in a little acetone and add an alcoholic solution of silver nitrate. (*Eq.*)

(*e*) *Reaction with metals.*—Repeat experiment 168, page 137.

181a. Preparation of Triphenylmethane from Triphenylchloromethane.—When the addition-product of triphenylchloromethane and aluminium chloride is treated with ether, the halogen atom in the former is replaced by hydrogen.

Attach to a 250-cc. flask, by means of a cork, a drying tube containing anhydrous calcium chloride. Have ready a beaker containing cold water into which the flask can be sunk up to the neck and can be held in place by means of a wire. Add to the flask 29 grams of carbon tetrachloride, 73 grams of benzene, and

25 grams of anhydrous aluminium chloride in the form of lumps. Place the flask in the water and let it stand at least 24 hours.

Connect the flask with a return condenser, place it in water and add through the condenser 30 grams of ether. Shake occasionally and let the mixture stand at least 24 hours. Pour the mixture onto 200 grams of ice and 5 cc. of concentrated hydrochloric acid. Add 100 cc. of carbon disulphide and shake until two layers have formed. Separate and dry the oil with calcium chloride. Filter into a flask and distil off the carbon disulphide. Transfer the residue to a small flask and distil, using a short glass tube as an air-condenser. Collect the fraction boiling between 330° and 356°. The distillate, which should weigh about 33 grams, is dissolved in 135 cc. of boiling alcohol. The solution is stirred as it cools. When cold, filter off the triphenylmethane by suction and wash twice with 10 cc. of cold alcohol. Weigh the product after drying in the air, determine its melting-point, and calculate the yield from the carbon tetrachloride used. The yield should be about 60 per cent of the theoretical. Triphenylmethane melts at 92°.

CHAPTER XVIII

AROMATIC AMINES

182. Preparation of Aniline (SECTION **494**).—Provide a 1-liter flask with a cork and tubes arranged for distillation with steam (§28, page 19); the tubes will be needed later in the preparation and should be ready for use. Place in the flask 25 grams of nitrobenzene and 50 grams of granulated tin, and connect it with a reflux air-condenser. Add to the mixture 125 cc. of concentrated hydrochloric acid in the following way: Add about 10 cc. of the acid and shake vigorously. If reaction does not take place in a minute or two, warm gently until there is an evolution of hydrogen and the reaction produces sufficient heat to keep the flask warm. When the reaction subsides, add another portion of 10 cc. of acid, and shake. Continue in this way until about one-half the acid has been added. If the reaction becomes too vigorous and there is chance of vapor escaping from the flask, place the latter in cold water. Care must be taken not to keep the flask so cold that the reaction does not proceed rapidly. The last half of the acid may be added in portions of about 20 cc. When all the acid has been added, heat the flask on a boiling water-bath, shaking occasionally, until no drops of nitrobenzene can be seen floating on the surface of the liquid. The odor of nitrobenzene should also disappear. From 1/2 to 1 hour is required to complete the reaction in this way.[1] Add to the hot solution 50 cc. of water, place the flask in cold water, and add a solution of 90 grams of sodium hydroxide in 150 cc. of water until most of the precipitate first formed has dissolved and the solution shows a strong alkaline reaction. The mixture must not be cooled too strongly; it is necessary only to keep it

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[1] If the preparation can not be completed in one exercise it is well to stop at this point; if the alkali to liberate the aniline is added, and the mixture allowed to cool, it is necessary to heat the flask to boiling before the contents are distilled with steam. The distillation requires about an hour.

from boiling in order to prevent loss of aniline. Distil with steam. The aniline passes over at first as a colorless oil. As the compound is somewhat soluble in water (about 1 part in 30), the distillation should be continued after the drops cease to form; change the receiver at this point and collect about 100 cc. of the solution. Combine the two distillates and saturate the solution with sodium chloride, using 20 grams of salt for each 100 cc. of solution. Extract twice with ether using about 200 cc. each time (§31, page 21). Separate the ether, place it in a bottle, and add 3 or 4 sticks of potassium hydroxide. Stopper the bottle and let the solution stand over night. Filter the solution into a dry flask. The water extracted from the ethereal solution forms with the potassium hydroxide a saturated solution of the alkali; care should be taken not to allow this to get into the flask. Distil off the ether on a water-bath (see §34, page 23). Transfer the residue to a small dry flask, wash out the first flask with a few cubic centimeters of the dry ether which has just been distilled off, and add the solution to the aniline. Distil over a free flame using an air-condenser, heating cautiously until the small amount of ether has come over, and collect the fraction boiling at 180°-184°. Calculate the percentage yield obtained.

Aniline boils at 182° (183.7° corrected), and has the specific gravity 1.024 at 16°. The yield should be from 85 to 90 per cent.

183. Properties of Aniline (SECTIONS **490, 494**).—(*a*) *Solubility of aniline.*—Determine whether aniline is soluble in the following: water, dilute sodium hydroxide, dilute hydrochloric acid, concentrated sulphuric acid, alcohol, and benzene.

(*b*) *Salts of aniline.*—Add 2 cc. of aniline to 5 cc. of water and add 1 cc. of concentrated sulphuric acid. Heat to boiling and set the solution aside to crystallize. (*Eq.*)

Heat together in a small beaker about 5 cc. of aniline, 5 cc. of water, and 10 cc. of concentrated hydrochloric acid. When the solution is cold, filter off the crystals by suction; do not wash them with water in which they are very soluble. Dry the crystals in a beaker on the steam-bath. The salt will be needed for the following experiments.

(*c*) *Double salts containing aniline.*—Make a saturated solution of about 1 gram of aniline hydrochloride in a little water. To one-half of the solution add a few drops of a solution of platinum chloride, and to the other a few drops of saturated solution of stannous chloride, and cool. (*Eqs.*)

(*d*) *Base-forming property of aniline.*—Make a saturated aqueous solution of aniline by shaking about 1 cc. of the amine with 16 cc. of water. Test the clear solution with litmus paper, and add some of it to a solution of aluminium sulphate or chloride. Compare the results with those obtained with methylamine (experiment 113*b*, page 98). Explain.

(*e*) *Hydrolysis of salts of aniline.*—Dissolve a little aniline hydrochloride in water and test the solution with litmus paper. Is the result in accord with those obtained in (*d*) above? Explain.

(*f*) *Reaction of salts of aniline with bases.*—Add to a concentrated aqueous solution of aniline hydrochloride a solution of sodium hydroxide. (*Eq.*)

(*g*) *Aniline and acetyl chloride.*—Add acetyl chloride, drop by drop, to 1 cc. of aniline as long as an evident reaction takes place. Add about 15 cc. of water and heat to boiling, filter hot, and cool in running water. (*Eq.*) Filter off the precipitate by suction, wash twice with cold water, and dry the crystals on a porous plate for half an hour. Determine the melting-point of the crystals. Acetanilide melts at 112°. Amines are frequently identified by converting them into acetyl derivatives.

(*h*) *Aniline and bromine.*—Add bromine-water, drop by drop, to an aqueous solution of aniline until the solution becomes yellow. Tribromoaniline, which is precipitated, crystallizes from alcohol and melts at 116°.

(*i*) *Aniline and nitrous acid.*—Dissolve about 1 cc. of aniline in 2 cc. of concentrated hydrochloric acid and 5 cc. of water. Cool the solution in running water. Add a cold solution of about 0.5 gram of sodium nitrite in 5 cc. of water. Shake, and heat gently. Observe that a gas is given off, and note the odor of the solution. (*Eq.*)

(*j*) *Aniline and ferric chloride.*—Add to an aqueous solution of aniline a few drops of a dilute solution of ferric chloride.

(*k*) *Aniline and hypochlorites.*—Add to a dilute aqueous solution of aniline a solution of bleaching powder or of sodium hypochlorite.

(*l*) *Aniline and potassium bichromate.*—Mix on a watch-glass a drop of aniline with 3 drops of concentrated sulphuric acid, and add 2 drops of a solution of potassium bichromate. Note the color, and heat on the steam-bath for a few minutes.

(*m*) *Aniline and methyl iodide.*—Mix together 3 cc. of aniline and 2 cc. of methyl iodide, and let the mixture stand in a stoppered tube until the next exercise. (*Eq.*) Remove the crystals, dry them on a porous plate, and then treat them with a strong solution of sodium hydroxide. (*Eq.*) Note the odor. Is it like that of aniline?

NOTES—(*a*) The solubility of many amines in dilute hydrochloric acid serves to distinguish them from other nitrogen compounds. Amines which contain a number of strongly negative groups are insoluble in the acid.

(*g*) Acetyl chloride is a useful reagent to distinguish primary and secondary amines from tertiary amines. Alcohols and phenols also react with acetyl chloride.

(*h*) Many amines give a precipitate of an insoluble substitution-product when treated with bromine water; certain phenols give a similar reaction.

184. Properties of Methylaniline (SECTIONS **491, 502**).—(*a*) *Methylaniline and acetyl chloride.*—Add acetyl chloride, drop by drop, to about 1 cc. of methylaniline, add water, and heat to boiling. Cool. (*Eq.*) The acetyl derivative formed melts at 102°.

(*b*) *Methylaniline and nitrous acid.*—Repeat experiment 183*i*, page 155, using methylaniline in place of aniline. Is an oil formed? Compare the results in the two experiments. (*Eq.*)

185. Properties of Dimethylaniline (SECTIONS **492, 504**).—(*a*) *Dimethylaniline and acetyl chloride.*—Repeat experiment 184*a*, page 156, and compare the results obtained when primary, secondary, and tertiary amines are treated with acetyl chloride.

(*b*) *Dimethylaniline and nitrous acid: nitroso-dimethylaniline.*—Dissolve 5 grams of dimethylaniline in a mixture of 10 cc. of concentrated hydrochloric acid and 40 cc. of water. Cool the mixture in ice-water, and add, slowly with stirring, a solution of 3 grams of sodium nitrite in 20 cc. of water. At the end of 15 minutes filter off the salt by suction, wash with dilute hydrochloric acid, and crystallize a little of it from warm (about 60°) dilute hydrochloric acid. Shake up the rest with an excess of a solution of sodium hydroxide. Dissolve a little of the precipitate in ether, filter the solution, and let it evaporate. Boil some of the free amine with sodium hydroxide, note the odor of the gas given off, and test it with moist litmus paper. Write equations for all the reactions.

186. Use of Benzenesulphonyl Chloride in Distinguishing the Three Types of Amines (SECTION **473**).—Shake together for 2 or 3 minutes 0.5 cc. of aniline, 50 cc. of a strong aqueous solution of sodium hydroxide (1 to 4) and 2 cc. of benzenesulphonyl chloride. Warm gently until the odor of the chloride disappears. Filter and add hydrochloric acid to the filtrate. (*Eqs.*)

Repeat the experiment using methylaniline and then dimethylaniline. Test the solubility in dilute hydrochloric acid of the substances separated in these two cases by filtration. Write equations for all reactions, and state clearly how the reagent serves to distinguish from one another the three classes of amines.

NOTE.—A few primary amines yield products with benzenesulphonyl chloride which do not dissolve in a dilute solution of sodium hydroxide. This is due to the fact that a difficultly soluble sodium salt is formed, which is partially hydrolyzed. Such compounds are converted into sodium salts by strong solutions of the base.

CHAPTER XIX

DIAZO COMPOUNDS

187. Preparation of Phenol from Aniline (SECTION **513**).—Prepare some iodo-starch paper for use as an indicator for nitrous acid as follows: Grind about 1 gram of starch with a few cubic centimeters of water and pour the mixture into 200 cc. of boiling water. Cool the solution and dissolve in it a crystal of potassium iodide. Insert pieces of filter-paper into the solution, and hang them up to dry in a place free from acid vapors. The moist paper can be used in the following preparation.

In a 500 cc. beaker pour 25 cc. of concentrated sulphuric acid into 200 cc. of water, and add to the warm solution 20 grams of aniline slowly and with vigorous stirring. Cool, and add 100 grams of ice. Dissolve 16 grams of sodium nitrite in 100 cc. of water, and add the solution in small quantities, with stirring, to the solution of aniline sulphate, until the amine has been diazotized. This can be determined by testing the solution for nitrous acid, which will be present when the nitrite has been added in excess. The amount of nitrite which has been dissolved is a slight excess over that required for the reaction. When the larger portion of the nitrite has been added, stir vigorously, place a drop of the solution on a piece of iodo-starch paper. If free nitrous acid is present a blue spot will form. (*Eq.*) Continue the addition of nitrite until the solution, after thorough stirring and standing 15 to 20 seconds, produces an immediate blue color with the iodo-starch paper. Pour the solution of the diazonium salt into a flask, and heat it at 40°-50° on a water-bath for half an hour. Distil with steam (§28, page 19) and collect about 300 cc.of distillate. As long as any phenol distils over the distillate will give a color with a solution of ferric chloride. Saturate the solution of phenol with sodium chloride, and extract three times with ether, using 100 cc. each time. Let the ether solution stand over night with about one-fifth its volume of anhydrous sodium sulphate. Filter the ether, and distil it off from a flask on a water-bath

(§34, page 23.) Wash the drying agent with some of the recovered ether, and add this solution to the flask. Pour the residue into a small flask, and distil using an air-condenser. Collect the fraction boiling at 180°-183°. Calculate the percentage yield.

Phenol melts at 43°, boils at 183°; it is soluble in about 15 parts of water at 16°. The yield in this preparation should be about 15 grams.

NOTE.—In the preparation of diazonium salts it is advisable to keep the reaction-mixture cold during the addition of the nitrite solution, even in the case when the resulting salt is to be decomposed by water; in this way the formation of by-products is largely avoided.

A small amount of *p*-hydroxydiphenyl, $C_6H_5.C_6H_4OH$, is formed as the result of the condensation of the diazonium salt with some of the phenol formed in the reaction. The compound can be obtained by filtering the hot solution from which the phenol has been distilled. On cooling, *p*-hydroxydiphenyl separates out in plates which melt at 164°.

188. Preparation of Iodobenzene from Aniline (SECTIONS **513**, **483**).—Mix together in a beaker 150 cc. of water, 12 cc. of concentrated sulphuric acid, and 10 grams of aniline. Cool the solution, and add 100 grams of ice. Diazotize the solution by adding a solution of 8 grams of sodium nitrite dissolved in 40 cc. of water in the way described in the above experiment (preparation of phenol). Pour the solution of the diazonium salt into a liter flask and add a solution of 22 grams of potassium iodide in 50 cc. of water. Place the flask in a water-bath heated to 70°-80° until the evolution of nitrogen ceases. Make the solution strongly alkaline by adding a solution of sodium hydroxide, and distil with steam as long as an oil comes over. It is necessary to have the end of the tube through which the steam enters the flask pass to the bottom of the latter, so that the steam passes through the heavy oil, and keeps it constantly in motion. Separate the iodobenzene, and dry it with calcium chloride. Filter it into a small flask and distil, using an air-condenser. Calculate the percentage yield.

