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Research Article

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## Green Synthesis of Fulgenic Acids from Stobbe Condensation Method

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### ABSTRACT

One pot synthesis of acid esters by Stobbe condensation of alkylidene / arylidene succinates and aldehydes or ketones, their subsequent hydrolysis to diacids were reported. The Stobbe condensation of various aromatic aldehydes or ketones with dimethyl succinate gives different types of diacids [2a, (Z)-2-benzylidene-3-(diphenylmethylene) succinic acid], [2b, (Z)-2-(diphenylmethylene)-3-(1-phenylethylidene) succinic acid], [2c, (E)-2-((4-chlorophenyl)(phenyl)methylene)-3-(diphenylmethylene) succinic acid], [2d, (2E,3Z)-2-benzylidene-3-(furan-2-ylmethylene) succinic acid] through green approach. The improved yields of Fulgenic acid were observed by the green approach method as compared with other classical methods employed so far.

**Keywords:** Green synthesis, Stobbe condensation, aryl aldehydes & ketones and their products.

### ARTICLE INFO

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### 1. Introduction

The earlier classical method [1, 2] involved use of hazardous solvents like benzene, ether etc for the formation

of Fulgenic acid and their anhydride forms. Also classical method consumed more time for the formation of required

products. The present work describes ecofriendly one pot synthesis method for Stobbe condensation in which solvent free condition improves the yield. As compared to classical condensation methods reported previously [3], in which extensive use of solvents and hazardous chemicals were involved; green method requires fewer amounts of dry solid reagents, for the formation of acid esters [4]. Moreover, heat energy consumption by the reaction is also averted.

Stobbe condensation under solvent free condition using solid potassium tertiary butoxide was done with dimethyl succinate and aromatic, aliphatic aldehyde and ketone which leads to the formation of the acid- esters, which on saponification yielded the corresponding diacids[5]. Organic photochromic compounds such as Fulgenic acids are potential candidates for application in erasable optical [6] information media. This green approach not only increases the product's yield, but also maintains & raises its photochromic strength. Fulgenic acids (cyclized forms) are the promising materials in optical memory devices, optical switches and sensors, especially dyes and inks. These are representative class of photochromic organic [7, 8, 9] molecules which exhibits several interesting properties for diverse applications in fields such as data storage or high resolution spectroscopy. The cyclized products of Fulgenic acid prepared by using different reagents [10, 11, 12] can be used in the preparation of photosensitive glasses, photosensitive toys, Optical data recording [13] device like CD, photosensitive dyes and inks for security purpose, Variable density filters. These Optical data recording devices should be capable of ultrafast parallel access of stored information, good thermal stability and good fatigue resistance with proficient in non-destructible read-out [14, 15].

## 2. Materials and Methods

### 2.1 Reagents

Diethyl succinate, Potassium tertiary butoxide, p-chloro benzophenone, Benzaldehyde, anhydrous methanol, ethylene dichloride, conc. H<sub>2</sub>SO<sub>4</sub>, 8% alcoholic KOH, Acetophenone, Furfural were used as raw materials. Benzene, Petroleum ether, n-Hexane were used for double solvent recrystallisation of the obtained product. All the above solvents were purified by the reported procedures [16].

### 2.2 Instrumentation:

The Infrared spectra were obtained on a Bruker AVANCE 520 Fourier transform Infrared spectrometer using KBr pellets from SAIF Punjab University Chandigarh, India. High resolution <sup>1</sup>H-NMR spectra was recorded on a Bruker Avance II 400 MHz spectrometer in D<sub>2</sub>O with TMS as an internal standard. Melting points were measured on a digital Electrothermal 9100 Melting Point Apparatus and reported without correction. UV and Visible spectra were measured for a 10<sup>-4</sup> M in Toluene solution. The pH-metric titrations were conducted in aq. Ethanol (50:50, v/v) on an automatic recording ECIL pH-meter (Model pH 821) having a glass-calomel electrode assembly. Molecular weights of the acidic products were determined by titrimetric method as their equivalent weights. The general

procedure for Stobbe condensation and saponification of Stobbe condensation products were similar to those described earlier. These general procedures for Stobbe condensation were modified by using green method [17, 18].

