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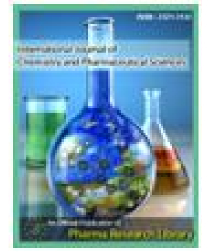

Research Article **Open Access**

One Pot Synthesis of Fulgenic Acids from Stobbe Condensation Method

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A B S T R A C T

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-(diphenylmethylene) -3-(furan-2-yl-methylene) succinicacid)],[2b, 2- (diphenylmethylene)-3-methylene succinic acid], [2c,(Z)- 2 -(furan-2-yl-methylene)-3-methylene succinic acid))], [2d,(2-methylene)-3-(propan-2-ylidene)succinicacid)]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.

A R T I C L E I N F O

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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. bThe present work describes eco-friendly 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 [7-9] 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 [10-12] 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, benzophenone, Formaldehyde, anhydrous methanol, ethylene dichloride, conc. H_2SO_4, 8% alcoholic KOH, Acetone, Furfural were used as raw materials. Benzene, Petroleum ether, n-Hexane were used for double solvent re-crystallization of the obtained product. All the above solvents were purified by the reported procedures [16].

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 ^{1}H-NMR spectra was recorded on a Bruker Avance II 400 MHz spectrometer in D_2O 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^{-4} 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].

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_2CO_3. On further acidification, finally, it gives acid ester which was again recrystallized with n-Hexane /Benzene -pet. ether. Further on esterification, with anhydrous CH_3OH, Ethylene dichloride and conc. H_2SO_4 at room temperature it gives diester .Once again the dieters 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 2nd acid ester. Finally, the obtained 2nd acid ester was saponified with alc. KOH at room temperature for 2 hours and followed by acidification and re-crystallization which would give a solid crystalline natured diacids (2a, 2b, 2c, 2d).

Spectroscopic data of Fulgenic acids

[2a, (Z)-2-(diphenylmethylene) -3-(furan-2-yl-methylene) succinicacid)]

Bluish purple colored crystalline solid nature diacid (by using benzophenone (16.3998 g, 0.09) mole and Formaldehyde (2.703g, 0.09 mol). ^{1}H NMR,$\boldsymbol{\delta}$;7.40, 7.40,7.40,7.40(s, 4H,-CH),δ ;7.39,7.384,7.39,7.40(s, 4H,-CH),$\boldsymbol{\delta}$;11.00(s, 2H,2-COOH),$\boldsymbol{\delta}$;7.598,7.60, (s, 2H,-CH)7.32,7.32,7.31(s, 3H,-CH) (FTIR; cm^{-1}) C =O (1726cm^{-1}),-OH (2861cm^{-1}), -CH (3258cm^{-1}), C=C (1586cm^{-1}); for melting point&UV –VIS. Spectroscopic data, refer table 1&table2.

[2b, 2- (diphenylmethylene)-3-methylene succinic acid]

Blackish green colored crystalline solid nature diacid [by using Furfural (8.64 g, 0.09 mol) & Formaldehyde (2.703 g, 0.09 mol)]

^{1}H NMR,$\boldsymbol{\delta}$; 7.39, 7.38, 7.384, 7.40(s,3H, -CH); $\boldsymbol{\delta}$ 7.40, 7.40, 7.40(s,3H, -CH),11.00(s,2H,2-COOH); $\boldsymbol{\delta}$7.140, 7.138 (s,2H,-CH); (FTIR;cm^{-1}) C=O (1727cm^{-1}),-OH (2687cm^{-1}),-CH (3304cm^{-1}), C=C (1648cm^{-1}); for melting point &UV – VIS. Spectroscopic data, refer table 1& table2.

