

GREEN SYNTHESIS OF TETRALONES AND INDENONES

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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 of diacids and the formation of Tetralones and Indenones by different reagents are reported.

Key Words : green synthesis, anhydrides, Stobbe condensation, and their products.

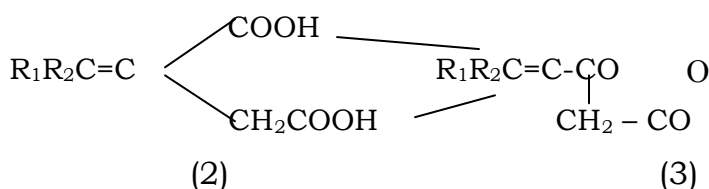
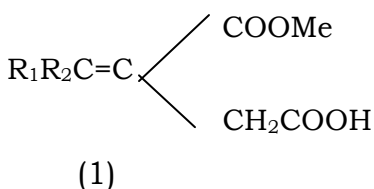
INTRODUCTION:

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 Tetralones Indenones, 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) $R_1R_2=Ph,h$,
 (b) $R_1R_2=2-C_{10}H_7,H$,
 (c) $R_1R_2=2\text{-furyl},H$,
 (d) $R_1R_2=Ph,Me$,
 (e) $R_1R_2=Me,Me$
 (f) $R_1R_2=Ph,Ph$
 (g) $R_1R_2=Et,Me$

EXPERIMENTAL

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 assembly¹ H 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 weight 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 SPECTORAL DATA

Compound s	Yields (%)		m.p (°C)	Eq.wt	¹ H NMR (δ , ppm)
	Classic al	Gree n			
1a	90	94	-	220	3.76(s,3H,OMe),3.30(s,2H,CH ₂),7.17(s.5H,Ar),7.80(s,1H,CH)
1b	75	78.84	-	270	3.76(s.3H,OMe),3.66(s.2H,CH ₂),7.20-7.96(M,7H,Ar),8.06(s,3H,CH)
1c	80	84.28	182	210	3.76 (s.3H,OMe),3.68(s.2H,CH ₂),6.10-7.50(m,3H,Ar),7.64(s.1H,CH)
1d	90	92.18	-	234	2.02(s.3H,Me),3.25(s.2H,CH ₂),3.65(s.mH,OMe),7.15(s.5H,Ar).
1e	60	68.12	-	172	3.72 (s.H,OMe),3.10(s.2H,CH ₂),6.10-5.50(m,3H,Ar),6.64(s.1H,CH)-
1f	95	96.82	123	296	2.46 (s.2H,Me),3.58(s.2H,CH ₂),6.10-7.50(m,3H,Ar),7.64(s.1H,CH)-
1g	65	72.89	105	186	1.76 (s.3H,Me),3.68(s.2H,CH ₂),6.10-4.50(m,3H,Ar),5.64(s.1H,CH)-



2a	62	65.89	165	104	3.76(s,3H,OMe),3.30(s,2H,CH ₂),7.17(s.5H,Ar),7.80(s,1H,CH)
2b	69	72.14	183	128	1.79(s.3H,OMe),3.16(S.2H,CH ₂),7.20-7.96(M,7H,Ar),8.06(s,3H,CH)
2c	78.12	79	187	98	2.76(s.2H,OMe),3.46(S.2H,CH ₂),7.207.96(M,7H,Ar),8.06(s,4H,CH)
2d	58.68	65.88	164	110	2.36(s.H,Me),3.66(S.2H,CH ₂),.207.96(M,7H,Ar),8.06(s,3H,C H)
2e	86	87.82	172	80	1.16(s.3H,OMe),3.66(S.2H,CH ₂),7.20-7.96(M,7H,Ar),8.06(s,4H,CH)
2f	59.83	62.61	149	98	1.376(s.3H,OMe),3.66(S.2H,CH ₂),7.20-7.96(M,7H,Ar),8.06(s,5H,CH)-
2g	68.28	69.71	-	-	-1.42(s,3H,OMe,3.30(s,2H,CH ₂),7.17(s.5H,Ar),7.80(s, 1H, CH)

3a	85	86.88	155	-	2.56(s,3H,OMe,3.30(s,2H,CH ₂),7.17(s.5H,Ar),7.80(s, 1H, CH)
3b	88	89.16	206	-	1.75(s.3H,OMe),3.66(S.2H,CH ₂),7.20-7.96(M,7H,Ar),8.06(s,5H,CH)
3c	80	81.12	152	-	3.79(s,3H,OMe,3.42(s,3H,CH ₂),7.19(s.5H,Ar),7.82(s,2H,CH)
3d	85	86.17	-	-	3.68(s,3H,OMe,3.30(s,2H,CH ₂),7.17(s.5H,Ar),7.80(s,3H,CH)
3e	86.12	87.18	-	-	3.71(s,2H,OMe,3.8s,2H,CH ₂),7.18(s.5H,Ar),7.28(s,4H,CH)
3f	71.92	74	-	-	3.12(s,H,OMe,3.10(s,2H,CH ₂),7.15(s.5H,Ar),7.80(s,1H,CH)
3g	61.28	64	-	-	3.26(s, Me,2.30(s,2H,CH ₂),7.13(s.5H,Ar),7.80(s,1H,CH)



Results and Discussions

Stobbe condensation 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 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.

REFERENCES

- S. Jabbar, (1994), studies in the synthesis and structure of Indenones, Ph.D.Thesis, Nagpur University.
- S. Deshmukh, (1992), Cyclization reaction, Ph.D.Thesis, Nagpur University.
- S.Banerjee and G.Bhagavant, (1981), Indian J.Chem.20B,362.
- G. Gupta and S.Bhanerjee, (1990), Indian J.Chem.,29B,787.
- G.Bhagavant and S. Banerjee, (1975), Curr.Sci.(India),44,846.
- S. Banerjee, (1977), Indian J.Chem.,16B,487.
- S. Banerjee, (2013), Journal of chemistry, vol.2013, Article ID 152370.