Iodobenzene boils at 188° (corrected). The yield should be about 20 grams.

189. Preparation of p-Tolunitrile: Sandmeyer Reaction (SECTION **513**).—CAUTION.—In this preparation cuprous cyanide is to be used. The compound is made from copper sulphate and potassium cyanide. As the reaction involves the liberation of cyanogen, a very poisonous gas, it should be carried out under the hood with a good draught, and care should be taken not to breathe any of the gas liberated. Care should be exercised also in handling the potassium cyanide.

Dissolve 50 grams of copper sulphate in 200 cc. of hot water, place the solution in a 2-liter flask on a water-bath heated to boiling under the hood, and add in small portions a solution of 55 grams of potassium cyanide dissolved in 100 cc. of water. Leave the solution heating on the water-bath, and prepare the diazo compound as follows: Add 20 grams of *p*-toluidine to a mixture of 45 cc. of concentrated hydrochloric acid and 100 cc. of water, and stir. Place the vessel containing the solution in cold water, add 100 grams of ice, and diazotize with a solution of 16 grams of sodium nitrite in 60 cc. of water, taking precaution to avoid an excess of the nitrite solution. (See experiment 187 above.) HOOD.—Pour the diazo solution into the hot solution of cuprous cyanide; add about 10 cc. at a time and shake vigorously. Avoid running the solution down the side of the flask; it should fall directly into the solution of the cyanide. This precaution is taken to avoid as much as possible the formation of cresol, $CH_3.C_6H_4.OH$, as the result of the interaction of the diazo compound with water. The addition of the diazo solution should take about 15 minutes. Leave the flask on the water-bath for about 15 minutes more, and when the evolution of nitrogen ceases, distil with steam under the hood. If the tolunitrile solidifies in the condenser, turn off the water in the latter for a short time; the steam will warm the water in the condenser, and the nitrile will melt. Distil as long as an insoluble substance comes over in appreciable amounts. If only a small amount of cresol has been formed the nitrile will solidify in the receiver. Separate the crystals and let them dry spontaneously on a porous plate. As tolunitrile melts at 38°, the crystals should not be put in a warm place. Weigh the crystals, and calculate the percentage yield. Save the preparation for a future experiment.

If much cresol has been formed during the reaction the product will not solidify. In this case, extract with a small amount of ether, shake the ethereal solution with an equal volume of a solution of sodium hydroxide, and dry over calcium chloride. Pour off the solution, distil off the ether, and distil, using an air-condenser.

p-Tolunitrile melts at 38° and boils at 218°. The yield should be about 13 grams.

190. Preparation of Diazoaminobenzene (SECTION **514**).—Dissolve 10 grams of aniline in a mixture of 100 cc. of water and 20 cc. of concentrated hydrochloric acid. Add 100 grams of ice. When the solution is cold add a solution of 8 grams of sodium nitrite in 40 cc. of water. Dissolve 10 grams of aniline in a mixture of 7 cc. of concentrated hydrochloric acid and 50 cc. of water, and add 50 grams of ice. Pour the solutions of aniline hydrochloride slowly with stirring, into the solution of the diazo compound. (*Eq.*) Dissolve 25 grams of hydrated sodium acetate in 50 cc. of water, and add the solution to the mixture. At the end of half an hour, add about 300 cc. of water, stir, and filter by suction; wash the precipitate with cold water. Press the diazoaminobenzene on a porous plate, and let it stand until dry; do not heat it. Weigh the product and calculate the percentage yield.

Crystallize a little of the compound from petroleum ether as follows: Digest for 2 or 3 minutes 2 grams of the diazoaminobenzene with 100 cc. of petroleum ether, filter hot, evaporate to about 50 cc, and set aside the solution to crystallize.

Diazoaminobenzene crystallizes in yellow plates, which melt at 98°; it explodes when heated above its melting-point. It is insoluble in water, and is soluble in benzene, ether, and alcohol. The yield obtained in the above preparation is about 15 grams.

NOTE.—The sodium acetate is added to interact with the excess of hydrochloric acid present:

$$HCl + CH_3COONa = NaCl + CH_3COOH$$

The salt is frequently added to solutions containing strong acids when it is desired to bring about a reaction which does not take place in the presence of such acids.

191. Preparation of Aminoazobenzene (SECTION **515**).—Mix in a small beaker 10 grams of diazoaminobenzene, 20 grams of aniline, and the aniline hydrochloride prepared as follows: Dissolve 5 cc. of aniline in 10 cc. of concentrated hydrochloric acid, cool in running water, filter by suction, press on a porous plate.

Allow the salt to dry for about 5 minutes. Heat for 1 hour on a water-bath the mixture so that the temperature of the latter is between 50° and 60°; stir frequently. Dissolve the product in 50 cc. of glacial acetic acid, and pour the solution slowly into 400 cc. of water, stirring vigorously. After about 5 minutes filter by suction, wash with water and set aside to dry.

Convert a part of the aminoazobenzene into the chloride as follows: Dissolve 2 grams of the compound in 10 cc. of alcohol and pour the solution into a boiling mixture of 20 cc. of concentrated hydrochloric acid and 200 cc. of water. Boil for 10 minutes and set aside to crystallize. Filter and wash the crystals with water containing some hydrochloric acid.

Crystallize the rest of the aminoazobenzene as follows: Dissolve the substance in alcohol in the proportion of 1 gram of aminoazobenzene to 10 cc. of alcohol. Heat to boiling and add water until the solution begins to cloud; set aside to crystallize. Filter off the crystals and wash them with a mixture of equal volumes of alcohol and water.

Aminoazobenzene crystallizes in yellow prisms, melts at 127°, and distils undecomposed above 360°. It crystallizes well from hot water in which it is difficultly soluble.

192. Preparation and Properties of Phenylhydrazine (SECTION **517**).—(*a*) In a beaker pour slowly, with stirring, 20 grams of aniline into 170 cc. of concentrated hydrochloric acid. Cool the beaker to 0° in a freezing mixture of ice and salt, and add, drop by drop, from a separatory funnel, a mixture of 20 grams of sodium nitrite dissolved in 100 cc. of water, until a drop of the solution when diluted with a few drops of water produces a blue color with iodo-starch paper. (See experiment 187, page 158). The mixture should be stirred during the addition of the sodium nitrite. Dissolve 120 grams of hydrated stannous chloride in 100 cc. of water, cool the solution with ice-water, and pour it slowly into the solution of the diazo compound. After an hour filter off by suction the precipitate of phenylhydrazine hydrochloride, using a porcelain funnel or a filter-plate and hardened filter-paper. Remove as much of the mother-liquor as possible by pressing the crystals, and then transfer them to a flask and add an excess of a solution of sodium hydroxide. Extract with ether, dry over anhydrous potassium carbonate, and distil off the ether. The resulting oil can be used for the following experiments. If it is desired to keep the phenylhydrazine, it should be distilled; as it decomposes slightly on distillation it is better to distil it under diminished pressure (§24, page 15). The compound can also be purified by freezing it and pouring off the liquid which does not solidify.

Phenylhydrazine is nearly colorless when pure; it melts at 17.5°, boils at 242°, and has the specific gravity 1.097 at 23°. The yield in this preparation should be about 10 grams.

(*b*) *Conversion of phenylhydrazine into benzene.*—Dissolve 35 grams of copper sulphate in 100 cc. of water in a 500 cc. flask connected with a reflux condenser. Heat the solution to boiling, remove the flame, and drop into the solution from a separatory funnel suspended in the condenser 10 grams of phenylhydrazine dissolved in 10 cc. of acetic acid and 50 cc. of water. As soon as the phenylhydrazine has been added, arrange the condenser for distillation, and distil as long as an oil comes over. Separate the oil and shake it with anhydrous calcium chloride until no drop of water can be seen, and the benzene is clear. Distil the oil and note its boiling-point.

Benzene, the product of the reaction, boils at 80.4°. The yield should be about 6 grams.

Add 2 drops of phenylhydrazine to Fehling's solution.

(*c*) *Formation of a urea derivative from phenylhydrazine: phenylsemicarbazide.*—Dissolve 1 cc. of phenylhydrazine in 1 cc. of glacial acetic acid and 5 cc. of water, and add a solution of 0.5 gram of potassium cyanate dissolved in 2 cc. of water. Heat to boiling, cool, and shake. Filter off the precipitate, wash with cold water, and crystallize it from boiling water. Phenylsemicarbazide melts at 172°.

(*d*) *Formation of a phenylhydrazone.*—Dissolve 2 drops of phenylhydrazine in 12 cc. of alcohol, and add 12 cc. of water. Add to the solution 2 drops of benzaldehyde and boil for half a minute. Cool, shake thoroughly, and filter by suction (§43, page 30). Wash with 10 cc. of 50 per cent alcohol, and recrystallize the precipitate from 25 cc. of boiling 50 per cent alcohol. Cool, filter off the crystals, and wash them with 10 cc. of 50 per cent alcohol. Dry the crystals, and determine their melting-point.

Benzalphenylhydrazone is a white crystalline compound which melts at 156°.

NOTES.—(*b*) The reaction between phenylhydrazine and copper sulphate takes place according to the following equation:

$$C_6H_5NH.NH_2 + CuSO_4 = C_6H_6 + N_2 + Cu + H_2SO_4$$

(c) Phenylhydrazine is a derivative of ammonia, and its salts, therefore, react in many cases like ammonium salts and the salts of amines. The preparation of phenylsemicarbazide from phenylhydrazine salts is analogous to the preparation of urea from ammonium salts; the equations for the two reactions are similar. (See SECTION **223.**)

$$\begin{aligned} NH_4Cl + KCNO &= NH_4CNO + KCl \\ NH_4CNO &= NH_2.CO.NH_2 \\ C_6H_5NH.NH_2.HCl + KCNO &= C_6H_5NH.NH_3.CNO + KCl \\ C_6H_5NH.NH_3CNO &= C_6H_5NH.NH.CO.NH_2 \end{aligned}$$

(*d*) Phenylhydrazine is a valuable reagent for identifying aldehydes. The method of preparing the phenylhydrazones is illustrated by this experiment.

CHAPTER XX

AROMATIC ALCOHOLS, PHENOLS, AND ETHERS

193. Preparation of Benzyl Alcohol from Benzaldehyde (SECTION **523**).—Place in a 250-cc. bottle 20 grams of benzaldehyde and a cold solution of 18 grams of potassium hydroxide in 12 cc. of water. Close the bottle with a cork or a rubber stopper, shake it vigorously until an emulsion is formed, and set aside over night or longer. (*Eq.*) Add enough water to dissolve the crystals of potassium benzoate formed, and extract the solution three times with ether, using about 50 cc. each time. Save the aqueous solution. Dry the ethereal solution with anhydrous copper sulphate, distil off the ether (§34, page 23), and distil the benzyl alcohol. Weigh the alcohol and calculate the percentage yield.

Benzyl alcohol boils at 206°. The yield in the preparation should be about 7 grams.

Add an excess of hydrochloric acid to the filtered aqueous solution of potassium benzoate, filter off the precipitate of benzoic acid, and wash it with cold water. Crystallize the acid from boiling water. Weigh the acid and calculate the percentage yield.

Benzoic acid melts at 121.4°; it is soluble in 345 parts of water at 20°, and in 17 parts at 100°.

194. Properties of Benzyl Alcohol (SECTION **523**).—(*a*) *Benzyl alcohol and hydrochloric acid.*—Mix 2 cc. of benzyl alcohol and 4 cc. of concentrated hydrochloric acid. Heat the mixture slowly and note any change produced. (*Eq.*) Observe the odor of the substance formed.

(*b*) *Oxidation of benzyl alcohol.*—Mix together 1 cc. of concentrated nitric acid, 4 cc. of water, and 3 drops of benzyl alcohol. Boil the mixture for about 2 minutes and note the odor from time to time. The characteristic odor of benzaldehyde is first observed, and then disappears as the aldehyde is oxidized further to benzoic acid. Cool the solution in running water; if the oxidation has progressed far enough benzoic acid will crystallize out. (*Eq.*)

(*c*) *Benzyl alcohol and acetyl chloride.*—Add acetyl chloride, drop by drop, to about 2 cc. of benzyl alcohol as long as evident reaction takes place. Pour the product into cold water and shake. (*Eq.*)

195. Preparation of Diphenylcarbinol from Benzophenone (SECTION **524**).—In a 500-cc. flask dissolve 15 grams of benzophenone and 15 grams of potassium hydroxide in 150 cc. of alcohol. Add 15 grams of zinc dust, connect the flask with a reflux condenser and boil for 1 1/2 hours. (*Eq.*) Filter hot, add water until the solution clouds, and set aside to crystallize. Filter off the crystals by suction, and wash with dilute alcohol. A second crop of crystals may be obtained from the filtrate.

Diphenylcarbinol melts at 67.5°-68°. The yield is nearly theoretical.

Warm a few of the crystals with concentrated hydrochloric acid. (*Eq.*)

196. Preparation of Diphenylethylcarbinol by the Grignard Reaction (SECTION **426**).—In a 200-cc. flask surrounded by cold water and provided with a return condenser, place 5 grams of magnesium powder, and add slowly through the condenser from a separatory funnel a solution of 38 grams of ethyl iodide dissolved in 50 cc. of ether which has been dried over sodium. If a reaction does not take place promptly, add a small crystal of iodine. Toward the end of the reaction it may be necessary to heat the flask by surrounding it with warm water. When the magnesium has passed into solution add, drop by drop, through the condenser, a solution of 10 grams of benzophenone in 10 grams of dry benzene. If the reaction ceases, place warm water around the flask for a few minutes. Cool the reaction-mixture, and pour it slowly into about 200 cc. of ice-water which contains about 10 cc. of dilute sulphuric acid. Extract twice with ether, using about 100 cc. each time. Shake the ether with a little sodium hydroxide solution if it is colored by iodine. Filter the ether solution, and distil off the ether; dissolve the residue in 50 cc. of hot petroleum ether and set the solution aside to crystallize. Weigh the product and calculate the yield from the benzophenone used.

Diphenylethylcarbinol melts at 95°. The yield should be from 10 to 12 grams.

PHENOLS

197. Properties of Phenol (SECTIONS 528, 529).—(*a*) *Solubility of phenol.*—-CAUTION.—Do not touch phenol; it causes painful blisters when brought into contact with the skin. Determine the solubility of phenol in the following: Water, a solution of sodium hydroxide, and a solution of sodium carbonate. Use about 1 gram of phenol in each case, and add the liquids in portions of about 2 cc. until solution is complete; shake thoroughly after each addition of the solvent.

