



GREEN SYNTHESIS OF FULGENIC ACID FROM BENZALDEHYDE & FORMALDEHYDE VIA STOBBE CONDENSATION METHOD

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Abstract

One pot synthesis of acid ester by Stobbe condensation of alkylidene / arylidene succinates and aldehydes or ketones, their subsequent hydrolysis to diacids were reported. The Stobbe condensation of aromatic aldehyde and aliphatic aldehyde with dimethyl succinate gives diacid [2a, (Z)-2-benzylidene-3-methylene succinic acid] through green approach. The improved yield of Fulgenic acid was observed by the green approach method as compared with other classical methods employed so far.

Key Words: Green synthesis, Stobbe condensation, aromatic aldehyde and aliphatic aldehyde and their products.

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

Dimethyl succinate, Potassium tertiary butoxide, benzaldehyde, formaldehyde, anhydrous methanol, ethylene dichloride, conc. H₂SO₄, 8% alcoholic KOH, were used as raw materials. Benzene, Petroleum ether, were used for double solvent crystallization 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 ¹H-NMR spectra was recorded on a Bruker Avance II 400 MHz spectrometer in D₂O 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].

2.3 Experimental procedure (Material synthesis)

A mixture of dimethyl succinate (9.0 g, 0.09 mole) and benzaldehyde(9.54 g, 0.09 mole) 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% Na₂CO₃. On further acidification, finally it gives acid ester which was again recrystallized with Benzene -pet. ether. Further on esterification, with anhydrous CH₃OH, Ethylene dichloride and conc. H₂SO₄ at room temperature it gives diester .Once again the diester was mixed withformaldehyde(2.70 g, 0.09 mole) and Potassium tertiary butoxide, the same procedure was repeated and recrystallization was done with 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 recrystallization which would give a solid crystalline natured diacids(2a).

2.4Spectroscopic data of Fulgenic acid [2a, (Z)-2-benzylidene-3-methylene succinic acid]

Black colored crystalline solid nature diacid (by using benzaldehyde(9.54 g, 0.09 moles) withformaldehyde (2.70 g, 0.09 moles)

¹H NMR, δ ;7.60,7.61,7.48,7.46,7.34, (s,5 aromatic H,) ; δ ;7.22,6.18,5.58(s,3H,-CH), δ ;11.00(s,2H,2-COOH),

FTIR; cm^{-1} C=O (1722 cm^{-1}), -OH (2867 cm^{-1}), -CH (3248 cm^{-1}), C=C (1586 cm^{-1}).; for **melting point&UV -VIS**. Spectroscopic data, refer **table 1&table2**

3.Results and Discussions:

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 tertiarybutoxide through green context.

Compound	Yields (%)		m.p. (°C)	Mol.wt.
	Classical	Green		
2a	72	89.49	216	218

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

Compound	$\lambda_{\text{max}}(\text{nm})$	
	-COOH	C=O
2a	204(1.57)	245(3.22)

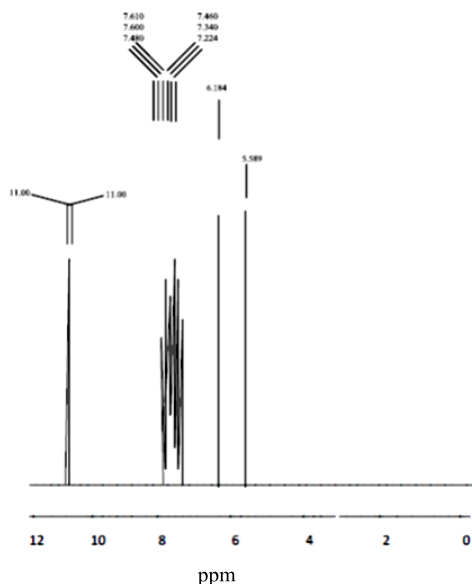
Table 2. UV -Visible maximum absorption of different groups in Fulgenic acid

TheFulgenic acid (2a) was having much purity as compared with classically prepared one. It was having sharp melting and boiling point, also having sharp NMR peak values. In previous methods[20], tremendous heat wasused, due to which obtained diacidsbear impuritywith less percentage yield.The UV graphsshowsharp and similar peaks,which alsoimproved the purity of diacids.

