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Research Article

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## One Potsynthesis of Itaconic Acids from Stobbe Condensation Method

Yadav Hanuman Singh\*<sup>1</sup>, Gadegone Sunita<sup>2</sup> and Pande Hemant<sup>3</sup>

<sup>1,3</sup>Dr. Ira Nimdeokar Research Center for Chemistry, Hislop College, Nagpur 440001, India

<sup>2</sup>Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur 440009, India

### 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, (E)-2-(Butan-2-ylidene) succinic acid], [2b, (Z)-2-Ethylidene succinic acid], [2c, 2-Methylene succinic acid], [2d, (Z)-2-Hexylidene succinic acid], [2e, (Z)-2-(Hexan-3-ylidene) succinic acid] through green approach. The improved yields of Itaconic 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, Itaconic acid and their products.

### ARTICLE INFO

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#### \*Corresponding Author

Yadav Hanuman Singh  
Dr. Ira Nimdeokar Research  
Center for Chemistry, Hislop  
College, Nagpur 440001, India  
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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 Itaconic acid and their anhydride forms. Also classical method consumed more time for the formation of required products. The present work describes eco-friendly one pot International Journal of Chemistry and Pharmaceutical Sciences

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 Itaconic 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. Itaconic 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 Itaconic 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. Experimental

**Reagents:** Diethyl succinate, Potassium tertiary butoxide, p-chlorobenzophenone, anhydrous methanol, ethylene dichloride, 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 [20].

### 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 [21, 22].

### General experimental procedure (Material synthesis)

A mixture of dimethyl succinate (9.0 g, 0.09 mole) and aldehydes or ketones were added drop-wise 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 anhyd. 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 diester 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 as olidcrystalline natured diacids (**2a, 2b, 2c,2d,2e**).

### Spectroscopic data of Itaconic acids

#### a[**2a, (E)-2-(Butan-2-ylidene) succinic acid**]

Brown colored crystalline solid nature diacid (by using ketone i.e. Benzaldehyde(9.54 g, 0.09 mole)

<sup>1</sup>H NMR,  $\delta$ ;  $\delta$  ;3.51,2.00(s, 2H,-CH),  $\delta$ ; 1.820, 1.060, 1.089, 0.998(s,4H,-CH); 11.00(s, 2H, 2-COOH), (FTIR;cm<sup>-1</sup>)C=O (1742cm<sup>-1</sup>), -OH (2864cm<sup>-1</sup>), -CH (3248cm<sup>-1</sup>), C=C (1586cm<sup>-1</sup>) & aromatic chloride (1206cm<sup>-1</sup>); for melting point & UV-VIS. Spectroscopic data, refer table 1 & 2.

#### b [**2b,(Z)-2-Ethylidene succinic acid**]

Bluish yellow colored crystalline solid nature diacid

[by using ketone i.e. acetophenone (10.813g,0.09 mol)] <sup>1</sup>H NMR,  $\delta$ ;6.300(s,1H, -CH); $\delta$ 3.561,2.00(s,2H, -CH), 11.00 (s,2H,2-COOH); (FTIR;cm<sup>-1</sup>) C=O (1735cm<sup>-1</sup>), -OH (2625cm<sup>-1</sup>), -CH (3328cm<sup>-1</sup>), C=C (1608cm<sup>-1</sup>);for melting point & UV-VIS. Spectroscopic data, refer table 1 & table 2

#### c [**2c, 2-Methylene succinic acid**]

Pale yellow colored crystalline solid nature diacid[by using ketone i.e. acetone(5.22 g, 0.09mol)] <sup>1</sup>H NMR,  $\delta$ ;6.76, 3.561,6.080(s,3H,-CH);  $\delta$ 11.00(s,2H 2-COOH) ; (FTIR; cm<sup>-1</sup>) C=O (1842cm<sup>-1</sup>), -OH (2984 cm<sup>-1</sup>), -CH (3242 cm<sup>-1</sup>), C=C (1306 cm<sup>-1</sup>), aromatic aldehyde (1740), aromatic -CH (2972 cm<sup>-1</sup>);for melting point & UV-VIS. Spectroscopic data, refer table 1 & table 2