[2c,(Z)-2-(furan-2-yl-methylene)-3-methylenesuccinicacid]

Pale green colored crystalline solid nature diacid [by using Acetone (5.228 g, 0.09 moles) and Formaldehyde (2.703 g, 0.09 mole)] ^{1}H NMR,$\boldsymbol{\delta}$; 8.42(s,2H,-CH); $\boldsymbol{\delta}$ 8.17(s,2H,-CH); $\boldsymbol{\delta}$11.00(s,2H 2-COOH); $\boldsymbol{\delta}$6.85(s,2H,-CH); $\boldsymbol{\delta}$6.66(s,1H) $\boldsymbol{\delta}$6.07(s,1H) ; 8.42, 8.17, 6.84, 6.07 (4H,-CH); (FTIR;cm^{-1}) C=O (1852cm^{-1}) ,-OH (2917cm^{-1}) , -CH (3226cm^{-1}) , C=C (1389cm^{-1}) , aromatic aldehyde (1747) ,aromatic -CH (2922cm^{-1});for melting point & UV –VIS. Spectroscopic data, refer table 1&table2.

[2d , (2-methylene)-3-(propan-2-ylidene) succinic acid)]

Purple orange colored crystalline solid nature diacid [by using Furfural (8.64 g, 0.09mol) and benzophenone (16.3998 g, 0.09 moles)

^{1}H NMR,$\boldsymbol{\delta}$; 8.42(s,2H,-CH); $\boldsymbol{\delta}$8.17(s,2H,-CH); $\boldsymbol{\delta}$11.00(s,2H 2-COOH); $\boldsymbol{\delta}$6.85(s,2H,-CH); $\boldsymbol{\delta}$6.66(s,1H) $\boldsymbol{\delta}$6.07(s,1H); (FTIR;cm^{-1}) C=O (1872cm^{-1}) ,-OH (2997cm^{-1}), -CH (3202cm^{-1}), C=C (1366cm^{-1}) , aromatic aldehyde (1740), aromatic-CH (2972cm^{-1});for melting point&UV –VIS. Spectroscopic data, refer table 1&table2.

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.

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

Compound	Yields (%)		m.p. (^{0}C)	Mol.wt.
	Classical	Green		
2a	79.45	89.81	315	360.36
2b	84.25	94.14	287	294.30
2c	85.54	96.81	284	208.17
2d	81.18	92.75	304	170.16

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

Compounds	λ_{max}(nm)	
	-COOH	C=O
2a	206(1.87)	246(3.12)
2b	204(1.45)	250(4.38)
2c	207(1.64)	236(5.22)
2d	209(2.74)	248(3.28)

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 $C_{22}H_{16}O_5$ showed characteristic stretching frequencies of C=O (1726cm^{-1}), -OH (2861cm^{-1}), -CH (3258cm^{-1}), C=C (1586cm^{-1}).

The presence of two carboxyl groups was further supported by ^{1}H NMR spectrum which showed two signals on δ ;11.00 (s, 2H, 2-COOH) (fig.1). Similarly, ^{1}H NMR spectrum also showed two –CH_3 groups on δ;2.42(m), and other aromatic hydrogens on δ ;7.29, 7.28, 7.310,7.290(s,4H,-CH δ; 7.14, 7.12, 7.15, 7.14(s,4H, CH), δ;7.24,7.25,7.33,7.31(s,4H,-CH) δ;7.17,7.13, 7.18, 7.19(s,4H,-CH). The diacid (2b) having molecular formula $C_{18}H_{14}O_4$also showed characteristic stretching frequencies Of C=O (1727cm^{-1}),-OH (2687cm^{-1}) , -CH (3304cm^{-1}), C=C (1648cm^{-1}) .The presence of two carboxyl groups were further supported by ^{1}H NMR spectrum which showed two signals on δ ;11.00(s, 2H, 2-COOH). Similarly, ^{1}H NMR spectrum also showed other aromatic hydrogens 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 $C_{10}H_8C_5$ also showed characteristic stretching frequencies C=O (1852cm^{-1}),-OH (2917cm^{-1}), -CH (3226cm^{-1}), C=C (1389cm^{-1}), aromatic aldehyde (1747), aromatic -CH (2922cm^{-1}).^{1}H NMR spectrum also showed the required peak values for two carboxylic groups, one Furfural ring δ; 8.42, 8.17, 6.84, 6.07 (4H,-CH)(fig. 3). Likewise the diacid (2d) having molecular formula $C_8H_{10}C_4$ also showed characteristic stretching frequencies C=O (1872cm^{-1}),-OH (2997cm^{-1}), -CH (3202cm^{-1}), C=C (1366cm^{-1}), aromatic aldehyde (1740),aromatic -CH (2972cm^{-1}).^{1}H NMR spectrum also showed the required peak values for two carboxylic groups(fig. 4).

