



Green Synthesis of Anhydride and Photochromic Fulgide of Benzophenone from Strobe Condensation Products

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Abstract

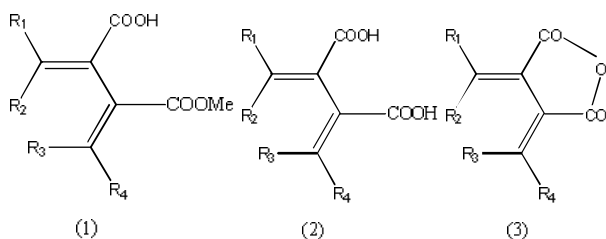
Photochromic materials are those which react reversibly to light. Photochromism is therefore distinguished from the familiar photographic processes, which because of the chemical development of the images, are essentially irreversible. Many organic materials, and a few inorganic ones, show this phenomenon. One pot synthesis of acid esters by Stobbe condensation of alkylidene / arylidene succinates and aldehydes or ketones, their subsequent hydrolysis to diacids and the formation of photochromic fulgides by cyclisation using different reagents are reported.

Key Words : green synthesis, anhydrides, Stobbe condensation, cyclised products.

Introduction:

Photochromism is observed in anhydrides obtained from the diacids of Stobbe condensation products ^{1,2}. To study, compare and correlate the photochromic properties with the structures and also in the course of green synthesis of different photochromic fulgides, and cyclized products, various anhydrides were synthesized by Stobbe condensation of dimethyl succinate with different carbonyl compounds followed by subsequent saponification and dehydration of the products.

The present work describes ecofriendly one pot synthesis method for Stobbe condensation in which solvent free condition improves the yield. 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. The diacids were converted to the respective anhydride on treatment with acetyl chloride under anhydrous conditions.



(a) $R_1R_2=Ph, Ph$ & $R_3R_4=Ph, Ph$ (a) $R_1R_2=Ph, Ph$ & $R_3R_4=Ph, Ph$





Experimental:

The acid anhydride (3a) is prepared by taking Benzophenone as an initial reactant. It is esterified and saponified at room temperature up to 1 hr. Finally it gives diacid (2a). Then diacid (2a) is further cyclised with conc. H_2SO_4 at room temperature up to 2 hrs. which gives acid anhydride (3a).

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. 1H NMR spectra in $CDCl_3$ at 60 MHz on a Varian EM-360 spectrometer (chemical shifts in δ , ppm) using TMS as internal standard. IR spectra in KBr pellets and nujol mull and UV spectra were measured in ethanol on a DMS-80 (Varian) spectrophotometer. Molecular weights of the acidic products were determined by titrimetric method³ as their equivalent weights.

The general procedure for green Stobbe condensation and saponification of Stobbe condensation products were similar to those described earlier³⁻⁵. The anhydrides were synthesised⁶ by refluxing corresponding acids with acetyl chloride⁷ under anhydrous conditions for 2 hours.

Physical And Spectral Data (Table 1)

Compound	Yields (%)		m.p. (°C)	Eq.wt.	1H NMR (δ , ppm)
	Classical	Green			
1a	90	94	-	476	11.0(1-OH), 7.38(s, 8 CH), 7.40(s, 8 CH) 7.33(s, 4CH), 2.21(CH ₃)
2a	62	75.89	165	416	11.0(2 -OH), 7.38(s, 8 CH), 7.40(s, 8 CH) 7.33(s, 4CH)
3a	85	94.88	155	428	7.782(s, CH), 7.7598(s, 3 CH), 7.5460(s, CH), 7.52, 7.50(s, 2CH), 7.44, 7.42, 7.40(s, 3CH)

Physical And Spectral Data (Table 2)