### 2.3 General experimental procedure (Material synthesis)

A mixture of dimethyl succinate (9.0 g, 0.09 mole) and aldehydes or ketones were added dropwise to a suspension of Potassium tertiary butoxide (10.08 g, 0.09 mole). The reaction mixture was ground in mortar and pestle for 10 minutes and allowed to stand for another 20 minutes. Then 3N HCl was added in small amounts. Alcohol was distilled off under reduced pressure and reaction mixture was extracted with ether at room temperature. Acidic substances were separated by using 10% Na<sub>2</sub>CO<sub>3</sub>. On further acidification, finally it gives acid ester which was again recrystallized with n-Hexane /Benzene -pet. ether. Further on esterification, with anhydrous CH<sub>3</sub>OH, Ethylene dichloride and conc. H<sub>2</sub>SO<sub>4</sub> at room temperature it gives diester. Once again the diesters was mixed with aldehydes or ketones and Potassium tertiary butoxide, the same procedure was repeated and recrystallization was done with n-Hexane /Benzene -pet. ether which gives 2<sup>nd</sup> acid ester. Finally the obtained 2<sup>nd</sup> acid ester was saponified with alc. KOH at room temperature for 2 hours and followed by acidification and recrystallization which would give a solid crystalline natured diacids (**2a, 2b, 2c, 2d**).

### 2.4 Spectroscopic data of Fulgenic acids

#### 2.4. a [**2a, (Z)-2-benzylidene-3-(diphenylmethylene) succinic acid**]

**Bluish Red colored crystalline solid nature diacid** (by using benzaldehyde (9.5508 g, 0.09 mol) and benzophenone (16.3998 g, 0.09 mole)

<sup>1</sup>H NMR, δ; 7.40, 7.40, 7.40, 7.40 (s, 4H, -CH), δ; 7.39, 7.384, 7.39, 7.40 (s, 4H, -CH), δ; 11.00 (s, 2H, 2-COOH), δ; 7.598, 7.60, (s, 2H, -CH) 7.32, 7.32, 7.31 (s, 3H, -CH)

(FTIR; cm<sup>-1</sup>) C=O (1721 cm<sup>-1</sup>), -OH (2862 cm<sup>-1</sup>), -CH (3238 cm<sup>-1</sup>), C=C (1586 cm<sup>-1</sup>); for **melting point & UV - VIS**. Spectroscopic data, refer **table 1 & table 2**

#### 2.4. b [**2b, (Z)-2-(diphenylmethylene)-3-(1-phenyl ethylidene) succinic acid**]

**Bluish green colored crystalline solid nature diacid** [by using acetophenone (10.813 g, 0.09 mol) & benzophenone (16.3998 g, 0.09 moles)]

<sup>1</sup>H NMR, δ; 7.39, 7.38, 7.384, 7.40 (s, 3H, -CH); δ 7.40, 7.40, 7.40 (s, 3H, -CH), 11.00 (s, 2H, 2-COOH); δ 7.140, 7.138 (s, 2H, -CH); δ 2.241 (s, -CH<sub>3</sub>); δ 6.83, 6.826 (s, 2H, -CH);

(FTIR; cm<sup>-1</sup>) C=O (1728 cm<sup>-1</sup>), -OH (2674 cm<sup>-1</sup>), -CH (3323 cm<sup>-1</sup>), C=C (1628 cm<sup>-1</sup>); for **melting point & UV - VIS**. Spectroscopic data, refer **table 1 & table 2**

#### 2.4. c [**2c, (E)-2-((4-chlorophenyl)(phenyl)methylene)-3-(diphenylmethylene) succinic acid**]

**Pale yellow colored crystalline solid nature diacid** [by using p-chloro benzophenone (19.4994 g, 0.09 moles) and benzophenone (16.3998 g, 0.09 moles)]

<sup>1</sup>H NMR, δ; 7.405, 7.403, 7.39, 7.401, 7.436, 7.418 (s, 6H, CH); δ 7.320, 7.321, 7.33, 7.31, 7.32, 7.30 (s, 6H, -CH); δ 11.05, 11.02 (s, 2H 2-COOH); δ 7.379, 7.378, 7.377, 7.376, 7.368, 7.401, 7.412 (s, 7H, -CH);

(FTIR;  $\text{cm}^{-1}$ ) C=O ( $1876\text{cm}^{-1}$ ), -OH ( $2991\text{cm}^{-1}$ ), -CH ( $3212\text{cm}^{-1}$ ), C=C ( $1346\text{cm}^{-1}$ ), aromatic aldehyde ( $1744$ ), aromatic -CH ( $2962\text{cm}^{-1}$ ), C-Cl ( $758\text{cm}^{-1}$ ); for melting point & UV -VIS. Spectroscopic data, refer table 1 & table 2.