#### d[**2d ,(Z) 2-Hexyldene succinic acid**]

Reddish yellow colored crystalline solid nature diacid[by

using ketone i.e. Benzophenone (16.38 g, 0.09mol)] <sup>1</sup>H NMR,  $\delta$ ; ,6.334,3.561,2.182,1.29,1.2847,1.266 (s,6H,-CH);  $\delta$ 11.00(s,2H 2-COOH);; (FTIR;cm<sup>-1</sup>)C=O (1842cm<sup>-1</sup>), -OH (2981cm<sup>-1</sup>), -CH (3258cm<sup>-1</sup>), C=C (13415cm<sup>-1</sup>), aromatic aldehyde (1740), aromatic -CH (2952cm<sup>-1</sup>); for melting point & UV-VIS. Spectroscopic data, refer table 1 & 2.

#### e[**2e ,(Z)-2-(Hexan-3-ylidene ) succinic acid**]

Pale yellow colored crystalline solid nature diacid[by using

aldehyde i.e. Furfural (8.64 g, 0.09mol)]. <sup>1</sup>H NMR,  $\delta$ ; 7.41, 7.411, 7.40, 7.38, 7.330, 7.382 (6H,-CH);  $\delta$ 11.00(s,2H 2-COOH);  $\delta$ 6.85(s,2H,-CH);  $\delta$ 6.66(s,1H)  $\delta$ 6.07(s,1H) ; (FTIR;cm<sup>-1</sup>)C=O (1887cm<sup>-1</sup>), -OH (2945cm<sup>-1</sup>), -CH (3642cm<sup>-1</sup>), C=C (1346cm<sup>-1</sup>), aromatic aldehyde (1740), aromatic -CH (2972cm<sup>-1</sup>); 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 [16] 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, Itaconic acids were prepared via Stobbe condensation using potassium tertiarybutoxide through green context.

**Table 1:** Improved yield of Fulgenic acid in green reaction method

Compounds	Yields (%)		m.p. ( $^{\circ}$ C)	Mol.wt.
	Classical	Green		
2a	61.45	89.85	222	172.18
2b	64.58	94.24	287	144.13
2c	75	96.78	298	130.10
2d	60.18	90.64	245	200.23
2e	62.08	85.84	286	200.23

**Table 2:** UV –Visible maximum absorption of different groups in Fulgenic acid

Compounds	$\lambda_{max}$ (nm)	
	-COOH	C=O
2a	206(1.51)	241(3.42)
2b	204(1.75)	244(4.60)
2c	207(1.44)	242(5.12)
2d	208(1.25)	249(4.72)
2e	203(1.48)	241(4.18)

The Itaconic acids (2a, 2b, 2c, 2d, 2e) 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 [17], 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  $C_8H_{12}O_4$  showed characteristic stretching frequencies of C=O ( $1742\text{ cm}^{-1}$ ), -OH ( $2817\text{ cm}^{-1}$ ), -CH ( $3448\text{ cm}^{-1}$ ), C=C ( $1546\text{ cm}^{-1}$ ). 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 one -CH<sub>2</sub> group on  $\delta$ ; 3.561(s), and other aromatic hydrogens on  $\delta$ ; 2.00, 1.060(s, 4H, -CH<sub>3</sub>).

The diacid (2b) having molecular formula  $C_6H_8O_4$  also showed characteristic stretching frequencies of C=O ( $1764\text{ cm}^{-1}$ ), -OH ( $2648\text{ cm}^{-1}$ ), -CH ( $3317\text{ cm}^{-1}$ ), C=C ( $1686\text{ cm}^{-1}$ ). 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 one -CH<sub>3</sub> groups on  $\delta$ ; 2.050, and other aromatic hydrogens on the corresponding peak values  $\delta$ ; 3.00(ethylene), 3.561(CH<sub>3</sub>)(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.