(*b*) *Acidity of phenol.*—Test an aqueous solution of phenol with litmus paper and with Congo paper. Test a dilute solution of hydrochloric acid with the two indicators. Do you observe a difference? A much higher concentration of hydrogen ions is required to affect the coloring matter on the Congo paper than to affect litmus. From the results obtained in experiment (*a*) above what conclusion can be drawn in regard to the relative acidity of phenol and carbonic acid? Test a solution of picric acid (trinitrophenol), acetic acid, benzoic acid, and salicylic acid, with the two indicators.

(*c*) *Phenol and acetyl chloride.*—Add acetyl chloride, drop by drop, as long as an evident reaction takes place, to about 0.5 gram of phenol. (*Eq.*) Pour the product into water and note the odor.

(*d*) *Phenol and ferric chloride.*—Add a few drops of a dilute aqueous solution of ferric chloride (1 part of the 10 per cent reagent with 3 parts of water) to an aqueous solution of phenol.

(*e*) *Identification of phenol by converting it into s-tribromophenol.* Dissolve about 0.1 gram of phenol in 5 cc. of water and add an aqueous solution of bromine until a permanent yellow color is formed. Filter off the precipitate and wash it with a solution of sulphur dioxide or of acid sodium sulphite until there is a strong odor of sulphur dioxide. Wash with water. Dissolve the compound in 10 cc. of hot alcohol, filter, add 20 cc. of hot water, and set aside to crystallize. Filter off the crystals and dry them on a porous plate. Determine the melting-point of the crystals; the 2, 4, 6-tribromophenol which is formed melts at 93°.

NOTES.—(*d*) If the ferric chloride solution contains much free acid it will not give the usual test—the production of a marked color. If this occurs make up a reagent for this and the following experiments as follows: Add to a 10 per cent solution of ferric chloride a solution of sodium hydroxide, drop by drop, until a permanent precipitate is just formed on shaking. If too much alkali is added, a little of the solution of ferric chloride can be used to almost dissolve it. Filter the solution, which should have a deep yellow color and mix with three volumes of water.

(*e*) When bromine is added in excess to an aqueous solution of phenol, a compound of the formula $Br_3C_6H_2.OBr$, is formed, which is converted by sulphur dioxide into tribromophenol, $Br_3C_6H_2.OH$. On account of the great insolubility of this compound in cold water, it is of value in detecting the presence of phenol in dilute aqueous solutions. Salicylic acid, and a few other compounds are converted into tribromophenol by bromine water.

198. General Reactions of Phenols (SECTION **540**).—(*a*) *With ferric chloride.*—Add a dilute aqueous solution of ferric chloride (see note to experiment 197*d*, above) to dilute aqueous solutions of pyrocatechol, quinol, resorcinol, cresol, α-naphthol, β-naphthol, and pyrogallol. If no color appears, dissolve a little of the substance in alcohol and add a drop of ferric chloride solution.

(*b*) *With bromine water.*—Add bromine water to the solutions of the phenols listed above.

(*c*) *Preparation of phthaleins from phenols* (SECTION **558**).—Put in a dry test-tube about 0.1 gram of phenol, in a second tube 0.1 gram of resorcin, and in a third 0.1 gram of thymol. To each tube add about 0.1 gram phthalic anhydride and 2 drops of concentrated sulphuric acid. Place the tube for 3 minutes in an oil-bath heated to 160°. Cool, add 5 cc. of a solution of sodium hydroxide, and observe the color by transmitted and reflected light. If the solution appears to be too concentrated, pour off a little and dilute with water. (*Eqs.*)

NOTES.—(*a*) Most phenols give a color when treated with a solution of ferric chloride. The reaction is valuable in testing for compounds of this class.

(*b*) Most monhydroxy phenols which dissolve in water give a precipitate when treated with bromine water.

199. Preparation and Properties of Anisol (SECTION **541**).—(*a*) Add to 50 cc. of methyl alcohol, contained in a 250-cc. flask, 2.5 grams of sodium; the metal should be cut into about half a dozen pieces and added slowly, and the flask should be kept cold by immersion in water. When the sodium has reacted, add to the solution 10 grams of phenol and 20 grams of methyl iodide. Attach a reflux condenser to the flask, and heat on a water-bath, until a drop of the solution, when diluted with water, no longer shows an alkaline reaction. The reaction is complete in about an hour. Distil off the excess of methyl alcohol on a water-bath, and add about 25 cc. of water to the residue. Extract with a small amount of ether, dry the ethereal solution with calcium chloride, and distil off the ether on a water-bath. Distil the residue over a free flame. Calculate the percentage yield from the phenol used.

Anisol boils at 155°. The yield is nearly the theoretical.

(*b*) *Solubility of anisol.*—Determine if anisol is soluble in the following: dilute hydrochloric acid, dilute sodium hydroxide, and cold concentrated sulphuric acid.

CHAPTER XXI

AROMATIC ACIDS

200. Preparation of Benzoic Acid from Benzyl Chloride (SECTION **546**).—In a 500-cc. flask provided with a return condenser like that shown in Fig. 17, page 27, place 20 grams of benzyl chloride, 100 cc. of water, 40 cc. of concentrated nitric acid, and half a dozen small pieces from a broken porous plate to prevent bumping. Place the flask on a wire gauze and boil for about 4 hours. When the oxidation is complete, the oil, which at first floats, becomes heavier than the aqueous solution, and when the flame is removed for an instant sinks to the bottom of the flask. Cool under running water, shaking vigorously to avoid the formation of large lumps. Filter by suction and wash with cold water. Dissolve the crystals in the smallest amount of boiling water, about 900 cc., add 2 grams of bone-black, boil for 3 minutes, and filter hot; set aside over night to crystallize. Filter off the crystals by suction, and wash with cold water. Let the acid stand in the air until dry. Weigh and determine the melting-point. If the acid does not melt sharply, sublime a little of it (§35, page 24), and determine the melting-point again. Calculate the percentage yield. How could you readily distinguish a solution of phenol from one of benzoic acid? How could you distinguish a solid acid from a solid phenol? How could you obtain pure benzoic acid from sodium benzoate?

Benzoic acid melts at 121.4° and boils at 249°. One hundred parts of water at 17.5° dissolve 0.268 parts, and at 75° dissolve 2.19 parts of the acid. It is readily soluble in alcohol and in ether. The yield should be about 14 grams.

NOTE.—In oxidizing aromatic compounds with nitric acid, the latter is usually diluted with water in order to prevent nitration. An acid of the specific gravity 1.15 is ordinarily used.

201. Identification of Benzoic Acid: Conversion into Benzanilide.—To definitely identify as benzoic acid an unknown substance which has the melting-point and physical properties of this acid, it should be converted into a solid derivative, and the properties of this compound determined. Benzanilide, $C_6H_5CO.NHC_6H_5$, is conveniently prepared and melts sharply. Proceed as follows: To about 0.2 gram of the acid in a dry test-tube add about 0.4 gram of phosphorus pentachloride; warm and stir the mixture until a homogeneous liquid is obtained. Cool, shake with about 5 cc. of water, decant off the latter, and add slowly about 1 cc, of aniline. Dissolve the product in a boiling mixture of 25 cc. of alcohol and 25 cc. of water. Filter the solution if necessary, cool, and filter off the crystals; wash with a little dilute alcohol, and dry the compound at 100°. Determine the melting-point. Benzanilide crystallizes in pearly, white scales which melt at 160°.

202. Preparation of Benzamide (SECTION **549**).—HOOD.—Place in a small flask 5 grams of benzoic acid and 9 grams of phosphorus pentachloride (weighed under the hood), and shake and warm on the steam-bath until a clear liquid is formed. Cool, and add the liquid to 150 grams of ice and 50 cc. of concentrated ammonia in a beaker. Stir occasionally until the liquid has changed to a solid. If the substance when pressed with a glass rod appears to be plastic, the reaction is not complete; it must be more or less granular. Filter by suction, wash with dilute ammonia, and crystallize from the smallest possible amount of boiling water (about 50 cc). Weigh the product and determine its melting-point. A small amount of amide can be recovered from the mother-liquor.

Benzamide melts at 128°-130°. The yield is about 4 grams. Determine whether benzamide shows the properties of an acid amide, and describe in your notes the test applied and the result obtained.

203. Preparation of p-Toluic Acid from the Nitrile (SECTION **551**).—Hydrolyze the tolunitrile obtained in experiment 189, page 159, by heating it with sulphuric acid as follows: For each gram of nitrile use 6 grams of concentrated sulphuric acid and 2 cc. of water. Heat on a sand-bath the mixture contained in a flask provided with a wide-bore reflux condenser, until the acid sublimes freely into the condenser. Cool, dilute with about 3 volumes of water, filter off the crystals, and wash them several times with cold water. Dissolve the toluic acid in hot alcohol, add about 1 gram of bone-black, and boil for 5 minutes. Filter hot, and add boiling water until the solution clouds. Set aside the solution to crystallize. Filter off the crystals, wash with cold water, and dry on a porous plate. Determine the percentage yield. A further amount of acid can be obtained from the mother-liquor. Save the acid for a later experiment.

p-Toluic acid melts at 180° and boils at 275°. The yield of acid is the theoretical, although some of it is lost in the purification.

204. Preparation of Cinnamic Acid by Perkin's Synthesis (SECTION **553**).—Place in a small round-bottomed flask provided with a reflux air-condenser, in the end of which is a drying tube containing calcium chloride, 20 grams *of freshly distilled* benzaldehyde, 30 grams of acetic anhydride, and 10 grams of freshly fused and pulverized anhydrous sodium acetate. (See experiment 66, page 44.) Heat the mixture in an oil-bath at 170°-180° for 8 hours. Pour the mixture into 500 cc. of water, place about 100 cc. of a 10 per cent solution of sodium carbonate in the flask, and shake to dissolve most of the residue. Add this solution to the mixture of water and cinnamic acid, heat to boiling, and add solid sodium carbonate as long as anything dissolves and the solution has a strong alkaline reaction. Stir vigorously during the addition in order to bring the oil in contact with the sodium carbonate. A small insoluble residue is left. Filter the solution hot and add an excess of hydrochloric acid. Filter off the acid when the solution has cooled, and wash it with cold water. Dissolve the acid in boiling water, add about 2 grams of bone-black, boil for 5 minutes, filter hot, and set aside to crystallize. Weigh the acid, after drying on a porous plate, determine its melting-point, and calculate the percentage yield from the sodium acetate used.

Cinnamic acid melts at 134°; it is soluble in 3,500 parts of water at 17° and in 100 parts at 100°. The yield is from 12 to 14 grams.

205. Properties of Cinnamic Acid (SECTION **553**).—(*a*) *Test for the double bond in cinnamic acid.*—Dissolve about 0.5 gram of the acid in carbon tetrachloride and add, drop by drop, a solution of bromine in the same solvent. If no reaction takes place in 1 minute, warm the solution gently. (*Eq.*) How does the rate at which this reaction proceeds compare with the rate with which ethylene and bromine react?

(*b*) *Oxidation of cinnamic acid.*—Stir about 0.1 gram of the acid with about 5 cc. of cold 10 per cent solution of potassium permanganate and note the odor. (*Eq.*) What acid would be obtained by the further oxidation of cinnamic acid?

NOTE.—(*a*) The rate at which bromine is added to a double bond is determined by the nature of the radicals linked to the carbon atoms joined by the double bond; negative atoms or groups markedly retard the reaction. In the case of certain compounds which contain four negative groups, for example tetraphenylethylene, $(C_6H_5)_2C = C(C_6H_5)_2$, addition does not take place at all.

206. Preparation of Terephthalic Acid from p-Toluic Acid (SECTION **561**).—Dissolve 5 grams of the toluic acid prepared in experiment 203 in a solution of 3 grams of sodium hydroxide in 250 cc. of water. Heat the solution on a water-bath and add a solution of 12 grams of potassium permanganate in 250 cc. of water until the color of the permanganate persists after heating for 5 minutes. Add to the hot solution enough alcohol to react with the excess of permanganate, and filter hot. Wash the precipitate of manganese dioxide with a little hot water, and add an excess of concentrated hydrochloric acid to the filtrate. Filter off the terephthalic acid when the solution has cooled. Weigh the acid and calculate the yield. Sublime a little of the acid.

Terephthalic acid is almost insoluble in hot and cold water. It sublimes without melting. It can be identified most readily by converting it into its dimethyl ester as described below.

207. Preparation of Dimethyl Terephthalate.—In a dry test-tube warm together on the steam-bath or in hot water about 0.2 gram of terephthalic acid and 0.6 gram of phosphorus pentachloride. (*Eq.*) Cool the mixture and add in small portions, keeping the mixture cold in running water, 4 cc. of methyl alcohol. (*Eq.*) Warm the mixture cautiously for a short time until reaction is complete. Cool again, add 20 cc. of water, filter by suction, and wash the precipitate with 10 cc. of water. Dissolve the dimethyl terephthalate in a boiling mixture of 8 cc. of methyl alcohol and 2 cc. of water. Filter hot, using a small funnel. Cool, filter off the crystals by suction, and wash them with a mixture of 3 cc. of methyl alcohol and 3 cc. of water. Dry the crystals on a porous plate and determine their melting-point.

Dimethyl terephthalate melts at 140°.

CHAPTER XXII

AROMATIC ALDEHYDES, KETONES, AND QUINONES

208. Properties of Benzaldehyde (SECTIONS **564-567**).—(*a*) *Oxidation of benzaldehyde.*—Leave a few drops of benzaldehyde on a watch-glass exposed to the air for a few days. (*Eq.*)

Grind a pinch of starch with a few cubic centimeters of cold water and pour the mixture into about 50 cc. of boiling water. Cool, and dissolve in the solution a crystal of potassium iodide. Divide the solution into two portions. Shake one of these with 2 drops of benzaldehyde and expose both to sunlight for some time. Explain. (See SECTION **565**.)

(*b*) *Test for the aldehyde group in benzaldehyde.*—Shake up a few drops of benzaldehyde with about 15 cc. of water, and test parts of the solution with Fehling's solution, Tollen's reagent, and Schiff's reagent. Compare the results with those obtained with acetaldehyde. For the test with phenylhydrazine see experiment 192*d*, page 163. If this experiment has not been performed, do it now.

(*c*) *Benzaldehyde and sodium hydrogen sulphite.*—Shake about 1 cc. of benzaldehyde with 5 cc. of a saturated solution of sodium hydrogen sulphite. Filter off the crystals by suction and wash them with a little alcohol until odorless. Dissolve the crystals in warm water; to one-half of the solution add a solution of sodium carbonate, and to the other dilute sulphuric acid. Explain the cause of the appearance and odor produced.

(*d*) *Benzaldehyde and sodium hydroxide.*—Shake up a few drops of benzaldehyde with a solution of sodium hydroxide, and then warm the mixture. Is a resin formed? Compare the results with those obtained in the case of acetaldehyde (experiment 108*d*, page 86). For the behavior of benzaldehyde with alkalies see experiment 193, page 165.