#### 2.4. d [2d, (2E,3Z)-2-benzylidene-3-(furan-2-yl methylene) succinic acid]

Orange colored crystalline solid nature diacid [by using Furfural (8.64 g, 0.09mol) and Benz aldehyde (9.5508 g, 0.09mol)]

$^1\text{H NMR}$ ,  $\delta$ ; 8.17, 8.42, 6.87 (s, 3H, Furan);  $\delta$ ; 7.60, 7.60 (s, 2H,  $\text{C}_6\text{H}_6$ );  $\delta$ ; 11.00 (s, 2H, 2-COOH);  $\delta$ ; 7.40, 7.40, 7.33 (s, 3H,  $\text{C}_6\text{H}_6$ );  $\delta$ ; 6.07, 7.81 (s, 2H, ethylene)

(FTIR;  $\text{cm}^{-1}$ ) C=O ( $1862\text{cm}^{-1}$ ), -OH ( $2897\text{cm}^{-1}$ ), -CH ( $3226\text{cm}^{-1}$ ), C=C ( $1356\text{cm}^{-1}$ ), aromatic aldehyde ( $1745$ ), aromatic -CH ( $2975\text{cm}^{-1}$ ); for melting point & UV -VIS. Spectroscopic data, refer table 1 & table 2

### 3. Results and Discussion

Stobbe condensation generally involves the use of metal alkoxide [19] as a catalyst in refluxing alcohol, particularly, butanol. On the other hand, the use of butanol is discarded and instead of that, dry solid potassium tertiary butoxide was taken for the reaction. The advantages are short reaction time, good yield, less by-products. Stobbe condensation via green approach generally involves the use of metal alkoxide as a catalyst in refluxing alcohol, and environment- friendly reaction conditions. In this research article, Fulgenic acids were prepared via Stobbe condensation using potassium tertiary butoxide through green context.

The Fulgenic acids (2a, 2b, 2c, 2d) were having much purity as compared with classically prepared one. They were having sharp melting and boiling point, also having sharp NMR peak values. In previous methods [20], tremendous heat was used, due to which obtained diacids bear impurity with less percentage yield. The UV graphs show sharp and similar peaks, which also proved the purity of diacids. The diacid (2a) exhibited a molecular formula  $\text{C}_{24}\text{H}_{18}\text{O}_4$  showed characteristic stretching frequencies of C=O ( $1721\text{cm}^{-1}$ ), -OH ( $2862\text{cm}^{-1}$ ), -CH ( $3238\text{cm}^{-1}$ ), C=C ( $1586\text{cm}^{-1}$ ). The presence of two carboxyl groups was further supported by  $^1\text{H NMR}$  spectrum which showed two signals on  $\delta$ ; 11.00 (s, 2H, 2-COOH) (fig. 1).

Similarly,  $^1\text{H NMR}$  spectrum also showed four -CH group on  $\delta$ ; 7.40 and other aromatic hydrogen's are on  $\delta$ ; 7.39, 7.384, 7.39, 7.40 (s, 4H, -CH),  $\delta$ ; 7.598, 7.60, (s, 2H, -CH) 7.32, 7.32, 7.31 (s, 3H, -CH). The diacid (2b) having molecular formula  $\text{C}_{25}\text{H}_{20}\text{O}_4$  also showed characteristic stretching frequencies of C=O ( $1728\text{cm}^{-1}$ ), -OH ( $2674\text{cm}^{-1}$ ), -CH ( $3323\text{cm}^{-1}$ ), C=C ( $1628\text{cm}^{-1}$ ). The presence of two carboxyl groups were further supported by  $^1\text{H NMR}$  spectrum which showed two signals on  $\delta$ ; 11.00 (s, 2H, 2-COOH). Similarly,  $^1\text{H NMR}$  spectrum also showed  $\delta$ ; 7.39, 7.38, 7.384, 7.40 (s, 3H, -CH);  $\delta$  7.40, 7.40, 7.40 (s, 3H, -CH);  $\delta$  7.140, 7.138 (s, 2H, -CH);  $\delta$  2.241 (s, -CH<sub>3</sub>);  $\delta$  6.83, 6.826 (s, 2H, -CH) and other aromatic hydrogen on the corresponding peak values (fig. 2). The obtained peak values were too much sharp & accurate for their corresponding