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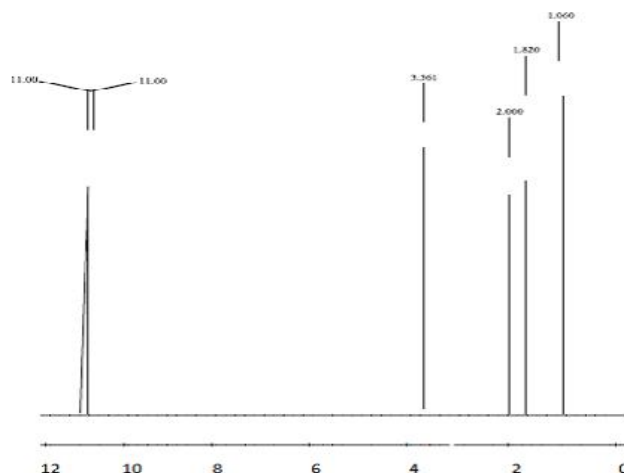
Likewise the diacid (2c) having molecular formula  $C_5H_6O_4$  also showed characteristic stretching frequencies C=O ( $1872\text{ cm}^{-1}$ ), -OH ( $2997\text{ cm}^{-1}$ ), -CH ( $3212\text{ cm}^{-1}$ ), C=C ( $1356\text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectrum also showed the required peak values for two carboxylic groups (fig. 3).

Similarly, the diacid (2d) having molecular formula  $C_{10}H_{16}O_4$  also showed characteristic stretching frequencies C=O ( $1862\text{ cm}^{-1}$ ), -OH ( $2947\text{ cm}^{-1}$ ), -CH ( $3245\text{ cm}^{-1}$ ), C=C ( $1386\text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectrum also showed the required peak values for two carboxylic groups  $\delta$ ; 11.00(s, 2H, 2-COOH) (fig. 4). Also the diacid (2e) having molecular formula  $C_{10}H_{16}O_4$  also showed characteristic stretching frequencies C=O ( $1882\text{ cm}^{-1}$ ), -OH ( $2977\text{ cm}^{-1}$ ), -CH ( $3242\text{ cm}^{-1}$ ), C=C ( $1356\text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectrum also showed the required peak values for two carboxylic groups  $\delta$ ; 11.00(s, 2H, 2-COOH) (fig. 5).

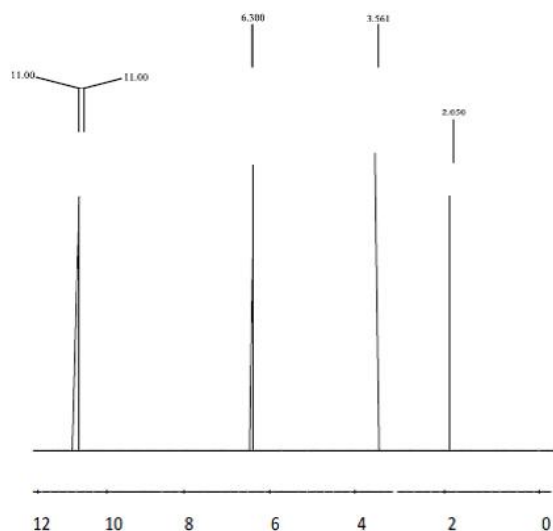
#### Structural determination:

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

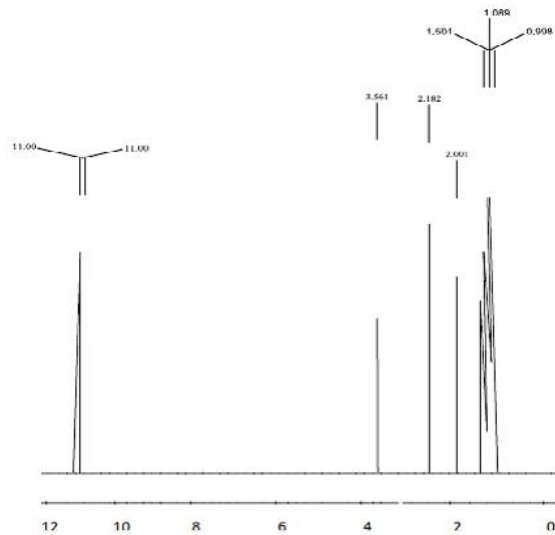
#### a Proton NMR Spectra



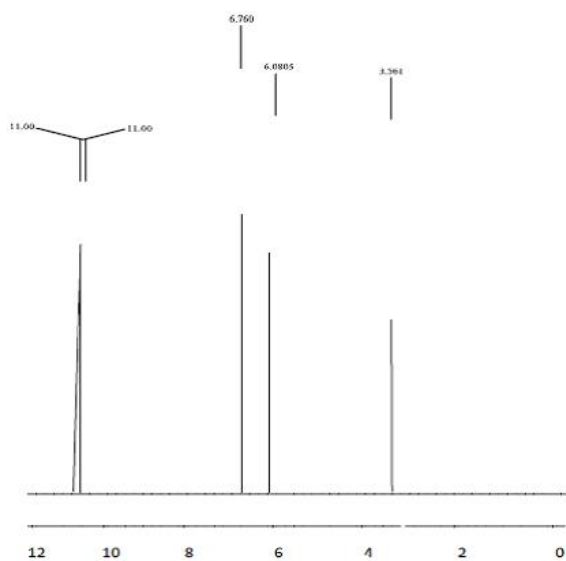
**Figure 1:** Proton NMR Spectra of diacid(2a) i.e. [2a, (E)-2-(Butan-2-ylidene) succinic acid]



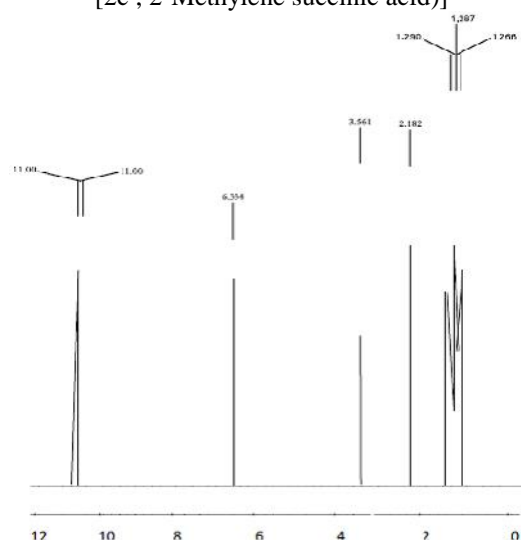
**Figure 2:** Proton NMR Spectra of diacid (2b) i.e. [2b,(Z)-2-Ethylidenene succinic acid]