Structural determination:

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

Proton NMR Spectra:

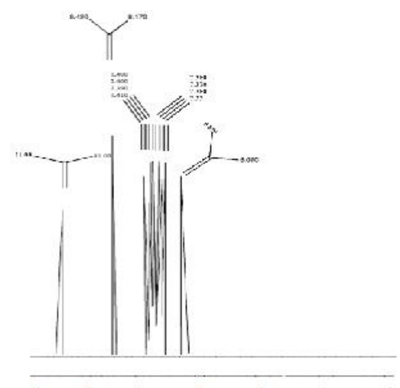


Figure 1: Proton NMR Spectra of diacid (2a) i.e. [2a, (Z)-2-(diphenylmethylene) -3-(furan-2-yl-methylene) succinic acid)]

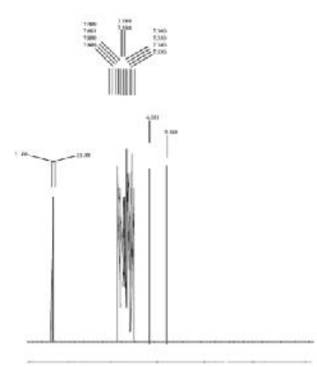


Figure 2: Proton NMR Spectra of diacid (2b) i.e. [2b, 2- (diphenylmethylene)-3-methylene succinic acid]

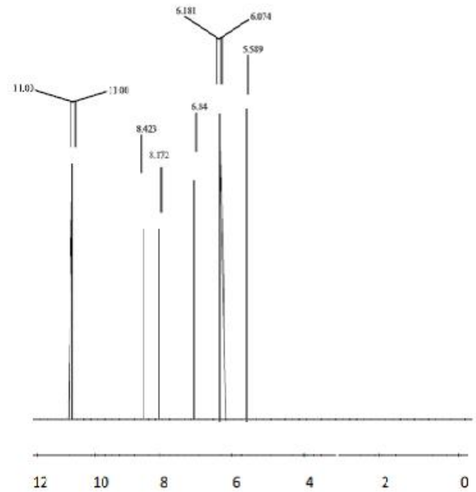


Figure 3: Proton NMR Spectra of diacid (2c) i.e [2c, (Z)- 2 -(furan-2-yl-methylene)-3-methylene succinicacid)]

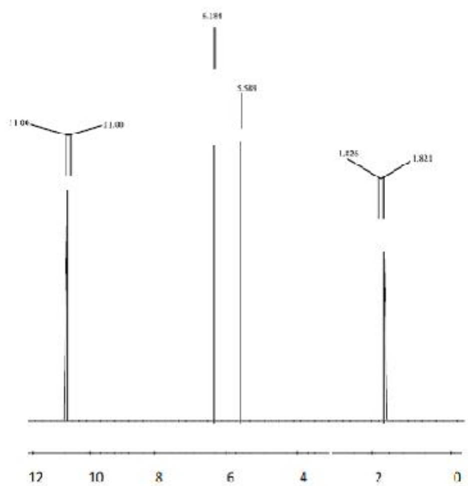


Figure4: Proton NMR Spectra of diacid (2d) i.e [2d, (2-methylene)-3-(propan-2-ylidene) succinic acid)]

IR Absorbtion spectra:

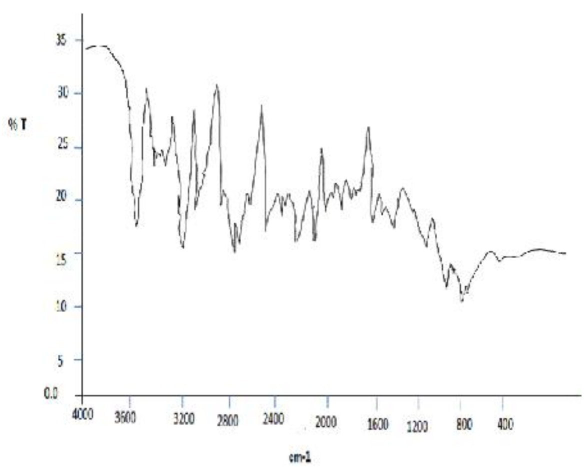


Figure 5:IR Absorbtion spectra of diacid (2a) i.e. [2a, (Z)-2-(diphenylmethylene) -3-(furan-2-ylmethylene) succinicacid)]

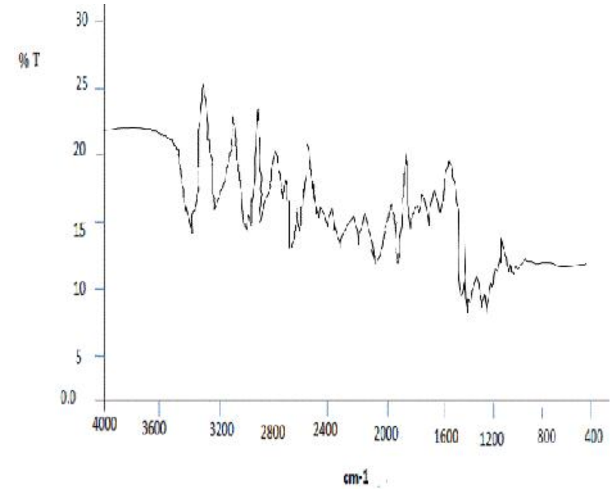


Figure 6: IR Absorbtion spectra of diacid (2b)i.e. [2b, 2- (diphenylmethylene)-3-methylene succinic acid]

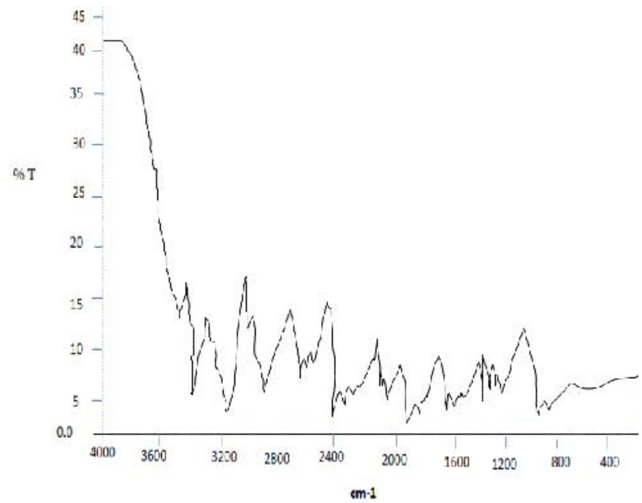


Figure 7: IR Absorbtion spectra of diacid (2c)i.e. [2c, (Z)- 2 -(furan-2-ylmethylene)-3-methylene succinic acid)]

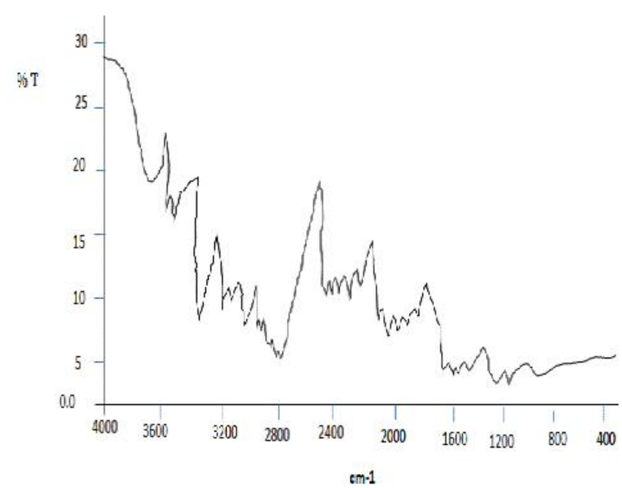


Figure 8: IR Absorbtion spectra of diacid (2d) i.e [2d, (2-methylene)-3-(propan-2-ylidene) succinic acid)]