(*e*) *Benzaldehyde and ammonia: hydrobenzamide.*—Mix together 3 cc. of benzaldehyde, 20 cc. of alcohol, and 10 cc. of a concentrated solution of ammonia. Set aside the mixture until the product which separates becomes solid. Heat on the steam-bath, and add alcohol until the solid dissolves. Set aside to crystallize. Determine the melting-point of the crystals. Compare the behavior of formaldehyde, acetaldehyde, and benzaldehyde with ammonia.

Hydrobenzamide, $(C_6H_5CH)_3N_2$, crystallizes from alcohol in octahedra which melt at 110°.

209. Preparation of Benzophenone (SECTIONS **572** and **425**). In a dry 500-cc. flask put 28 grams of benzene, 30 grams of anhydrous aluminium chloride in the form of lumps, and 27 grams of benzoyl chloride. The aluminium chloride should not be exposed to the air any longer than necessary, as it rapidly absorbs moisture. Attach to the flask by means of a cork a small drying tube containing anhydrous calcium chloride, place the flask under a hood in a beaker containing water, and let the reaction proceed for at least 24 hours. To determine whether the reaction is complete, pour a few drops of the material into a few cubic centimeters of water in a test-tube. Shake the tube and observe whether the characteristic odor of benzoyl chloride is present. If the chloride is present, the mixture should stand for several hours and then be tested again. When benzoyl chloride can no longer be recognized by its odor, pour into the flask rapidly a mixture of 200 cc. of water, 100 grams of shaved ice or snow, and 50 cc. of concentrated hydrochloric acid. Shake under running water until two layers are formed. Add 50 cc. of benzene and separate the solution from the acid. Shake the former with a solution of sodium hydroxide to remove any benzoic acid that may be present. Dry the solution with calcium chloride and filter it into a distilling flask, provided with a thermometer. Distil, using a water condenser, until the temperature of the vapor reaches 250°. Replace the water condenser by an air condenser and collect in a weighed 200-cc. beaker the material boiling between 285° and 305°. Record the weight of the distillate, which should change to a mass of crystals. Dissolve it in warm alcohol (5 cc. for each gram of benzophenone) and add to the cooled solution cold water until a permanent cloud is formed. The volume of the water used should be about one-third that of the alcohol. After standing over night, filter off the crystals and add water to the filtrate as before. Weigh the two crops of crystals, calculate the yield and determine the melting-point of the crystals.

Benzophenone melts at 48°, and boils at 306.1° (corr.). The yield in the preparation is about 25 grams.

210. Preparation of Benzophenoneoxime (SECTION **573**).—In a flask provided with a reflux condenser dissolve 5 grams of benzophenone in 50 cc. of alcohol, and add a solution of 5 grams of hydroxylamine hydrochloride in 15 cc. of water; to this add a solution of 10 grams of sodium hydroxide in 15 cc. of water, and heat the mixture on a water-bath for an hour. Pour the product into about 200 cc. of water, filter if necessary, and add to the filtrate dilute sulphuric acid until the solution is just acidic to litmus paper. After an hour filter off the benzophenoneoxime. Weigh the product when dry and calculate the percentage yield, which should be nearly theoretical. Recrystallize the oxime from about 25 cc. of hot alcohol.

Benzophenoneoxime melts at 141°.

211. Beckmann's Rearrangement of an Oxime (SECTION **573**).—In a small flask dissolve 2 grams of benzophenoneoxime in 30 cc. of ether dried over sodium, and add slowly in small portions 3 grams of finely divided phosphorus pentachloride. At first it may be necessary to cool the solution; toward the end of the reaction the mixture should be heated on the steam-bath until the phosphorus pentachloride has dissolved. When this has taken place, pour the ethereal solution with vigorous stirring into 400 cc. of cold water. Stir until a solid has formed, and then filter it off by suction and wash with cold water. Crystallize the benzanilide from the smallest amount of boiling alcohol, and determine the melting-point of the dried crystals. Write equations for the reactions involved in the rearrangement.

Benzanilide melts at 160°.

212. Preparation of Quinone (SECTION **577**).—Mix is a large beaker 250 cc. of water, 50 cc. of pure concentrated sulphuric acid, and 50 grams of sodium bichromate or the equivalent weight of potassium bichromate. When the salt has dissolved, set the beaker in cold water and cool the solution to 20°. Mix in a beaker 150 cc. of water and 10 grams of aniline; pour into the mixture, with stirring, 10 cc. of pure concentrated sulphuric acid. Cool the solution to 20° and add it, stirring vigorously, in four portions to the solution of sodium bichromate. The beaker in which the reaction takes place should be surrounded by cold water and the temperature should be kept between 35° and 40°. About 6 to 8 minutes are required for the addition of the solution of aniline sulphate. When this has been accomplished, remove the beaker from the water and let it stand for about 15 minutes. Transfer the product to a large flask, and cool it in running water to about 15°. Add to the flask 300 cc. of ether and shake. Let the flask stand for a few minutes. In order to facilitate the separation of the ether into a distinct layer, add to it 25 cc. of acetone, and give to the flask a gentle rotary motion. In a few minutes decant off carefully as much of the ether as possible into a separatory funnel; if some of the aqueous layer flows into the funnel it can be separated. Draw off the ethereal solution, place it in a flask, and distil the ether off from a water-bath through a long water-jacketed condenser (see §34, page 23). Extract the solution of quinone once more with this recovered ether, and evaporate it off as before. Crystallize the residue of quinone from the smallest possible amount of boiling ligroin, or distil it with steam in the ordinary way except that no water is put into the flask containing the quinone. Dry the crystals of quinone in a desiccator; the compound is volatile at room temperature, and if left exposed to the air for a number of hours an appreciable quantity is lost.

Quinone melts at 116°. The yield in this preparation is 5 to 6 grams.

213. Properties of Quinone (SECTION **577**).—(*a*) *Reduction of quinone.*—Shake up a crystal of quinone with 10 cc. of water. Note the odor and color of the solution; add to one-half of it a solution of sodium hydrogen sulphite. (*Eq.*) To the other half add a dilute solution of potassium iodide and a few drops of dilute hydrochloric acid. (*Eq.*)

(*b*) *Unsaturation of quinone.*—Dissolve a few crystals of quinone in 5 cc. of carbon tetrachloride and add, drop by drop, a solution of bromine in carbon tetrachloride. (*Eq.*)

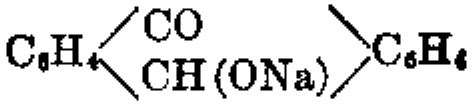
(*c*) *Formation of quinhydrone.*—Make a saturated solution of quinone in water and add to the solution, drop by drop, a strong aqueous solution of hydroquinone. Examine the tube after about 1 minute. If crystals have not formed, repeat, using a more concentrated solution of hydroquinone. (*Eq.*) Add a solution of ferric chloride to a strong solution of hydroquinone. (*Eq.*) Add an ammoniacal solution of silver nitrate to an aqueous solution of hydroquinone.

214. Preparation of Anthraquinone (SECTION **579**).—In a 250-cc. round-bottomed flask provided with a reflux condenser place 5 grams of anthracene and 50 cc. of glacial acetic acid. Heat the liquid to boiling over a wire gauze and add, drop by drop, from a separatory funnel placed in the upper end of the condenser, a solution made by dissolving 10 grams of chromic acid anhydride in 10 cc. of water and then adding 25 cc. of glacial acetic acid. Boil the solution for 10 minutes after the oxidizing agent has been added, and then allow the mixture to cool spontaneously to the temperature of the room. Finally cool under running water. Filter by suction, and wash the crystals twice with a mixture of 2 volumes of water and 1 volume of glacial acetic acid, using 20 cc. of the mixture each time. Finally wash twice with water and allow the crystals to dry in the air.

Sublime a small amount of the dried anthraquinone (§35, page 24), and crystallize a little from boiling alcohol.

Anthraquinone sublimes at about 250° in yellow needles which melt at 273°. The yield in this preparation is 5 grams.

Boil together for about half a minute a trace of powdered anthraquinone with a little zinc dust and 10 cc. of a solution of sodium hydroxide. Filter the solution and shake it with air. Anthraquinone is partly reduced by zinc and sodium hydroxide to a red salt of the composition:



$$C_6H_4\left\langle\begin{matrix}CO\\CH(ONa)\end{matrix}\right\rangle C_6H_4$$

This salt is oxidized by air to anthraquinone. The reaction is a valuable one in the identification of this substance.

Compare the properties of anthraquinone with those of benzoquinone. Does the former oxidize an acidified solution of potassium iodide? Is it reduced by sulphurous acid?

NOTE.—After oxidation by chromic acid in acetic acid solution, the product is usually precipitated by pouring the solution into water. In the case of anthraquinone it is convenient to allow the mixture to cool as the compound crystallizes well from glacial acetic acid.

CHAPTER XXIII

AROMATIC COMPOUNDS CONTAINING TWO OR MORE UNLIKE GROUPS

215. Preparation of o-Nitrophenol (SECTION **584**).—(*a*) In a small beaker melt 20 grams of phenol on the steam-bath, and add it slowly with stirring to a mixture of 30 cc. of pure concentrated nitric acid and 100 grams of ice contained in a beaker. Stir the mixture and then let it stand for at least 3 hours; if more convenient it can be set aside until the next laboratory exercise. Decant off as much of the acid layer as possible through a funnel containing a filter-paper, which serves to collect the part of the oil that is suspended in water. Add about 200 cc. of water to the oil, stir, and decant off the liquid as before. Repeat the washing with 200 cc. of water. Place the filter-paper with the adhering oil in a liter flask, arranged for steam distillation (see Fig. 14, page 20). Wash the oil in the beaker into the flask using for the purpose 200 cc. of water, which should be measured. (This is done to facilitate the isolation of the *p*-nitrophenol which is not volatile with steam.) Distil with steam as long as any oil or solid condenses (about 30 minutes). If the oil solidifies in the condenser, turn off the water from the latter; when the water in the condenser becomes heated, the solid melts and runs into the receiver. Filter, dry, and weigh the *o*-nitrophenol. Recrystallize the product by dissolving it in 40 cc. of hot alcohol and adding 40 cc. of water; set aside over night to crystallize. Filter by suction and wash with a small amount of cold alcohol. Heat the filtrate to boiling and add an equal volume of water. Set aside and collect as before.

o-Nitrophenol melts at 45°. The yield is from 7 to 8 grams.

(*b*) The *p*-nitrophenol, which is not volatile with steam, may be obtained from the residue in the flask as follows: Cool in running water the solution in the flask to 40° and filter it rapidly through a large funnel. The volume of the solution should be about 300 cc. Add 2 grams of bone-black to the filtrate and boil it for about

15 minutes. Filter hot, and place in cold water. The solution should be cooled to at least 10°, and ice should be used if necessary. If crystals do not form, scratch the side of the beaker with a glass rod. After standing for about half an hour, filter off the crystals by suction and wash them with a little cold water. The yield is about 3 grams. By evaporating the mother-liquor to dryness on the steam-bath and extracting the residue with about 50 cc. of boiling benzene, about 2 grams more of the product can be obtained.

p-Nitrophenol melts at 114°; it crystallizes well from benzene in which it is readily soluble hot and difficultly soluble cold. When pure it crystallizes readily from hot water.

Compare the conditions used in the nitration of phenol with those used in making nitrobenzene (experiment 170, page 139), dinitrobenzene (experiment 172, page 141), and nitroacetanilide (experiment 219, page 182).

NOTE.—The yields are small in this preparation on account of the fact that compounds other than *o*- and *p*-nitrophenol are formed; among these are substances of a tarry nature from which it is difficult to separate the para-compound. It is on this account that special precautions are necessary in order to obtain *p*-nitrophenol in a crystalline condition,

216. Isolation of Eugenol from Cloves (SECTION **593**).—Distil 25 grams of cloves with steam as long as an oil separates in the condenser; during this time about 600 cc. of water will distil. Give the vessel containing the mixture a rotary motion so that the oil settles. Decant off most of the water, and pour the oil into a test-tube. By means of a pipette transfer about one-half the oil to a small test-tube, cover it with about 2 cc. of water, and add a dilute solution of sodium hydroxide (10 per cent) as long as it appears to dissolve the oil. (*Eq.*) Is a clear solution obtained? Add to a few cubic centimeters of the alkaline solution, bromine-water in excess. What does the reaction indicate? Divide the rest of the alkaline solution into two equal portions. To one add an excess of dilute hydrochloric acid. (*Eq.*) Set the two tubes aside and examine them carefully at the next exercise for an oil. Explain why sodium hydroxide did not dissolve the oil to a clear solution.

Separate from water, by means of a pipette, the rest of the oil obtained in the distillation with steam. Put it in a dry test-tube, avoiding getting water into the tube. Add about 2 cc. of carbon tetrachloride, and filter into a dry test-tube through a small funnel containing a paper moistened with carbon tetrachloride. Add a solution of bromine in carbon tetrachloride, drop by drop. What does the behavior indicate?

217. Preparation of Sulphanilic Acid (SECTION **598**).—In a small round-bottomed flask containing 25 grams of aniline, pour cautiously 80 grams of pure concentrated sulphuric acid. Heat the mixture for from 4 to 5 hours in an oil-bath at 180°-190°. In order to determine whether the reaction is complete, remove a drop of the mixture on a glass rod, and mix it on a watch-glass with a few drops of a solution of sodium hydroxide. If any aniline sulphate is present in the mixture, the aniline will separate as an oil; if sulphonation is complete, the sodium salt of sulphanilic acid, which is soluble in water, is formed. When the reaction is complete, pour the product into about 300 cc. of cold water. Filter, wash the precipitated sulphanilic acid with cold water, dissolve it in boiling water, avoiding an excess of the latter, add about 2 grams of bone-black, and boil for 5 minutes, stirring occasionally. Filter the hot solution and set aside to crystallize. Dry the crystals in the air; weigh them as soon as dry as the acid slowly loses its water of crystallization on standing. Calculate the percentage yield.

Sulphanilic acid crystallizes from water in plates, which contain 2 molecules of water of crystallization; it is converted into tribromoaniline by an excess of bromine water. The yield in this preparation is about 25 grams.