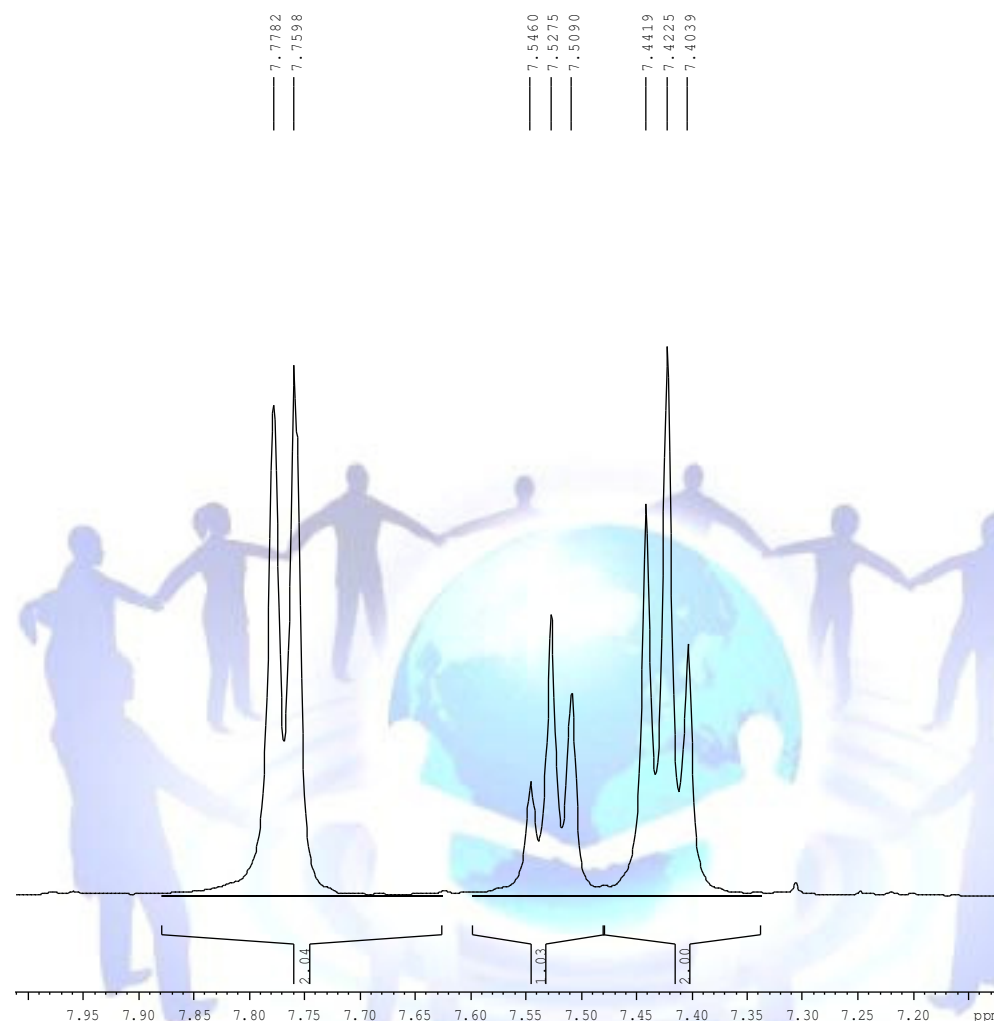
Compounds	IR(C=O) cm^{-1}	$\lambda_{max}(nm)$ (log ϵ)
1a	1715, 1698, 2045, 3147	227(2.5), 302(3.1)
2a	3200, 1695, 1564, 1563, 2546	257(1.3), 346(3.8), 165(4.3)
3a	1879, 1658, 1902, 1254	227(2.8), 356(1.9), 225(4.1), 210(4.06)





NMR Interpretation of 3a (ACID ANHYDRIDE)

101-NMR



BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

Current Data Parameters
NAME Nov25-2014
EXPNO 150
PROCNO 1

F2 - Acquisition Parameters
Date_ 20141125
Time 14.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 41.600 usec
DE 6.00 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 10.90 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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Results and Discussions:

Stobbecondensation generally involves the use of metal alkoxide¹ as a catalyst in refluxing alcohol, particularly, butanol. On the other hand, in the present paper, the use of butanol is discarded and instead of that, dry solid potassium tertiary butoxide is taken for the reaction. The advantages are short reaction time, good yield, less materials. Stobbecondensation generally involves the use of metal alkoxide¹ as a catalyst in refluxing alcohol, and environment- friendly reaction conditions.

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. As compared to classical condensation methods done by previous workers¹, plenty of solvents and hazardous chemicals were used by them. Instead, green method requires much less





amount of dry solid reagents; for which no heat energy is required for the formation of acid esters.

Acknowledgement:

The authors are grateful to SAIF Chandigarh, RSIC, CDRI, Lucknow for IR and PMR spectra, Principal, Hislop College, Nagpur for providing research facility and **Dr.SabaGani** for her help and interest.

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