groups which proved the dominancy of green approach on classical method. Likewise the diacid (2c) having molecular formula  $\text{C}_{30}\text{H}_{21}\text{ClO}_4$  also showed characteristic stretching frequencies C=O ( $1876\text{cm}^{-1}$ ), -OH ( $2991\text{cm}^{-1}$ ), -CH ( $3212\text{cm}^{-1}$ ), C=C ( $1346\text{cm}^{-1}$ ), aromatic aldehyde ( $1744$ ), aromatic -CH ( $2962\text{cm}^{-1}$ ), C-Cl ( $758\text{cm}^{-1}$ ).

The presence of two carboxyl groups were supported by  $^1\text{H NMR}$  spectrum which showed two signals on  $\delta$ ; 11.03, 11.05 (s, 2H, 2-COOH).  $^1\text{H NMR}$  spectrum also showed the required peak values  $\delta$ ; 7.405, 7.403, 7.39, 7.401, 7.436, 7.418 (s, 6H, -CH);  $\delta$  7.320, 7.321, 7.33, 7.31, 7.32, 7.30 (s, 6H, -CH);  $\delta$  7.379, 7.378, 7.377, 7.376, 7.368, 7.401, 7.412 (s, 7H, -CH) (fig. 3).

Similarly, the diacid (2d) having molecular formula  $\text{C}_{16}\text{H}_{12}\text{O}_5$  also showed characteristic stretching frequencies C=O ( $1862\text{cm}^{-1}$ ), -OH ( $2897\text{cm}^{-1}$ ), -CH ( $3226\text{cm}^{-1}$ ), C=C ( $1356\text{cm}^{-1}$ ), aromatic aldehyde ( $1745$ ), aromatic -CH ( $2975\text{cm}^{-1}$ ). The presence of two carboxyl groups were further supported by  $^1\text{H NMR}$  spectrum which showed two signals on  $\delta$ ; 11.00 (s, 2H, 2-COOH). Similarly,  $^1\text{H NMR}$  spectrum also showed  $\delta$ ; 8.17, 8.42, 6.87 (s, 3H, Furan);  $\delta$ ; 7.60, 7.60 (s, 2H,  $\text{C}_6\text{H}_6$ );  $\delta$ ; 7.40, 7.40, 7.33 (s, 3H,  $\text{C}_6\text{H}_6$ );  $\delta$ ; 6.07, 7.81 (s, 2H, ethylene) (fig. 4).

#### 3.1 Structural determination:

The Fulgenic acids which were prepared through green method were obtained in better yields as compared to the classical method. Their structural determination were done by using NMR-IR -UV- VIS. Spectral values.

##### 3.1. a Proton NMR Spectra:

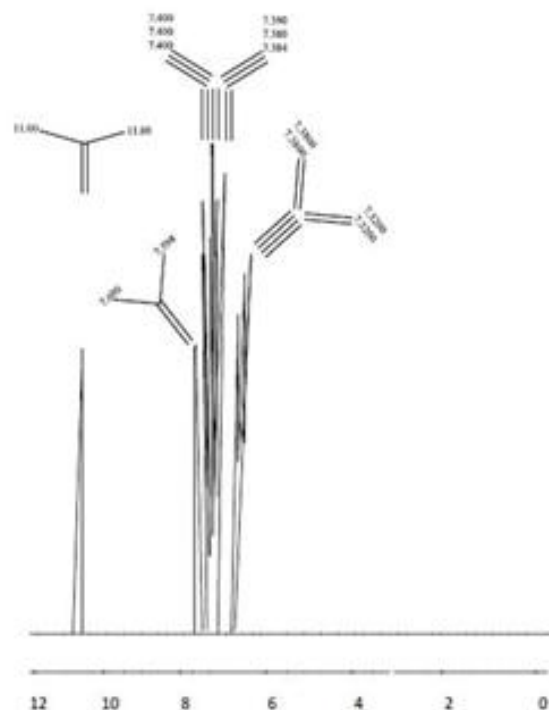
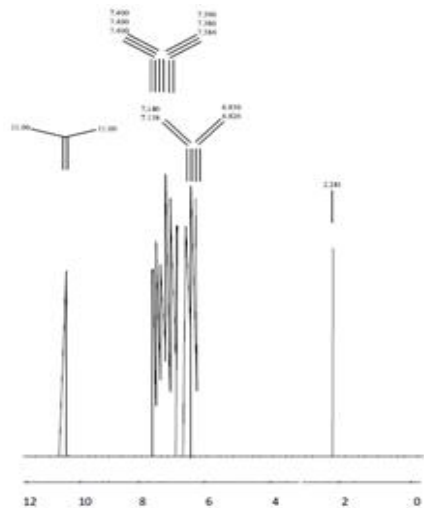
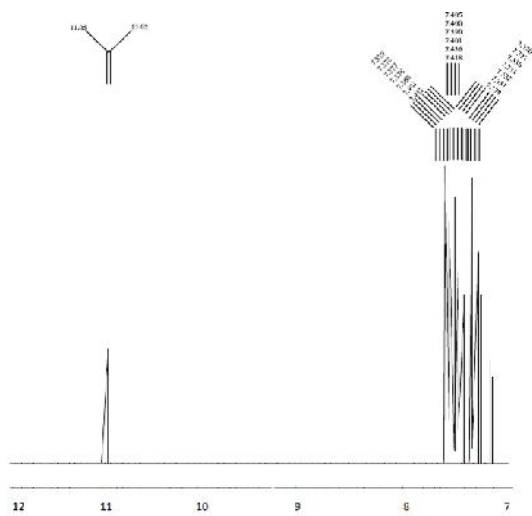