218. Preparation of m-Nitroaniline (SECTION **600**).—In a 100-cc. flask dissolve 10 grams of *m*-dinitrobenzene in 50 cc. of hot alcohol; cool the solution under running water so that small crystals are formed, and add 10 cc. of a *concentrated* solution of ammonia in water. HOOD.—Pass into the solution a rapid stream of hydrogen sulphide as long as heat is evolved by the reaction (*Eq.*); this requires about one-half hour. Heat on the steam-bath for 10 minutes. Pour the product into 200 cc. of water, filter by suction, and wash the precipitate with water. Put the mixture of *m*-nitroaniline and sulphur into a beaker, add 100 cc. of water and 20 cc. of concentrated hydrochloric acid, stir, and filter off the residue of sulphur by suction. Set the filtrate aside. Determine whether all the nitroaniline has been extracted from the sulphur by treating it on the filter with a little dilute hydrochloric acid, and adding ammonia to the filtrate. To the original filtrate from the sulphur add an excess of concentrated ammonia. Cool in running water, filter off the precipitated *m*-nitroaniline by suction, and wash it with a little cold water. Dissolve the nitroaniline in the smallest amount of boiling water (about 500 cc.), filter the hot solution, and set it aside to crystallize. Filter off the crystals, wash them with a little cold water, and dry on filter-paper. Calculate the percentage yield and determine the melting-point of the product.

m-Nitroaniline crystallizes in yellow needles, which melt at 114°. The yield in this preparation is from 5 to 6 grams.

219. Preparation of p-Nitroaniline (SECTION **600**).—Add slowly in small amounts with stirring, 20 grams of finely powdered acetanilide to 60 grams of fuming nitric acid (sp. gr. 1.52) contained in a beaker surrounded by ice and concentrated commercial hydrochloric acid. The temperature of the nitric acid should not be allowed to rise above 10°. The addition of the acetanilide requires about 20 minutes. When the substance has dissolved, pour the solution into about 300 cc. of cold water, stir vigorously, and filter by suction. *p*-Nitroacetanilide is precipitated, and the ortho compound formed remains in solution. Wash the precipitate three or four times with hot water. Remove as much water as possible by pressing the compound on the funnel, and then crystallize it from boiling alcohol. Let the solution cool, and filter off the crystals. By evaporating the filtrate to a small bulk, a further amount of the anilide can be obtained. Determine the melting-point and yield of the *p*-nitroacetanilide obtained.

p-Nitroacetanilide melts at 207°. The yield should be about 14 grams. The ortho compound can be obtained from the original solution in dilute nitric acid by extraction with chloroform.

To obtain *p*-nitroaniline from the anilide proceed as follows: HOOD.—In a beaker covered with a watch-glass boil the *p*-nitroacetanilide with ten times its weight of dilute hydrochloric acid (sp. gr. 1.12) for about 20 minutes. Cool the solution, add about an equal volume of water and an excess of concentrated ammonia. When the solution is cold, filter off the *p*-nitroaniline, wash it with cold water, recrystallize from hot dilute hydrochloric acid (1 vol. conc. HCl to 5 vols. H_2O). Weigh the compound, determine its melting-point, and calculate the percentage yield from the *p*-nitroanilide used.

p-Nitroaniline melts at 147°.

220. Hydrolysis of the Salts of the Nitroanilines.—Prepare a sample of aniline hydrochloride as follows: Mix together 1 cc. of aniline and 1 cc. of concentrated hydrochloric acid. Cool under running water, and place the solid which separates on a porous plate. When the liquid has been absorbed pour a little ether on the salt. Repeat the treatment with ether, and let the salt dry in the air. Prepare samples of the hydrochlorides of meta- and para-nitroanilines as follows: Mix together about 1 gram of the amine with 5 cc. of concentrated hydrochloric acid and 5 cc. of water. Heat to boiling, and then cool in running water. Filter the salt by suction, and wash the crystals with 10 cc. of alcohol and then with 10 cc. of ether. Dry the salts for a few minutes on filter-paper.

Shake up a little of the three salts with about 2 cc. of water and test the solutions for acid with litmus paper and with Congo paper. Explain the results.

NOTE.—Litmus is much more sensitive to hydrogen ions than the dye on Congo paper.

221. Properties of Salicylic Acid (SECTION **606**).—(*a*) *Salicylic acid and ferric chloride.*—Add a dilute solution of ferric chloride (see note to experiment 197*d*, page 168) to a dilute aqueous solution of salicylic acid. To one-half of the solution add dilute hydrochloric acid, drop by drop, and to the other half dilute acetic acid. Add a drop of ferric chloride to an alcoholic solution of salicylic acid. Repeat these tests with phenol and compare the results.

(*b*) *Salicylic acid and bromine.*—Add bromine water to a solution of the acid. (*Eq.*)

(*c*) *Formation of methyl salicylate.*—Warm together on a watch-glass about 0.05 gram of salicylic acid, 3 drops of methyl alcohol and 3 drops of concentrated sulphuric acid. (*Eq.*) Note the odor of the compound formed.

(*d*) *Decomposition of salicylic acid on heating.*—Heat rapidly in a dry test-tube a little of the acid (*Eq.*) and note the odor.

(*e*) *Detection of salicylic acid and benzoic acid in foods.*—If the sample to be tested is a liquid, acidify 100 cc. of it with 10 drops of dilute sulphuric acid, and extract the solution twice with ether or petroleum ether, using 50 cc. each time. If the material contains a substance insoluble in water, grind 50 grams of it with 100 cc. of water, and add enough of a dilute solution of sodium hydroxide to make the mixture alkaline. Mix thoroughly, filter through 3 layers of cheese-cloth, acidify with dilute sulphuric acid, and extract twice with ether or petroleum ether using 50 cc. each time. Separate the ethereal extract and filter it through a dry filter-paper. Shake 5 cc. of the extract with 5 cc. of water and add to the aqueous solution a dilute solution of ferric chloride containing no free acid; if salicylic acid is present, the characteristic color will develop. Evaporate the rest of the ethereal extract to dryness, dissolve the residue in the smallest possible amount of hot water. Let the solution cool, and remove the crystals by means of a spatula to a porous plate. When dry, determine their melting-point. Test a crystal with ferric chloride as in (*a*) above. Dissolve a crystal in a drop of ammonia, evaporate on the steam-bath, dissolve in a few drops of water, and add a drop of a solution of ferric chloride. If benzoic acid is present, a buff-colored precipitate of basic ferric benzoate is formed.

222. Properties of Tannic Acid (SECTIONS **613, 614**).—For the following experiments make a 1 per cent solution of tannic acid, by dissolving 0.5 gram of the acid in 50 cc. of water.

(*a*) *Tannic acid and ferric chloride.*—Add a few drops of a dilute solution of ferric chloride (see note to experiment 197*d*, page 168) to about 5 cc. of a solution of tannic acid. Dilute some of the solution of the acid with 50 parts of water and add a drop of ferric chloride.

(*b*) *Tannic acid and the salts of heavy metals.*—Add to a solution of the acid a solution of lead acetate. Repeat using copper sulphate.

(*c*) *Tannic acid and gelatin.*—Dissolve about 0.1 gram of gelatin in about 10 cc. of warm water, and add to one-half of the cold solution a solution of tannic acid. Reserve the rest of the solution for experiment (*f*) below.

(*d*) *Reducing action of tannic acid.*—Test a solution of the acid with Fehling's solution. Add a solution of tannic acid to an ammoniacal solution of silver nitrate.

(*e*) *Oxidation of tannic acid by air.*—Mix a little of the solution of the acid with a solution of sodium hydroxide and shake the mixture in contact with air.

(*f*) *Tannic acid in tea* (SECTION **616**).—Pour about 50 cc. of boiling water onto about 1 gram of tea. After 2 minutes decant off the clear solution; to 5 cc. of it add 2 drops of ferric chloride solution. If the shade of the color produced can not be clearly seen, dilute with water. Compare the color with that produced by the gall-nut tannic acid in experiment (*a*) above. Add 5 cc. of the solution to a dilute solution of gelatin. Compare the behavior of the tannic acid from tea with that from gall-nuts.

To the rest of the tea-infusion add a dilute solution of lead acetate, drop by drop, from a pipette as long as a precipitate is formed.

Devise and carry out an experiment to determine whether the amount of tannic acid present in a tea-infusion is greater when the tea is steeped for 2 minutes, or when it is boiled with water for 15 minutes.

(*g*) *Preparation of a tannin ink: removal of ink-stains* (SECTION **616**).—Dissolve 1 gram of tannic acid in 10 cc. of hot water, 0.5 gram of ferrous sulphate in 5 cc. of hot water, and 0.05 gram gum arabic in 5 cc. of hot water. Cool the solutions and mix them. Write on a piece of paper with some of the ink, using a new pen. Add a few drops of ferric chloride to a little of the ink and write with the mixture. Compare result in the two cases. Explain. Put the paper away, and examine the writing with the two samples of ink at the next exercise. Explain.

Put on a piece of cotton cloth some of the iron ink and on another piece some ordinary ink which probably contains a dye. When the ink-spots are dry, cut each piece of cloth into three parts in such a way that the pieces containing the iron ink can be distinguished from those containing the dye. Wash the pieces in water. Add a piece of each kind to a dilute solution of oxalic acid. Explain the result. Add a piece of each kind to a dilute solution of sodium hypochlorite. Place these pieces alternately in the solution of oxalic acid and sodium hypochlorite until the color is destroyed in both cases.

Prepare a 0.5 per cent solution of potassium permanganate by dissolving about one-fourth gram of the salt in 50 cc. of water. Add to the solution 5 drops of concentrated sulphuric acid. Place in the solution pieces of cloth containing the two kinds of ink. After about 2 minutes remove them, wash with water, and place them in a strong solution of sodium hydrogen sulphite. Repeat the treatment with the permanganate and sulphite until the ink is destroyed. If ink is removed in this way the fabric should be washed thoroughly in water, and then placed in a dilute solution of ammonia.

NOTES.—(*b*) The formation of insoluble compounds from tannic acid and the salts of metals is used in preparing mordants in dyeing. (See experiment 228, page 191.)

(*c*) The use of tannin in tanning leather is based on the fact that it forms a compound with the proteins in the hide, of which gelatine is an example.

(*g*) The removal of ink-spots from fabrics made of silk is best accomplished by means of potassium permanganate. If sodium hypochlorite is used, the chlorine present attacks the material, and converts it into a chlorinated product which has a faint yellow color that can not be readily destroyed. A neutral solution of potassium permanganate oxidizes ink; the reaction takes place more rapidly in a very faintly acid solution.

CHAPTER XXIV

DYES AND DYEING

223. Preparation of an Azo Dye: Methyl Orange (SECTION **629**).—Dissolve 10 grams of sulphanilic acid and 3 grams of anhydrous sodium carbonate in 150 cc. of water. To the solution first add 4 grams of sodium nitrite dissolved in 20 cc. of water, and then a mixture of 7 cc. of concentrated hydrochloric acid and 10 cc. of water. (*Eq.*) Dissolve 6 cc. of dimethylaniline in a mixture of 20 cc. of water and 10 cc. of concentrated hydrochloric acid. Cool the solution under running water, and pour it slowly and with stirring into the diazotized sulphanilic acid. (*Eq.*) Add a dilute solution of sodium hydroxide until the solution is just alkaline; this can be seen by the change in color. Add to the mixture 50 grams of salt dissolved in 150 cc. of water. In order to facilitate the separation of the dye, heat the mixture to boiling until gas-bubbles disappear. Allow the solution to cool to room temperature, and filter it with a large funnel, without the use of suction. When the liquid no longer passes through the filter-paper, transfer the precipitated dye, which is mixed with much water, to a funnel connected with a filter-bottle and pump, and remove the last part of the solvent by suction. It is well to proceed in the way described, and not to attempt to filter by suction at first; in this case the paper soon becomes clogged with the dye and filtration proceeds very slowly.

The salt may be purified by recrystallization from hot water (about 150 cc). Filter the boiling solution in the way described in §10, page 6. The yield should be about 12 grams.

Dissolve a little methyl orange in water and add alternately to the solution dilute hydrochloric acid and dilute sodium hydroxide as long as a change in color is observed. (*Eqs.*)

Dissolve about 0.2 gram of methyl orange in about 10 cc. of dilute hydrochloric acid, add about 1 gram of zinc dust and boil the solution as long as any change takes place. Methyl orange, like other azo dyes, is reduced to colorless compounds by hydrogen in acid solution at the N:N bond:

$$(CH_3)_2NC_6H_4N{:}NC_6H_4SO_3H + 4H = (CH_3)_2NC_6H_4NH_2 + H_2NC_6H_4SO_3H$$

224. Preparation of a Triphenylmethane Dye: Malachite Green (SECTION **637**).—Melt cautiously over a flame in a 6-inch evaporating dish 7 grams of fused zinc chloride, as long as bubbles are given off. Remove the flame and as the zinc chloride cools rotate the dish slowly so that when cold the chloride covers an area from 3 to 4 inches in diameter. Put into the dish 13 grams of dimethylaniline and 5 grams of freshly distilled benzaldehyde. Cover the dish with a watch-glass and heat on the steam-bath for 4 hours. Stir the contents frequently with a glass rod, which should be left in the mixture. Transfer the reaction-product to a flask; the part that can not be poured out of the evaporating dish can be treated repeatedly with hot water and thus removed. Distil with steam as long as any oil passes over. Discard the distillate.. Pour the water out of the flask and dissolve the material sticking to the side of the flask in the smallest amount of boiling alcohol. Filter the solution and set it aside to crystallize over night. The leuco base which separates may form at first as an oil, but on standing changes into masses of small crystals. Filter off the solid, dry, and weigh it. The yield of leuco base, $C_6H_5CH[C_6H_4N(CH_3)_2]_2$, should be from 7 to 10 grams.

To convert the leuco base into the color base it is oxidized by lead dioxide. The dye is finally obtained as the double chloride of the color base and zinc chloride. Prepare the lead dioxide as follows: Dissolve 8 grams of lead acetate in 50 cc. of water. Mix thoroughly 20 grams of fresh bleaching powder with 300 cc. of water and filter. Heat the solution of lead acetate, and add the solution of bleaching powder slowly, keeping the solution just below boiling. When all the lead has been precipitated and the solid has changed to a deep brown color, stop heating and let the precipitate settle. Pour off the liquid and wash the solid three times by decantation, using about 500 cc. of water each time.

Dissolve 5 grams of the leuco base in a mixture of 5 cc. of concentrated hydrochloric acid and 10 cc. of water. Pour this into a large beaker containing 400 cc. of water and 100 grams of ice. Stir, and add slowly, taking about 5 minutes for the operation, the lead dioxide from which as much water as possible has been removed by decantation. Next add a solution of 5 grams of sodium sulphate in 25 cc. of water; this is to precipitate the lead which has gone into solution as chloride. Filter, and to the filtrate add a solution of 5 grams of zinc chloride in 10 cc. of water. To precipitate the dye add 50 grams of powdered salt, and stir until the latter has dissolved. Filter with a large funnel, and finally transfer the dye, which is mixed with much water, to a funnel connected with a pump, and remove most of the solution by suction. Wash once with a solution of salt. Transfer the dye to a porous plate. When quite dry, weigh the compound. Write equations, using graphic formulas, for all the reactions involved in the preparation. The yield should be 7 grams.