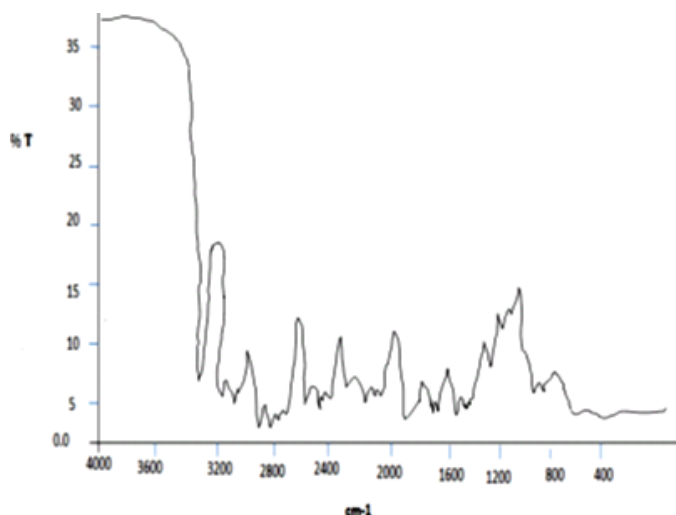
The diacid (2a)exhibited a molecular formula C₁₂H₁₀O₄ showed characteristic stretching frequencies of C=O (1722 cm^{-1}),-OH (2867 cm^{-1}), -CH (3248 cm^{-1}), C=C (1586 cm^{-1}).The presence of two carboxyl groups was further supported by ¹H NMR spectrum which showed two signals on δ ;11.00(s, 2H, 2-COOH)(**fig. 1**). Similarly , ¹H NMR spectrum also showed three-CH groupson δ ;7.22,6.18,5.58(s,3H,-CH), and other aromatic hydrogen's on δ ;7.60,7.61,7.48,7.46,7.34.

3.1Structural determination:-

The Fulgenic 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.



3.1. a Proton NMR Spectra
Fig. 1 Proton NMR Spectra of diacid(2a)



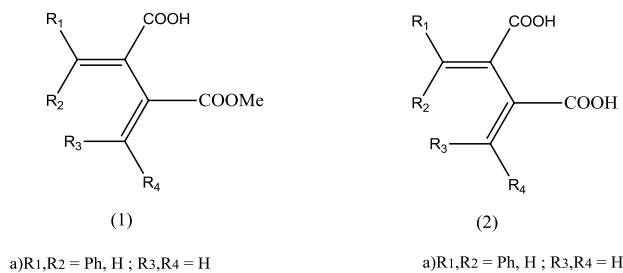
3.1.b IR Absorption spectra
Fig. 2 IR Absorption spectra of diacid (2a)

3.2 Reaction Schemes of Experimental Work

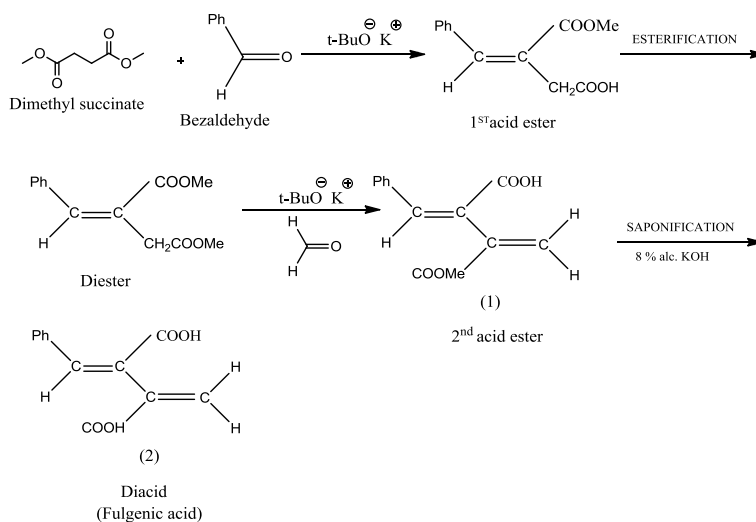
The Fulgenicacid (diacid) **2a** was prepared by using following schemes:

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.

Scheme 1



Scheme 2



4. Conclusion:

It was concluded that, the solvent free Stobbe condensation of aromatic aldehydes and aliphatic, aromatic 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**) 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.

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