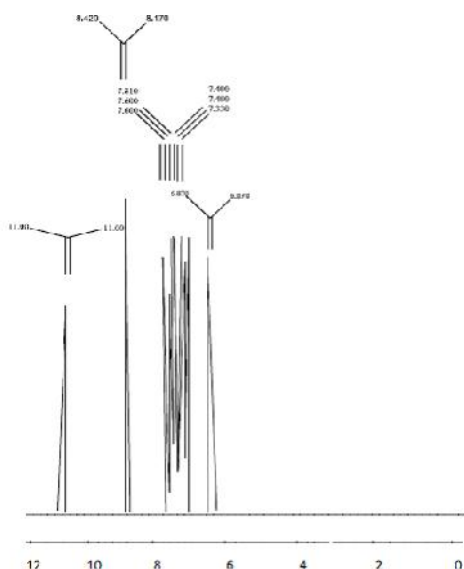
Figure 1: Proton NMR Spectra of di acid (2a) i.e. [2a, (Z)2-benzylidene-3-(diphenylmethylene) succinic acid]



**Figure 2:** Proton NMR Spectra of diacid (2b) i.e.[2b, (Z)-2-(diphenylmethylene)-3-(1-phenylethylidene) succinic acid]

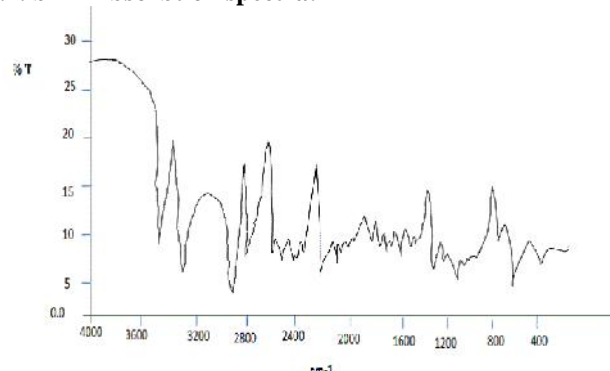


**Figure 3:** Proton NMR Spectra of diacid (2c) i.e [2c,(E)-2-((4-chlorophenyl)(phenyl)methylene)-3-(diphenylmethylene)succinic acid]