UV-Vis Absorption spectra

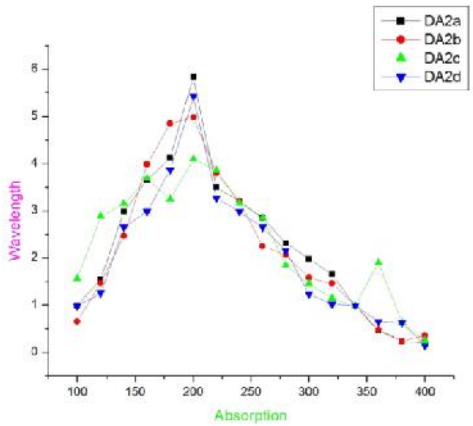
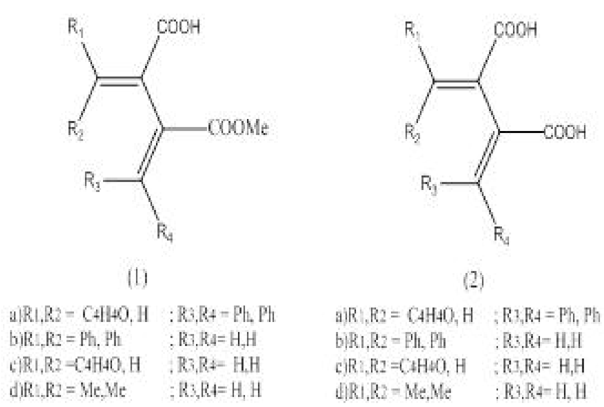


Figure 9: UV-Vis Absorption spectra of diacids (2a, 2b, 2c, 2d)

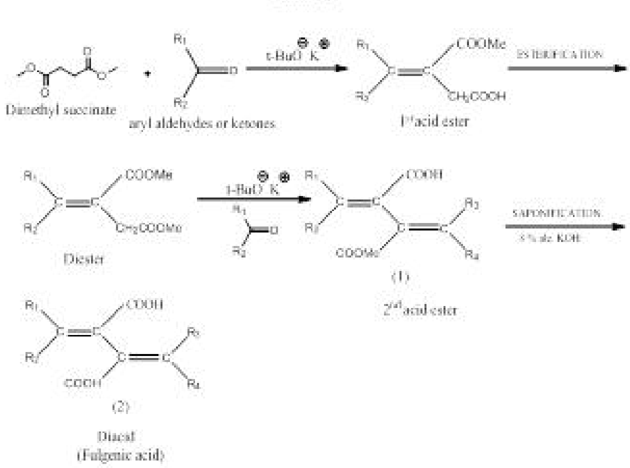
Reaction Schemes of Experimental Work

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 stepwise Stobbe condensation (twice) with different aldehydes and ketones through green approach, which are given as below.

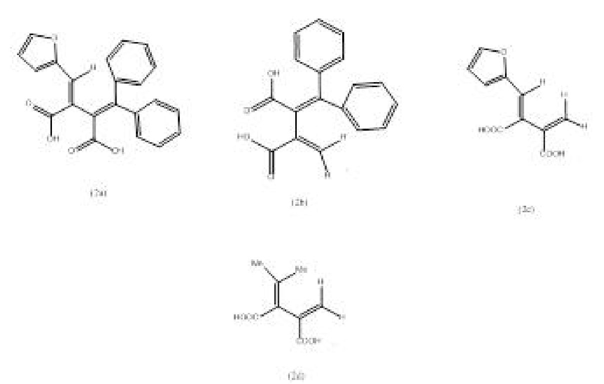
Scheme1



Scheme 2



Scheme3



structures of Fulgenic acids (diacids)

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 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.

5. Acknowledgement

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