226. Preparation of a Phthalein: Fluorescein (SECTIONS **639, 641**).—Melt cautiously over a flame in a 6-inch evaporating dish, 5 grams of anhydrous zinc chloride, as long as bubbles are given off. When the zinc chloride solidifies, add 10 grams of resorcin and 7 grams of phthalic anhydride. Cover the dish with a watch-glass, place it on a wire gauze, and heat very carefully over a flame about 2 cm. high, the top of which is 2 or 3 cm. below the gauze. (*Eq.*) The heating should be at such a rate that the mixture produces bubbles slowly. In about 15 minutes, when the bubbles cease to be formed and the mass becomes stiff, stop the heating, and add to the dish, after it has cooled somewhat, 100 cc. of water and 20 cc. of concentrated hydrochloric acid. Heat the mixture to boiling, and break up with a glass rod the mass on the bottom of the dish. In a few minutes pour off the liquid through a filter and grind the solid with a pestle. Add 100 cc. of water and 20 cc. of concentrated hydrochloric acid, and boil again. Finally filter and wash with water. Let the fluorescein, the insoluble residue, dry in the air. Weigh the product. The yield should be about 12 grams.

Fluorescein can be crystallized by dissolving it in hot alcohol or in hot glacial acetic acid, and adding water.

Dissolve a trace of fluorescein in a dilute solution of sodium hydroxide and examine the solution by reflected and by transmitted light.

226. Preparation of Eosin (SECTION **641**).—In a small flask cover 5 grams of fluorescein with 20 cc. of alcohol. Add slowly in small portions, taking 10 minutes for the operation, 4 cc. of bromine. Shake the flask frequently. When about one-half of the bromine has been added most of the fluorescein passes into solution as the dibrom-substitution-product; as the addition continues the tetrabrom-substitution-product crystallizes out. (*Eq.*) Allow the mixture to stand for an hour; filter and wash twice with a small amount of cold alcohol. The yield is about 7 grams.

Dissolve a little eosin in sodium hydroxide and examine the solution by transmitted and by reflected light.

Salts of eosin are used for dyeing. Prepare some of the ammonium salt as follows: Place in a desiccator about 25 cc. of concentrated ammonia. Place about a gram of powdered eosin on a small watch-glass and support it on a triangle in the desiccator. Cover the latter. At the next exercise test the solubility of the substance on the watch-glass; if it has been completely converted into the ammonium salt it will dissolve without a residue in water.

Dissolve some of the ammonium salt in a little water, and then use the solution as ink, with a new pen.

Dissolve about 0.1 gram of the salt in 200 cc. of water and dye a piece of silk by heating it with the solution for about 10 minutes.

DYEING

227. Dyeing with a Substantive Dye: Congo (SECTIONS **622, 625, 628**).—The cotton to be used in this and the experiments which follow should be heated for 10 minutes in a boiling solution of 1 gram of sodium carbonate in 500 cc. of water. Prepare in this way seven pieces of white cotton cloth about 6 inches square. Wash the cotton three times with water and let it stand under water until needed.

Dissolve 0.1 gram of Congo and 0.1 gram of sodium carbonate in 500 cc. of water. Heat the solution to a temperature just below boiling, and add pieces of white cotton cloth, woolen cloth, and silk about 6 inches square. Stir occasionally to obtain even dyeing. At the end of 10 minutes remove the fabrics and wash in hot water as long as the dye is removed. Cut the pieces in two, and place half of each material in a very dilute solution of hydrochloric acid. Let the samples stay in the air until dry.

228. Dyeing with an Adjective Dye: Mordants: Malachite Green (SECTIONS **624, 637**).—Mordant two pieces of boiled-out cotton cloth (see previous experiment) by allowing them to stand for 15 minutes in a cold solution of 0.2 gram of tannic acid in 200 cc. of water. Fix the tannic acid on one of the pieces by placing the cloth without washing into a solution of 0.2 gram of tartar emetic in 200 cc. of water, and allowing it to stand for 10 minutes.

Make a dye bath by dissolving 0.1 gram of malachite green in 500 cc. of water. Add to the bath a piece of boiled-out cotton which has not been mordanted, the piece of cotton mordanted with tannic acid from which most of the solution has been removed by pressure, the piece of cotton cloth on which the tannic acid was fixed by tartar emetic, a piece of wool, and a piece of silk. Dye for 15 minutes at a temperature just below boiling. Work the pieces over and over with a rod occasionally to obtain even dyeing.

Wash the dyed material in boiling water as long as color is removed. Dry. Compare the appearance of the three pieces of cotton cloth. Why is the piece which was treated with tannic acid and tartar emetic darker than the one mordanted with tannic acid alone?

229. Dyeing with an Ingrain Color: Primuline (SECTION **625**). Dye three pieces of boiled-out cotton cloth (see experiment 227) in a solution of 0.2 gram of primuline and 0.2 gram of sodium carbonate in 500 cc. of water, at a temperature just below boiling for 15 minutes. Wash the cloth twice in about 500 cc. of water.

Prepare a diazotizing bath by dissolving 10 cc. of concentrated hydrochloric acid in 500 cc. of cold water and then adding 0.2 gram of sodium nitrite. Place in the bath the three pieces of cloth which have been dyed with primuline, and allow them to stay 10 minutes. Stir occasionally. Prepare three baths in which the diazotized primuline is to be developed. Dissolve 0.1 gram β-naphthol in 1 cc. of a 10 per cent solution of sodium hydroxide, and add 100 cc. of water; dissolve 0.1 gram resorcinol in 2 cc. of the sodium hydroxide solution and add 100 cc. of water; dissolve 0.1 gram of phenol in 1 cc. of the sodium hydroxide solution and add 100 cc. of water.

Transfer the cloth from the diazo bath to a beaker containing about 500 cc. of water and stir. Put one piece of cloth in each of the developing solutions, and allow them to stay 5 minutes.

Wash the dyed cloth twice with water and dry.

CHAPTER XXV

HETEROCYCLIC COMPOUNDS

230. Formation of Thiophene (SECTION **654**).—Shake together in a test-tube 1 gram of red phosphorus and 2 grams of flowers of sulphur. Heat the mixture over a free flame until action begins. Prepare some sodium succinate by neutralizing 2 grams of succinic acid with a strong solution sodium carbonate and evaporating to dryness. HOOD.—Powder the residue and grind it with the phosphorus sulphide. Place the mixture in an 8-inch test-tube which is fitted with a glass tube bent at two right angles; the second bend of the tube should pass to the bottom of a test-tube placed in a beaker containing ice and concentrated hydrochloric acid. Heat under the hood the tube containing the mixture of sodium succinate and phosphorus trisulphide as long as anything distils. Note whether the oil is lighter or heavier than water.

Add to a drop of the oil a trace of isatin and 1 cc. of concentrated sulphuric acid. Test a sample of commercial benzene and one of benzene purified by crystallization from thiophene.

231. Formation of Furfuraldehyde (SECTION **656**).—Boil a small piece of gum arabic in a test-tube with 5 cc. of dilute sulphuric acid. Hold in the vapors escaping from the tube a piece of paper which has been moistened with a solution of 2 drops of aniline and 2 drops of glacial acetic acid in 2 cc. of water.

232. Properties of Pyridine (SECTIONS **659, 660**).—(*a*) *Base-forming property of pyridine.*—Dissolve about 1 cc. of pyridine in 5 cc. of water and test the solution with litmus paper.

Add a solution of pyridine to a solution of ferric chloride and to one of aluminium chloride. (*Eq.*)

(*b*) *Pyridine and mercuric chloride.*—Add an aqueous solution of pyridine to one of mercuric chloride. The crystalline precipitate has the composition $HgCl_2.C_5H_5N$.

(*c*) *Pyridine and oxidizing agents.*—Determine whether pyridine is oxidized by a solution of potassium permanganate, by concentrated nitric acid, or by a mixture of potassium bichromate and sulphuric acid.

(*d*) *Behavior of pyridine as an amine.*—Determine whether pyridine is a primary, secondary, or tertiary amine. Describe in detail the tests applied.

(*e*) *Pyridine and methyl iodide.*—Mix together in a test-tube 5 drops of pyridine and 5 drops of methyl iodide. Set aside and examine after a few hours. (*Eq.*)

233. Preparation of Quinoline by Skraup's Synthesis (SECTION **662**).—In a 1500-cc. flask place 15 grams of finely powdered hydrated ferrous sulphate, 24 grams of nitrobenzene and 38 grams of aniline; add cautiously 100 grams of pure concentrated sulphuric acid, and then, slowly with shaking, 120 grams of glycerol. Connect the flask with a long reflux water-condenser, the inner tube of which has a wide bore. Support the flask and condenser by means of damps. Do not use a gauze or bath, but heat the flask directly, cautiously, with a free flame. In a short time a vigorous reaction will begin, and a large amount of heat is evolved; when this occurs remove the flame. When the spontaneous boiling ceases, place a wire-gauze under the flask, and heat to boiling for 2 hours. Cool the flask slightly, add about 100 cc. of water and distil with steam as long as an oil passes over. This distillation serves to remove the excess of nitrobenzene. Cool the flask under running water, and add a cold solution of 100 grams of sodium hydroxide in 150 cc. of water. Distil over the quinoline with steam. When an oil no longer separates in the condenser, stop the distillation.

The aqueous distillate contains the quinoline formed in the reaction and a small amount of aniline. In order to separate the latter, advantage is taken of the fact that aniline is converted into a diazo compound by nitrous acid, whereas quinoline, being a tertiary amine, is not affected by this reagent. When the aqueous solution containing the diazo compound is heated, the latter is converted into a phenol. Quinoline can be readily separated from phenol by distillation with steam from an alkaline solution, in which the phenol is present as the sodium salt and is, therefore, non-volatile. To effect this separation treat the aqueous distillate as follows: Add to the distillate 10 cc. of concentrated sulphuric acid. There should be a small excess of acid over that required to dissolve the oil. Next add a few cubic centimeters of a solution of sodium nitrite and stir vigorously. Continue the addition until the solution smells strongly of the oxides of nitrogen. The quinoline is liberated from its salt by adding a solution of 40 grams of sodium hydroxide in 50 cc. of water. Distil again with steam as long as an oil passes over. Separate the oil, dry it with solid potassium hydroxide and distil. By extracting with ether the aqueous solution, from which the quinoline was finally separated, the yield can be slightly increased.

Quinoline boils at 238°. The yield in this preparation is about 38 grams.

NOTE.—The ferrous sulphate prevents rapid oxidation from taking place, and, as a result, reduces the violence of the reaction.

ALKALOIDS

234. General Reactions of Alkaloids (SECTION **670**).—Dissolve the amount of quinine sulphate that can be held on the point of a pen-knife in about 20 cc. of water. Observe the appearance of the solution. Add to 2 cc. of the solution drop by drop, a dilute (1 per cent) solution of tannic acid. Repeat using solutions of phosphomolybdic acid, picric acid, iodine in potassium iodide, and potassium mercuric iodide. The last-named solution can be prepared by adding an excess of a solution of potassium iodide to a solution of mercuric chloride.

235. Test for an Alkaloid in Tobacco: Nicotine (SECTION **672**).—In a small distilling flask boil together one cigarette, 25 cc. of water, and 2 cc. of dilute sulphuric acid. At the end of 10 minutes, add an excess of a solution by sodium hydroxide, connect the flask with a condenser, and distil over about 10 cc. of the solution. Test the distillate by adding to separate portions of it, drop by drop, solutions of the following: mercuric chloride, tannic acid, iodine in potassium iodide, and potassium mercuric iodide.

CHAPTER XXVI

PROTEINS

236. Detection of Nitrogen, Sulphur, and Phosphorus in Proteins.—The methods described below illustrate those commonly used in the analysis of proteins.

(*a*) *Analysis for nitrogen by means of soda-lime.*—HOOD.—Heat about 0.1 gram of casein with five times its weight of soda-lime in a dry test-tube over a small flame. Observe the odor of the gases which escape, and test them with moist litmus paper.

(*b*) *Analysis for phosphorus and sulphur by fusion with potassium nitrate.*—HOOD.—Fuse together cautiously in a small porcelain crucible about 0.1 gram of casein, 0.2 gram of potassium nitrate, and 0.1 gram of anhydrous sodium carbonate. When the mixture is colorless, let it cool; then add 10 cc. of water and heat to boiling. The fusion has converted the phosphorus into sodium phosphate. The acid radical is tested for in the usual way. Acidify about 2 cc. of the solution with nitric acid, and add a solution of ammonium molybdate. If no precipitate forms, warm gently (about 60°) and set aside. A yellow precipitate indicates the presence of phosphorus.

Acidify about 2 cc. of the solution from the fusion mixture, which contains a sulphate if sulphur is present, with hydrochloric acid, and add a solution of barium chloride. Heat the solution to boiling and set aside. Examine the tube for a white precipitate.

(*c*) *Analysis for sulphur by decomposition with sodium hydroxide.*—Boil about 0.1 gram of casein with 5 cc. of a 10 per cent solution of sodium hydroxide to which a drop of lead acetate solution has been added. If a black precipitate is not evident, filter the solution through a paper and observe if a precipitate is left on the paper. When proteins containing sulphur are decomposed by sodium hydroxide, sodium sulphide is formed; the latter is converted into lead sulphide by lead salts.

(*d*) *Analysis for nitrogen, phosphorus, and sulphur by fusion with sodium.*—Analyze a sample of dried egg-white for nitrogen, phosphorus, and sulphur by the method commonly used in the qualitative analysis of organic compounds (§58-61, page 39).

237. Precipitation Reactions of Proteins (SECTION **686**).—The protein solution to be used in the following experiments is prepared as follows: Beat egg-white for a short time to break the membranes, and squeeze it through cotton cloth. Mix with ten times its volume of water and filter through paper. This gives a solution which contains about 1 per cent of protein.

(*a*) *Strong mineral acids: Heller's test.*—Put 2 cc. of egg-white in a test-tube; incline the tube, and pour cautiously down the side concentrated nitric acid in such a way that the acid sinks to the bottom of the tube and two layers are formed. Shake the tube. Is the precipitate dissolved? Dilute 2 cc. of the egg-white solution with 100 cc. of water, and test 2 cc. of this solution as before with nitric acid. Determine whether the protein is precipitated from the 1 per cent solution by dilute hydrochloric acid and by dilute acetic acid, and if it is soluble in an excess of the acid.

(*b*) *Salts of the heavy metals.*—To 2 cc. of egg-white solution add 1 drop of a solution of mercuric chloride. For what purpose can this reaction be used?

Test in the same way the effect on the protein of a solution of lead acetate, of silver nitrate, and of copper sulphate. To the tube containing the precipitate with copper sulphate add 3 to 4 drops of a solution of sodium hydroxide, dilute, and note the color.