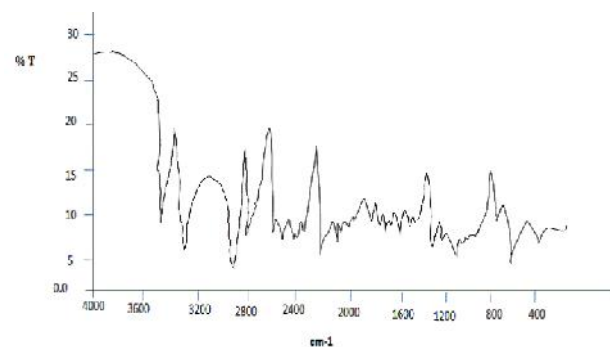


**Figure 4:** Proton NMR Spectra of diacid (2d) i.e [2d, (2E, 3Z) -2-benzylidene-3- (furan-2-ylmethylene) succinic acid]

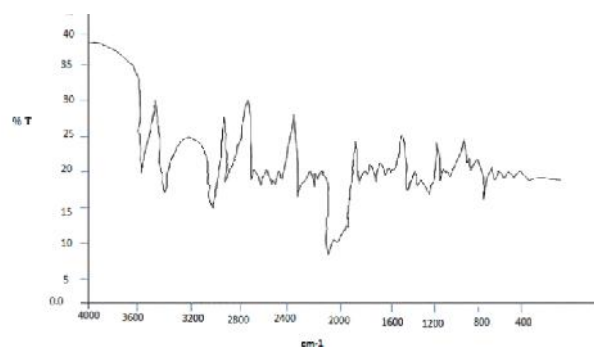
**2.1. b IR Absorbion spectra:**



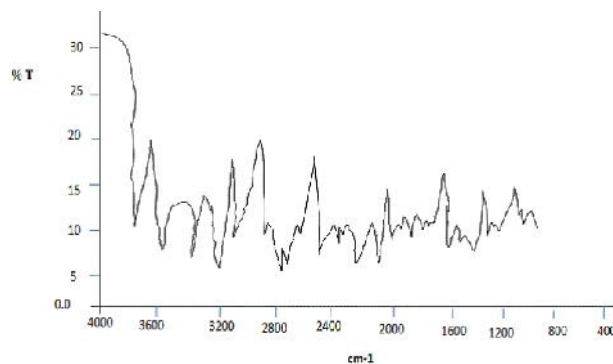
**Figure 5:** IR Absorbion spectra of diacid (2a) i.e. [2a, (2Z, 3Z)-2-3-bis(4-chlorophenyl)( phenyl) (methylene) succinic acid]



**Figure 6:** IR Absorbion spectra of diacid (2b)i.e.[2b, (2Z, 3Z) -2-(4-chlorophenyl) (phenyl)(methylene)-3-(1-phenyl ethylidene) succinic acid]



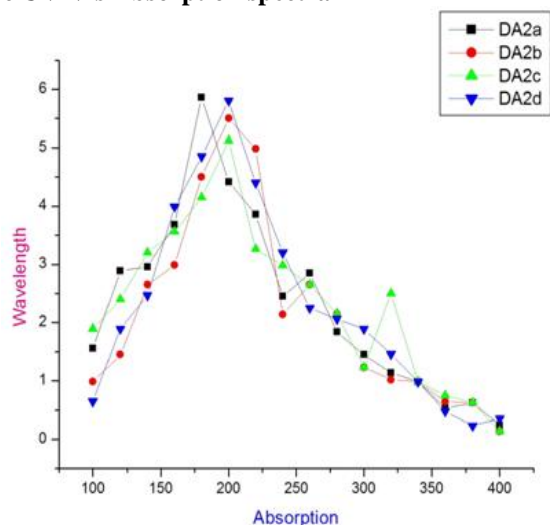
**Figure7:** IR Absorbion spectra of diacid (2c) i.e.[2c, (2Z, 3E)-2-3-bis (furan-2-ylmethylene) succinic acid]



**Figure 8:** IR Absorbion spectra of diacid (2d) i.e [2d , (2E,3Z)-2-benzylidene-3- (furan-2-ylmethylene) succinic acid]