**Figure 5:** Proton NMR Spectra of diacid (2e) i.e. [2e ,(Z)-2-(Hexan-3-ylidene ) succinic acid]

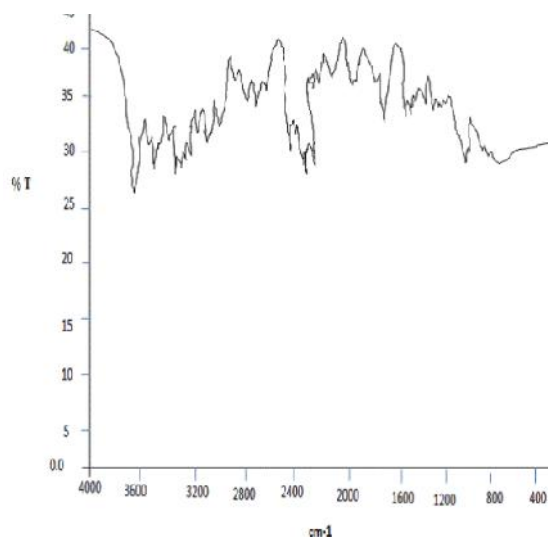


**Figure 3:** Proton NMR Spectra of diacid (2c) i.e. [2c , 2-Methylene succinic acid]

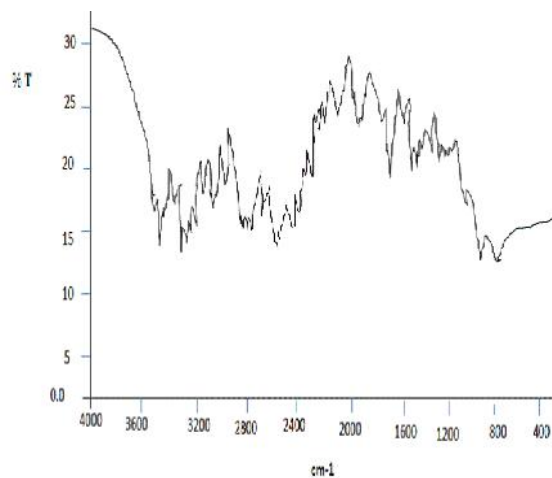


**Figure 4:** Proton NMR Spectra of diacid (2d) i.e. [2d ,(Z) 2-Hexyldene succinic acid]

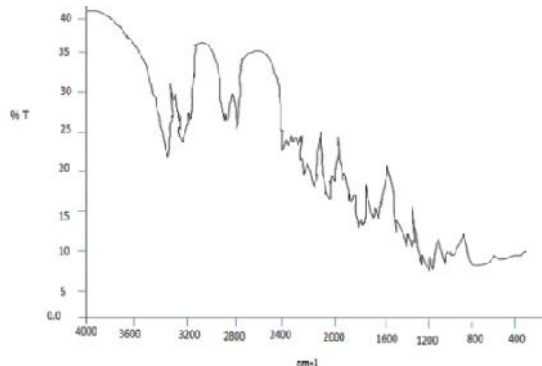
**b IR Absorbion spectra:**



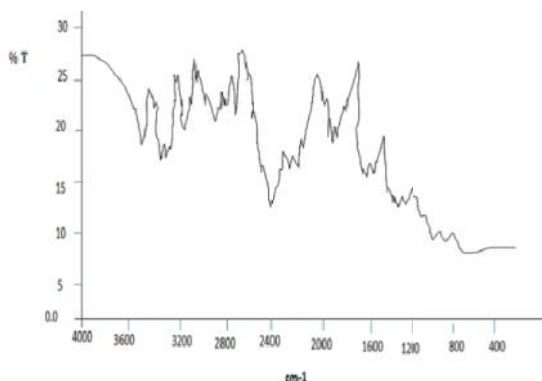
**Figure 6:** IR Absorbion spectra of diacid (2a)i.e. [2a, (E)-2-(Butan-2-ylidene) succinic acid]



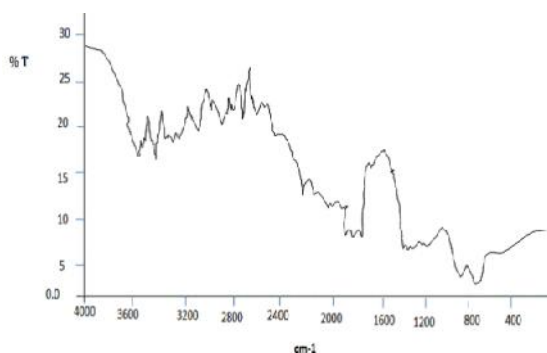
**Figure 7:** IR Absorbion spectra of diacid (2b)i.e. [2b, (Z)-2-Ethylidenene succinic acid]