(*c*) *Alkaloidal reagents in acid solutions. Hydroferrocyanic acid.*—Add to 2 cc. of egg-white solution 5 drops of glacial acetic acid and 1 drop of a solution of potassium ferrocyanide.

Tannic acid.—Add, drop by drop, to 2 cc. of egg-white solution a solution of tannic acid.

Picric acid.—Repeat with a solution of picric acid.

Potassium mercuric iodide.—Prepare the reagent by adding to a few drops of a solution of mercuric chloride a solution of potassium iodide until the precipitate first formed is dissolved. Add to 2 cc. of egg-white solution a drop of dilute hydrochloric acid and a drop of the reagent.

Bromine.—Add bromine-water to 2 cc. of the egg-white solution until a permanent yellow color is formed.

(*d*) *Coagulation by alcohol.*—Add to 5 cc. of the egg-white solution twice its volume of alcohol. Set aside until the next exercise. Filter and test the solubility of the precipitate in water. To do this, wash the precipitate with water, and test the solution for protein

(*e*) *Heat coagulation.*—Heat 2 cc. of the egg-white solution to boiling. To 2 cc. of the egg-white solution add 1 or 2 drops of a 0.5 per cent solution of acetic acid, and heat to boiling. Compare the results in the two cases (see note below).

Determine the temperature of coagulation of egg-white as follows: Add to 5 cc. of the protein solution 5 drops of a 0.5 per cent solution of acetic acid. The mixture should be faintly acid to delicate litmus paper. Put a thermometer in the solution, and place the test-tube in cold water in a beaker; heat the water and determine the temperature at which the solution clouds and when the precipitate separates in flocks. Stir from time to time with the thermometer.

NOTES.—(*a*) Heller's reaction is a very delicate test for most proteins; peptones are not precipitated by nitric acid.

(*c*) A reaction with potassium ferrocyanide takes place only in acid solution; neutral salts interfere to some extent with the reaction. Peptones are not precipitated by hydroferrocyanic acid.

(*d*) Alcohol precipitates proteins unchanged, but on standing the latter are converted into a form which is insoluble in water.

(*e*) Egg-white is faintly alkaline. Complete precipitation takes place only in faintly acid solution. The temperature at which coagulation takes place depends to a large extent on the amount of acid and of salts present.

238. Color Reactions of Proteins (SECTION **686**).—(*a*) *Biuret reaction.*—Add to 2 cc. of egg-white solution 2 cc. of a 10 per cent solution of sodium hydroxide and 2 drops of a 1 per cent solution of copper sulphate.

(*b*) *Xanthoproteic reaction.*—To 2 cc. of the egg-white solution add 5 drops of concentrated nitric acid and heat to boiling. Note the change in color. Cool the solution and make it alkaline with ammonia or sodium hydroxide.

(*c*) *Millon's reaction.*—To 2 cc. of the egg-white solution add 5 drops of Mellon's reagent. Is a precipitate formed? Heat to boiling.

(*d*) *Molisch reaction.*—Add to 2 cc. of egg-white solution 3 drops of a solution of α-naphthol in chloroform; shake and pour cautiously down the side of the test-tube concentrated sulphuric acid so that two layers are formed. If no color is produced, put the tube aside and examine in a few minutes.

(*e*) *Sulphur reaction.*—Add 1 drop of a solution of lead acetate to 2 cc. of the egg-white solution and then a dilute solution of sodium hydroxide until the precipitate is dissolved. Heat to boiling.

(*f*) *Hopkins-Cole reaction.*—Add to 2 cc. of the egg-white solution 5 drops of a solution of glyoxylic acid (see Appendix). Pour down the side of the tube concentrated sulphuric acid so that two layers are formed. If no color develops examine the tube in a few minutes.

NOTES.—(*a*) Excess of copper sulphate must be avoided in making the biuret test, since the color of the salt prevents the recognition of the color produced in the reaction. The presence of ammonium salts interferes with the test. In applying the reaction to solutions containing these salts a large excess of sodium hydroxide must be present. Compounds which give the biuret test must contain at least two —CO—NH— groups. The color formed in the reaction varies in shade with the complexity of the molecules.

(*b*) The color is produced as the result of the formation of nitro-derivatives of the compounds which contain a benzene ring, for example, tyrosine.

(*c*) The color produced in Millon's test is given by derivatives of benzene in which a hydrogen in the ring has been replaced by a hydroxyl group. The reaction serves as a test for the presence of tyrosine.

(*d*) If the Molisch test is positive, a carbohydrate is present in the protein molecule.

(*e*) If sulphur is present a black precipitate or brown coloration is produced. If the result is in doubt the solution should be filtered and the paper examined. The precipitate, which is lead sulphide, is formed as the result of the decomposition of the cystine by the alkali.

(*f*) The color produced is due to the formation of a compound from the glyoxylic acid in the reagent and the tryptophane in the protein. A similar color is produced when sulphuric acid is added to a protein solution in the presence of a trace of formaldehyde. The reaction is used as a test for formaldehyde in milk.

239. Study of the Composition of Gelatin and of Wool.—Apply the precipitation and color reaction of proteins to a solution of gelatin made by dissolving 1 gram of the substance in 100 cc. of hot water. Cool the solution before it is used. State what conclusion can be drawn from the results as to the presence or absence of certain amino-acids in gelatin.

Apply the color tests to a sample of wool.

240. Separation of Proteins by Salting Out (SECTION **679**).—(*a*) *Separation of a globulin from an albumin by means of sodium chloride.*—Add to 10 cc. of the egg-white solution finely powdered sodium chloride until the solution is saturated and a slight residue of salt is obtained (3.6 grams for each 10 cc. of solution). The globulin is precipitated. Filter the solution; add to the filtrate 2 to 3 drops of 0.5 per cent acetic acid, and heat to boiling. The albumin which was in solution is coagulated.

(*b*) *Separation of a globulin from an albumin by means of ammonium sulphate.*—Prepare a saturated solution of ammonium sulphate by dissolving 8 grams of the salt in 10 cc. of water. Add 10 cc. of this solution to 10 cc. of egg-white solution. In this way the latter solution is one-half saturated with ammonium sulphate, and the globulin is precipitated. Filter, and to one-half of the filtrate add 2 drops of a 0.5 per cent solution of acetic acid and boil. The albumin is coagulated. Saturate the other half with solid ammonium sulphate; the albumin is precipitated. Filter, and test the filtrate as before for protein.

241. Products of the Hydrolysis of Proteins.—(*a*) *Metaproteins.*—In a test-tube place 10 cc. of the egg-white solution and 1 cc. of a 10 per cent solution of sodium hydroxide. In a second tube place 10 cc. of the egg-white solution and 1 cc. of concentrated hydrochloric acid. Place the tubes in a beaker containing about 300 cc. of water at 50°, and allow them to stand from 15 to 20 minutes. The temperatures should not fall below 40°. The protein is partly converted into alkali-albumin and into acid-albumin.

Boil 2 cc. of the solution in each tube. Is protein precipitated? Add to 2 cc. of the alkali albumin a drop of dilute hydrochloric acid. Is the precipitate soluble in dilute alkali? Add to 2 cc. of the alkali albumin a drop of dilute hydrochloric acid; heat to boiling. Is the precipitate soluble in dilute alkali as before? Explain. Add to 2 cc. of the acid albumin a drop of dilute alkali. Is the precipitate soluble in dilute acetic acid? Add to 2 cc. of the solution of alkali albumin an equal volume of a saturated ammonium sulphate solution. Is the protein precipitated?

(*b*) *Proteoses and peptones.*—Stir 2 grams of Witte's peptone with 40 cc. of cold water, and filter from the small insoluble residue.

Add to 2 cc. of the solution 2 to 3 drops of 0.5 per cent solution of acetic acid and boil. Are the proteins coagulated?

242. Separation of Proteoses and Peptones.—Saturate 20 cc. of the solution prepared in experiment 241*b* above with ammonium sulphate (16 grams). Filter. Save the filtrate which contains the peptones. Place the filter-paper containing the precipitate in a beaker, and heat it with 25 cc. of water. Filter. This filtrate contains the proteoses. Apply to the solution of the peptones and to the solution of the proteoses the precipitation and color reactions given above. Compare the results in the two cases. In making the biuret test when ammonium salts are present, a large excess of alkali must be added; add a strong (1 to 1) solution of sodium hydroxide or about 10 cc. of a 10 per cent solution to 2 cc. of the solution to be tested.

243. The Proteins of Wheat (SECTION **690**).—(*a*) *Protein soluble in water (leucosin).*—Shake up about 1 gram of bread flour with 10 cc. of water, filter, and determine whether the filtrate contains protein by applying three or four tests.

(*b*) *Alcohol-soluble protein (gliadin).*—Add 25 cc. of water to 75 cc. of alcohol. Pour the mixture onto about 20 grams of bread flour. Stir occasionally during half an hour. Filter, and evaporate the filtrate to dryness. Observe the properties of the dried protein. Is it brittle? Moisten it with water and after a few minutes note its properties. Is it elastic? Prove that it is a protein by applying a number of tests.

(*c*) *Separation of gluten.*—Gluten is a mixture of glutenin and gliadin. In a porcelain dish mix 50 grams of bread flour with enough water to make a stiff dough (about 25 cc). Let the mixture stand for half an hour. Add about 100 cc. of water and work the dough, keeping it in the form of a ball. The starch passes into suspension in the water. Pour off the water, and add fresh water from time to time until all the starch is removed. Note the properties of the gluten.

The two proteins present can be separated by extracting the gliadin with 75 per cent alcohol. This is a tedious process. Grind a small part of the gluten in a mortar repeatedly with 10 cc. portions of 75 per cent alcohol. Finally heat the residue with some of the alcohol on the steam-bath. When all the gliadin has been removed the protein is no longer elastic. Dissolve the glutenin in dilute sodium hydroxide and apply a few of the protein tests.

NOTE.—Wheat contains the following proteins: Soluble in water, leucosin, about 0.4 per cent, and a proteose, about 0.3 per cent; soluble in 10 per cent sodium chloride, edestin, about 0.6 per cent; soluble in 75 per cent alcohol, gliadin, about 4.3 per cent; insoluble in neutral solvents, glutenin from 4.0 to 4.5 per cent.

244. Isolation of a Crystalline Protein: Edestin from Hemp Seed.—Grind in a mortar 25 grams of hemp seed; add the seed in small quantities at a time, and see that each seed is crushed. Dissolve 28 grams of sodium chloride in 700 cc. of water (4 per cent solution of sodium chloride) and heat to 60°. Add the hemp seed and stir frequently during 15 minutes. The temperature of the solution should be kept between 58° and 60° during the extraction of the protein. This can be accomplished by placing a *very small* flame under the beaker. If the temperature rises above 60°, the flame should be removed. Filter into a dry beaker through a large hot water funnel containing water at 60°. Cover the funnel with a watch-glass to prevent loss in heat from the solution. Receive the first part of the filtrate in a small beaker and return it to the funnel. Set the filtrate aside to cool slowly. When the solution is cold, decant off most of the liquid carefully and filter off the solid. Place a little of the suspended solid on a glass slide, cover, and examine under a microscope. Sketch the crystals. If crystals have not separated from the solution before the end of the laboratory period, leave the solution in a cool place. Test the edestin crystals by applying the following reactions: xanthoproteic, biuret, Hopkins-Cole, Millon, sulphur. Shake up some of the protein with 20 cc. of a 10 per cent solution of sodium chloride. Filter through a dry paper into a dry test-tube. If the first part of the filtrate is cloudy return it to the funnel. Pour some of the clear filtrate into water. Determine whether the protein is coagulated by heat, and whether it is salted out by sodium chloride and by ammonium sulphate.

NOTE.—During the extraction of edestins it is necessary to avoid a high temperature in order to prevent the coagulation of the protein.

245. Isolation of Casein from Milk (SECTION **696**).—To 50 cc. of milk add 150 cc. of water and heat the mixture to 30°. Add dilute acetic acid, drop by drop, as long as a precipitate is formed (about 1 cc. of a 10 per cent solution). Stir vigorously. It is necessary to avoid an excess of acid, since the latter dissolves some of the protein. Filter, During the filtration test small portions of the filtrate for protein by three or four color reactions. Heat 10 cc. of the filtrate to boiling. What protein is precipitated? Filter this off, and test the filtrate for a sugar with Fehling's solution, and for a phosphate with ammonium molybdate.

Wash the precipitate of casein with 50 cc. of water; press out as much water as possible, and then wash the precipitate twice with 20 cc. of alcohol. Squeeze out the alcohol, and press the casein between a number of pieces of filter-paper. Break up the casein and let it dry in the air. Determine whether it is soluble in water. To do this, grind in a mortar a little of the solid with 10 cc. of water, filter, and test the filtrate for a protein with concentrated nitric acid. If the filtrate is not clear, refilter it through two filter-papers. Determine if casein is soluble in sodium carbonate solution. Proceed as before; acidify the filtrate and test it for a protein.

Put into a mortar 10 cc. of water and 3 or 4 drops of a dilute solution of sodium hydroxide. Test the solution with red litmus paper. Next add some casein and grind it thoroughly in the alkaline solution. Test the solution again with red litmus paper. What conclusion can you draw in regard to the chemical nature of casein. Filter the solution through a wet filter-paper, and add to the filtrate a few drops of a solution of calcium chloride. Explain.

TEXTILE FIBERS

246. Appearance of Fibers.—Examine under a microscope a fiber of each of the following: Silk, wool, cotton, mercerized cotton, and linen.

247. Properties of Wool, Silk, and Cotton.—(*a*) *Effect of burning.*—Burn a thread of wool, of silk, and of cotton. Notice the odor produced during the burning. Explain. At the end of a few seconds blow out the flame and observe the appearance of the charred residue.

(*b*) *Action of sodium hydroxide.*—For this and the following experiments use pieces of the material about 1 inch square. Place in a test-tube a piece of cotton, a piece of silk, and a piece of wool; add about 10 cc. of a 10 per cent solution of sodium hydroxide. Heat the solution to such a temperature that the tube can just be held in the hand (about 65°); shake, and keep the tube hot by heating it occasionally until the wool dissolves. Heat to boiling for some minutes and note the effect. Explain the cause of the difference in behavior of the animal and vegetable fibers.

(*c*) *Action of concentrated hydrochloric acid.*—Shake pieces of cotton, silk, and wool with about 10 cc. of cold concentrated hydrochloric acid. One of the pieces should dissolve.

Place a piece of cotton and a piece of wool in a mixture of 1 cc. of concentrated hydrochloric acid and 5 cc. of water. Press out as much of the solution as possible. Set aside to dry and examine at the next exercise. Try to tear the material.