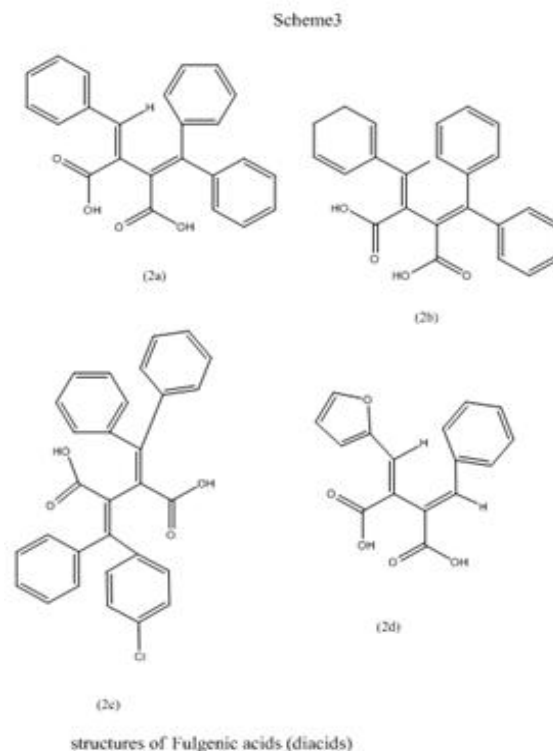
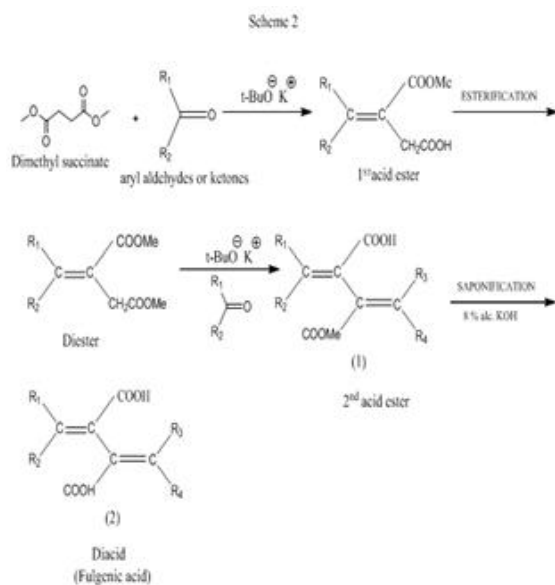
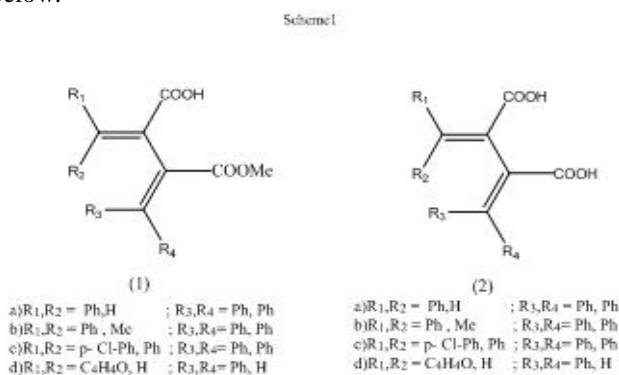
### 3.1. c UV-Vis Absorption spectra



**Figure 9:** UV-Vis Absorption spectra of diacids (2a, 2b, 2c, 2d)

### 3.2 Reaction Schemes of Experimental Work

The Fulgenic acids (diacids) **2a**, **2b**, **2c** and **2d** were prepared by using following schemes: The synthesis of different substituted fulgenic acids were possible by step wise Stobbe condensation (twice) with different aldehydes and ketones through green approach which are given as below.



## 4. Conclusion

It was concluded that, the solvent free Stobbe condensation of aromatic aldehydes and aliphatic, aromatic ketones with dimethyl succinate at room temperature occurred smoothly to give substituted acid esters which on further saponification gives diacid. The greener chemical reaction strategy managed to synthesize Fulgenic acid (**2a**, **2b**, **2c**, **2d**) successfully by simple and efficient means with improved yield. This methodology [21, 22] brought down not only the reaction time but also the uses of hazardous organic solvents (as possible). The prepared Fulgenic acid after cyclisation can also be used in the preparation of photosensitive glasses, photosensitive toys and other instruments, Optical data recording like CD, Preparation of photosensitive inks for security purpose, Variable density filters.

## 5. Acknowledgement

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## 6. References

1. S.Banerjee, S.Jabbar, Synthesis of Anhydrides from Stobbe Condensation Products. *Asian Journal of Chemistry*. **2002**, 14(3-4): 1655-1659
2. S.Banerjee, S.Jabbar, Stereochemistry in the Stobbe Condensation. *Asian Journal of Chemistry*. **2002**, 14(3-4): 1651-1654.
3. S.Banerjee, S.Jabbar, Aromatization of Stobbe Reaction Products. *Asian Journal of Chemistry*. **2002**, 14(3-4): 1799-1800.