**Figure 8:** IR Absorption spectra of diacid (2c) i.e. [2c, 2-Methylene succinic acid]

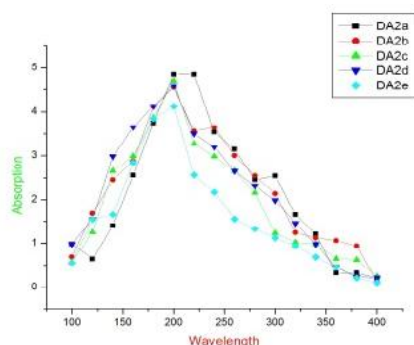


**Figure 9:** IR Absorption spectra of diacid (2d) i.e. [2d, (Z) 2-Hexyldene succinic acid]



**Figure 10:** IR Absorption spectra of diacid (2e) i.e. [2e, (Z)-2-(Hexan-3-ylidene) succinic acid]

### c. UV-Vis Absorption spectra

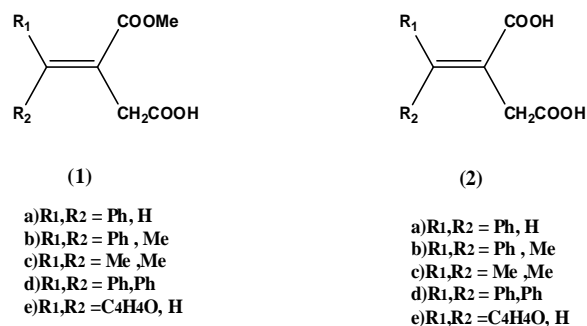


**Figure 11:** UV-Vis Absorption spectra of diacids (2a, 2b, 2c, 2d, 2e)

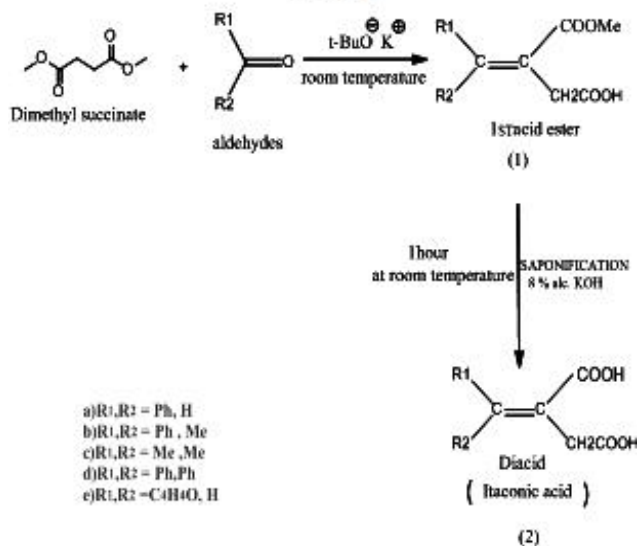
### Reaction Schemes of Experimental Work

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

Scheme1



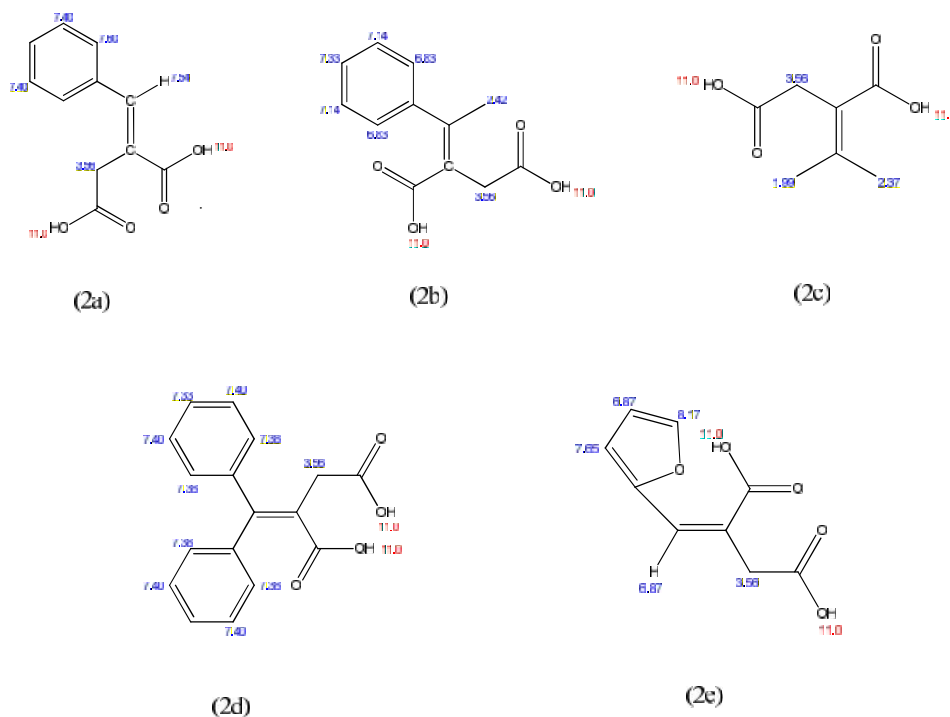
Scheme 2



### 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 Itaconic acid (2a, 2b, 2c, 2d, 2e) successfully by simple and efficient means with improved yield. This methodology [18, 19] brought down not only the reaction time but also the uses of hazardous organic solvents (as possible). The prepared Fulgenic acid after cyclization 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.

Scheme3



structures of Itaconic acids (diacids)

## 5. Acknowledgments

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