(*d*) *Examination of wool and of silk for sulphur.*—Add a few drops of a solution of lead acetate to about 20 cc. of a 10 per cent solution of sodium hydroxide. Divide the solution into two portions. In one dissolve a piece of wool and in the other a piece of silk.

(*e*) *Action of Millon's reagent* (SECTION **686**).—Millon's reagent is prepared by using the substances in the following proportions: One gram of mercury is dissolved in 2 cc. of hot concentrated nitric acid and the resulting solution diluted with 3 cc. of water.

Dilute 2 cc. of the reagent with 10 cc. of water, add to the solution pieces of cotton, silk, and wool, and heat to boiling.

(*f*) *Test of textile fabrics.*—Test the samples submitted, making use of the results obtained in (*a*), (*b*), (*c*), (*d*), and (*e*) above. The samples may consist of cotton, silk, or wool, or mixtures of any two of the fibers. It is a common practice to make fabrics in which the threads running in one direction are of one material, and those running in another are of a different material. Designs in pure silk are often woven into a fabric made of mercerized cotton. These designs can be readily developed by warming a sample of the material with Millon's reagent.

CHAPTER XXVII

THE IDENTIFICATION OF ORGANIC COMPOUNDS

248. Throughout the laboratory course outlined in the previous chapters, the typical reactions of a number of important classes of compounds have been illustrated by experiments. These reactions are made use of in the identification of organic compounds. Practice in such identifications is of great educational value, as it requires continuous thought on the part of the student, is an excellent review of many facts which have been learned, and has a practical significance.

No set analytical scheme is available as is the case in inorganic qualitative analysis. The subject is more complicated than the latter, and each compound requires special study. By the application of a few simple tests it is often possible to determine to what class a compound belongs. In order to facilitate the work the student should prepare a table which summarizes the behavior of certain typical compounds with a few important reagents. To do this proceed as follows: Divide a large sheet of paper into squares by drawing on it twenty horizontal and fifteen vertical lines. Place in the first vertical column on the left side of the paper the names of the following important classes of compounds, using a square for each class: paraffin hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, alcohols, phenols, acids, ethers, anhydrides, esters, aldehydes, ketones, amines, amides, nitriles, nitro compounds, halogen compounds, sulphonic acids, carbohydrates. In the squares that form the upper horizontal column write the following: water, cold solution of sodium hydroxide, hot solution of sodium hydroxide, solution of sodium carbonate, dilute hydrochloric acid, cold concentrated sulphuric acid, acetyl chloride, sodium, bromine, influence of substituents, influence of aromatic group, special reactions, and remarks. State briefly, as far as possible, in the appropriate squares, the behavior of the several classes of compounds with the reagents listed. It will take time and study to do this satisfactorily. The following references to the sections in the text-book and to the laboratory experiments will be of value in getting together the facts to be incorporated into the table. It is important that any notes under the experiments referred to should be read: paraffin hydrocarbons, **26, 27**, and experiment 70, page 47; unsaturated hydrocarbons, **38,** 46, and experiments 74 and 75, page 52; aromatic hydrocarbons, **429,** and experiments 164*d* to *h,* page 133; alcohols, **74, 83,** and experiment 79, page 57; phenols, **540,** and experiments 197, 198, page 167; acids, **124,** and experiments 90, 91, page 66; ethers, **147,** and experiment 96, page 73; anhydrides, **152,** and experiment 98, page 75; esters, **173,** and experiment 103, page 79; aldehydes, **188,** and experiment 108, page 86; ketones, **200,** and experiment 111, page 87; amines, **213, 505,** and experiments 113, 183, 184, 185, pages 89, 154, 156; amides, **231,** and experiment 116, page 92; nitriles, **244,** and experiment 127, page 97; alkyl halides, **255,** and experiment 132, page 101; acyl halides, **278,** and experiment 139, page 109; aryl halides, **480,** and experiment 180, page 148; carbohydrates, **386,** and experiments 148, 152, 156, pages 119, 123, 128; nitro compounds, **469,** and experiment 171, page 140; sulphonic acids, **477,** and experiment 174, page 144.

249. The properties of the members of any class are in general like those illustrated in the case of the simpler members, which have been studied by the student. It is important to remember, however, that increase in molecular weight generally leads to decreased solubility and chemical activity. For example, the anhydrides with low molecular weight of the homologues of acetic acid react promptly with water, whereas those of high molecular weight must be heated with water for some time to bring about hydrolysis. It is also important to remember that the presence of a second group in a compound often modifies the properties which a characteristic group gives to it; for example, monhydroxy phenols are insoluble in dilute hydrochloric acid, but aminophenol dissolves in this reagent on account of the presence of the amino group.

Before beginning to identify an unknown compound the student should study SECTIONS **405** to **408** inclusive, and solve problem 2 at the end of Chapter XVII in the text-book. The work should be done carefully with small amounts of the substance to be studied. About 10 grams of a pure compound is ordinarily enough for complete identification, including the preparation of a derivative and the determination of its physical properties. Solubilities can be determined with a crystal or a single drop. The first substances given to the student should be practically pure.

The work is begun by testing the purity of the sample to be identified. If it is a liquid the substance should be distilled very carefully from a small flask (§44, page 30). If the substance is a solid its melting-point should be determined. Record the result obtained, as it is to be used in the final identification. If the substance is impure it should be purified before being studied further. Burn some of the substance (experiments 164*d*, note, and 180*b*, pages 134, 148,) and determine if possible if it is an aromatic compound (experiment 164*e* and *f*, note). Next make a qualitative analysis (§57-61, pages 39, 42). If any element other than carbon, hydrogen, and oxygen is found, it is well to make tests to discover in what group the element is present. Study next the behavior of the substance with the reagents given in the table prepared as described above, and test with Tollen's and Schiff's reagent. If the substance appears to be a carbohydrate, apply the Molisch test.

250. When the class or classes to which the compound belongs and the melting-point or boiling-point have been determined, consult large texts, or other reference books on organic chemistry, which contain tables or lists of compounds with their physical properties. Such books as Richter, "Organic Chemistry;" Beilstein, "Handbuch der Organischen Chemie;" Mulliken, "Identification of Pure Organic Compounds;" Chemiker Kalender; Meyer and Jacobson, "Lehrbuch der Organischen Chemie;" and Van Nostrand's "Chemical Annual" are useful. Take into consideration compounds the melting-points of which lie within about four degrees on either side of the point observed. Such a range is necessary as the melting-points and boiling-points recorded are at times far from accurate. When one or more compounds are found the descriptions of which fit those of the substance under study, find out what derivative which possesses a satisfactory melting-point or boiling-point can be readily made.

It is best to prepare a solid whenever possible, since in this case much smaller amounts of substance can be used. Look up the properties of this derivative and its method of preparation, and convert about 1 gram of the substance to be identified into the derivative if the latter is a solid; if it is a liquid more will be required. Before making the preparation read carefully pages 29 to 32, where the special technique of handling small quantities is described. Determine the melting-point or boiling-point of the compound prepared; if this agrees with the number as given, the identification of the original substance may be considered satisfactory.

In the case of certain compounds it is difficult to transform them into other substances when only a small amount is available. In this case, if the compound is a liquid, it is often convenient to determine its specific gravity (§56, page 37) as an aid in its identification. At times both the melting-point and the boiling-point of a substance can be determined; these two constants often will serve to identify a compound. For the identification of a substance it is necessary to have at least two physical constants agree with those which have been recorded; these may be constants of the substance itself, or one may be a constant of the substance and one of a compound into which it has been converted. Reliance on one constant often leads to mistakes. For example, *o*-chlorotoluene boils at 154° and *m*-chlorotoluene at 156°. It would be very difficult to identify either substance by a determination of its boiling-point alone. The identification is readily accomplished, however, by converting the compounds into the corresponding benzoic acids; *o*-chlorobenzoic acid melts at 137° and *m*-chlorobenzoic acid at 153°.

251. In the following list, the derivative which can be conveniently prepared, in most cases, from the several classes of compounds is given. In some cases specific gravity determinations are made, although it is preferable to convert the compound into another substance if possible: paraffin hydrocarbons, specific gravity; unsaturated hydrocarbons, addition-products with bromine or hydriodic acid; aromatic hydrocarbons, solid nitrocompounds (experiment 172, note, page 142), or addition-products with picric acid (experiment 169*c*, page 138); alcohols, special tests or solid esters of aromatic acids; phenols, bromine substitution-products; monobasic fatty acids, solid anilides (experiment 91*c*, page 67), or esters; polybasic acids, characteristic salts; aromatic acids, amides (experiment 202, page 171) or nitroderivatives; ethers, specific gravity or conversion into iodides (experiment 96*j*, page 74); aromatic ethers, as above, or nitroderivatives; fatty anhydrides, anilides (experiment 98*e*, page 76); aromatic anhydrides, change to acids; esters, hydrolysis and identification of the acid or alcohol formed; fatty aldehydes, specific tests; aromatic aldehydes, nitroderivatives or special tests; ketones, oximes (experiment 210, page 176), or special tests (experiment 111*f*, page 88); fatty amines, salts with hydrochloric acid; aromatic amines, acetyl derivatives or special tests; amides, change to acids; nitriles, change to acids; nitro compounds, further nitration or reduction to amines; sulphonic acids, amides; carbohydrates, special tests, osazones, behavior with Fehling's solution, etc.

252. Study of Mixtures.—(See SECTION **408**).—The mixture should be treated in turn with twice its volume of water, dilute hydrochloric acid, dilute sodium hydroxide, and concentrated sulphuric acid. When sulphuric acid is used care must be taken to keep the mixture cold. If the mixture is a liquid it should be treated with solvents in a graduated cylinder. The volume of the liquid should be noted before and after shaking with the solvents; in this way it can be easily seen whether any of the mixture dissolves. If this occurs the mixture should be treated with small quantities of the solvent as long as any of its dissolves. The several solutions should be examined separately. The water solution should be carefully distilled. It is tested first with litmus paper to determine whether an acid or an amine is present. If an acid is present the solution should be neutralized with sodium hydroxide before distillation. The acid will remain in the flask as a sodium salt and other volatile substances will pass over. The boiling-point should be carefully noted during the whole distillation. If there is evidence of the presence of anything in solution, tests should be applied to the distillate for the classes of substances soluble in water.

The extract obtained by treatment with acid should be rendered alkaline. If a basic substance has been removed it will be precipitated; this should be separated and tested.

The extract obtained with sodium hydroxide is next treated with dilute hydrochloric acid. If an acid or phenol is present it will be precipitated, and is examined.

The concentrated sulphuric acid solution is poured very carefully onto twice its volume of cracked ice. Any substance which is precipitated is washed with a little water, separated, and examined. If two substances which belong to the same class of compounds are present in a mixture, it is usually necessary to separate them by fractional distillation.

A full record of all tests used should be placed in the notebook. The observed physical properties (melting-point, boiling-point or specific gravity) of the substance and of the compound prepared from it should be given together with the physical properties as recorded in the reference books.

APPENDIX

SCHIFF'S REAGENT

Dissolve about 0.2 gram of rosaniline in a small amount of boiling water. Cool and add 15 cc. of a saturated solution of sulphur dioxide in water, and allow the mixture to stand several hours until it becomes colorless or pale yellow; then dilute to 200 cc. with water. The reagent should be kept in a well-stoppered bottle of dark glass.

TOLLEN'S REAGENT

Make an ammoniacal solution of silver nitrate by dissolving 10 grams of the salt in 100 cc. of a solution of ammonia prepared by mixing equal volumes of concentrated ammonia (sp. gr. 0.9) and water. When ready to make a test, mix a portion of this solution with an equal volume of a 10 per cent aqueous solution of sodium hydroxide. The test should be made in the cold. The sodium hydroxide should be added immediately before use; on standing or on heating, the mixture so prepared deposits a black explosive precipitate.

FEHLING'S SOLUTION

Dissolve 34.64 grams of pure crystalline copper sulphate in distilled water, and dilute to 500 cc. Dissolve 70 grams of sodium hydroxide and 180 grams of pure Rochelle salt in 400 cc. of water, and dilute to 500 cc. The solutions should be kept in separate bottles until used. Fehling's solution is made by mixing equal volumes of the two solutions. A solution prepared in this way is of such a strength that 1 cc. of it will oxidize 0.005 gram of dextrose.

MILLON'S REAGENT

Dissolve 10 grams of mercury in 20 cc. of hot concentrated nitric acid, and dilute the resulting solution with 30 cc. of water.

HOPKINS-COLE REAGENT

In a large flask place 10 grams of powdered magnesium, cover the latter with distilled water, and add slowly, keeping the mixture cold, 250 cc. of a cold saturated solution of oxalic acid. When the reaction is complete, filter, make the filtrate slightly acid with acetic acid, and dilute to 1000 cc. with distilled water.

PREPARATION OF HYDROBROMIC ACID

The constant-boiling mixture of hydrobromic acid and water can be conveniently used to prepare alkyl bromides. The acid boils at 126°, contains about 47.5 per cent of hydrogen bromide, and has a specific gravity of about 1.48.

The acid can be prepared from potassium bromide or from bromine.

(*a*) *From potassium bromide.*—In a 250 cc. distilling flask pour slowly into 85 cc. of water 98 grams of pure concentrated sulphuric acid. To the mixture add 119 grams of powdered potassium bromide and distil slowly, using a water-jacketed condenser. Collect the fraction boiling at 124°-126°. The yield is 85 to 90 per cent of the theoretical.

(*b*) *From bromine.*—In a 200 cc. distilling flask place 162 cc. of water and 10 grams of red phosphorus; cover the side-arm of the flask with a cork (Fig. 16, page 26), connect the flask with a return condenser, and place it in a water-bath so that it is completely covered with cold water. Put 40 cc. of bromine in a small separatory funnel, and support the latter in the condenser at the top. Allow the bromine to flow into the flask slowly, *drop by drop.* When all the bromine has been added, support the flask on a wire gauze, connect it with a condenser and distil. Collect the part which boils at 124°-126°. The yield is about 95 per cent of the theoretical.

PREPARATION OF HYDRIODIC ACID

The constant-boiling aqueous solution of hydriodic acid can be conveniently used for the preparation of alkyl iodides. The solution contains about 57 per cent of hydriodic acid, boils at 127°, and has the specific gravity of 1.68 to 1.70. The exact composition varies with the pressure at which the acid is distilled. The solution is prepared as follows: In a 100 cc. distilling flask place 65 cc. of water and 70 grams of iodine. Put the flask in a water-bath containing cold water, and force it down so that the whole bulb of the flask is submerged. Hold the flask in place by means of a clamp and ring-stand. Add 6.5 grams of red phosphorus. Let the flask stand for about 5 minutes. Support it on a wire gauze, connect with a condenser and distil. Collect what boils at 126°-127°. The yield is about 95 per cent of the theoretical.

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