4. S. Banerjee; R. A. Tayade; B. D.Sharma.Green Synthesis of Acid Esters from Furfural via Stobbe Condensation, *Journal of Chemistry*, **2013**.
5. M.A. Wolak, N.B. Gillespie, C.J. Thomas, R.R. Birge, W.J. Lees.Optical properties of Photochromic fluorinated indolylfulgides, *Journal of Photochemistry and Photobiology A: Chemistry*. **2001**, 144(2): 83-91
6. M. Asiri. A convenient method for conversion of the Z- isomer to the E- isomer from a Mixture containing both isomers of Fulgides,Tetrahedron Letters. **2002**, 43: 6815–6817
7. S.S Deshmukh, S.Banerjee. Photochromism in Fulgides and Anhydrides, *Asian Journal of Chemistry*. **2001**, 13(2): 481-484
8. S. Jabbar, S.Banerjee.Synthesis of Fulgides and Anhydrides from Stobbe condensation Products, *Oriental Journal of Chemistry*. **2003**, 19(1): 229-232
9. .S. Jabbar, S.Banerjee.Cyclisation reaction of Stobbe condensation reaction, *Ultra Science*, 2002, Vol. 14, No. 3, 527-534
10. C.J. Thomas, M.A. Wolak, R.R. Birge, W.J. Lees.Improved synthesis of indolyl fulgides. *The Journal of organic chemistry* 2001, 66 (5), 1914-1918
11. M.A. Wolak, N.B. Gillespie, C.J. Thomas, R.R. Birge, W.J. Lees. Optical and thermal Properties of photochromic fluorinated adamantylidene indolylfulgides. *Journal of Photochemistry and Photobiology A: Chemistry*. **2002**, 147(1): 39-44.
12. M.A. Wolak, J.M. Sullivan, C.J. Thomas, R.C. Finn, R.R. Birge, W.J. Lees. Thermolysis of a fluorinated indolylfulgide features a novel 1, 5-indolyl shift. *The Journal of organic chemistry*. **2001**. 66 (13): 4739-4741.
13. M.A. Wolak, N.B. Gillespie, R.R. Birge, W.J. Lees.Thermolysis of fluorinated cycloalkylidene fulgides yields a new class of photochromic compounds. *Chemical Communications*. **2003**. 992-993
14. M. A. Wolak, R. C. Finn, R. S. Rarig Jr, C. J. Thomas, R. P. Hammond, R. R. Birge, J. Zubieta and W. J. Lees. Structural properties of a series of photochromic fluorinated Indolylfulgides, *Crystal Structure Communications*. July **2002**, 58(7): 389-393
15. M. A. Wolak , C. J. Thomas , N. B. Gillespie , R. R. Birge ,and W. J. Lees. Tuning the Optical Properties of Fluorinated Indolyl fulgimides, *J. Org. Chem.* **2003**, 68(2): 319–326
16. S.C. Murugavel, C.S. Swaminathan, P. Kannan. Synthesis and characterization of photo-crosslinkable poly (benzylidene phosphoramidate)s, *Polymer* , **1997**, 38(20): 5179–5183
17. V.R. Kamalraj, S. Senthil, P. Kannan. One -pot synthesis and the fluorescent behavior of 4-Acetyl-5-methyl-1, 2, 3-triazole regioisomers, *Journal of Molecular Structure*, **2008**, 892(1–3): 210–215.
18. J.Donnely, C.R Müller,L, Wiermans, C. J. Chuck, P. D.María. Upgrading biogenic Furans: blended C<sub>10</sub> C<sub>12</sub> platform chemicals *via* lyase-catalyzed carboligations and formation of novel C<sub>12</sub>– choline chloride-based deep-eutectic-solvents, *Green Chem.*, **2015**.
19. S. Nityanandan. C. Saravanan, S.Senthil; P. Kannan, Microwave assisted synthesis of Phctchromic Fulgides, *J. Chem. Sci.*, March **2010**, 122(2):183-188
20. S.Jabbar, studies in the synthesis and structure of Indenones, Ph.D. Thesis, Nagpur University, (Nagpur, India, **1994**)
21. P. J. A. Withers; J.J.Elser; J.Hilton; H.Ohtake; W. J.Schipper; K.C.van Dijk, Greening the global phosphorus cycle: how green chemistry can help achieve planetary P sustainability *Green Chem.*, **2015**, 17, 2087-2099
22. W. Wardencki; J.Curylo;J. Namiesnik, *Green Chemistry Current and Future Issues Polish Journal of Environmental Studies*, **2005**, 14(4): 389-395