Asian Journal of Chemistry Vol. 14, Nos. 3–4 (2002), 1655–1659

Synthesis of Anhydrides from Stobbe Condensation Products

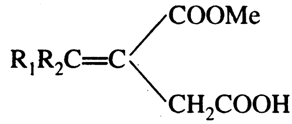
SABA JABBAR* and SHUBHRA BANERJEE†
Department of Chemistry, Dr. Ambedkar College, Nagpur-440 010, India

Synthesis of acid-esters by Stobbe condensation of dimethylsuccinate and aldehydes or ketones, their subsequent hydrolysis to diacids and the formation of anhydrides by different reagents are reported.

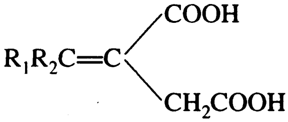
Key Words: Synthesis, Anhydrides, Stobbe, Condensation, Products.

INTRODUCTION

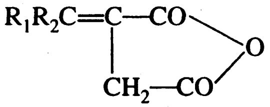
Photochromism is observed in anhydrides obtained from the diacids of Stobbe condensation products[1, 2]. To study, compare and correlate the photochromic properties with the structures and also in the course of synthesis of different indenones and cyclized products, various anhydrides were synthesised by Stobbe condensation of dimethylsuccinate with different carbonyl compounds followed by subsequent saponification and dehydration of the products.



(1)



(2)



(3)

(a) R_1R_2 = Ph, H,
(b) R_1R_2 = *p*-OMePh,
(c) R_1R_2 = 3,4,5-tri-OMePh, H,
(d) R_1R_2 = 2-$C_{10}H_7$, H,
(e) R_1R_2 = 2-furyl, H,
(f) R_1R_2 = Ph, Ph,
(g) R_1R_2 = *p*-ClC_6H_4, Ph,
(h) R_1R_2 = Ph, Me,
(i) R_1R_2 = Cyclo C_6H_{10},
(j) R_1R_2 = Cyclo C_5H_8,
(k) R_1R_2 = Me, Me,
(l) R_1R_2 = Et, Me,
(m) R_1R_2 = Cyclohexenyl.

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 assembly ^{1}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

---

†Department of Chemistry, Institute of Science, Nagpur 440 001, India.

TABLE-1

PHYSICAL AND SPECTRAL DATA OF ACID-ESTER (**1a–*l***), DIACIDS (**2a–m**) AND ANHYDRIDES (**3a–h**)*

Compd.	Yield (%)	m.p.+ (°C)	Eq. wt.$	pKa	λ_{max} (nm) (log ε)	IR (cm^{-1})	^1H NMR (δ, ppm)
1a	90	—	221 (220)	—	—	1710, 1680	3.76 (s, 3H, OMe), 3.30 (s, 2H, CH_2), 7.17 (s, 5H, Ar), 7.80 (s, 1H, CH)
1b	90	119^a	249 (250)	—	—	1705, 1665	3.76, 38.2 (s, 3H each, 2xOMe), 3.51 (s, 2H, CH_2), 6, 66–7.62, (m, 4H, Ar), 7.77 (s, 1H, CH)
1c	90	194^a	310 (310)	7.5	—	1710, 1687	3.72 (s, 3H, OMe), 3.72 3.77, 3.81 (s, 3H each, 3xOMe), 3.40, (s, 2H, CH_2) 6.60–6.85 (m, 2H, Ar), 7.78 (s, 1H, CH)
1d	75	—	272 (270)	—	225 (4.48) 265 (3.84) 290 (3.54)	1720, 1688	3.76 (s, 3H, OMe), 3.66 (s, 2H, CH_2), 7.20–7.96 (m, 7H, Ar), 8.06 (s, 1H, CH)
1e	80	182^a	211 (210)	6.1	226 (3.49) 353 4.12	1710, 1670	3.76 (s, 3H, OMe), 3.68 (s, 2H, CH_2), 6.10–7.50 (m, 3H, Ar), 7.64 (s, 1H, CH)
1f	95	123^a	297 (296)	—	227 (4.20) 266 (4.07)	1710, 1660	3.46 (s, 2H, CH_2), 3.50 (s, 3H, OMe), 7.20 (s, 10H, Ar).
1g	79	120^a	328 (330)	—	240 (4.28) 270 (4.23)	1708, 1665	3.38 (s, 2H, CH_2), 3.42 (s, 3H, OMe), 6.7–7.8 (m, 9H, Ar)
1h	90	—	236 (234)	—	—	1715, 1680	2.02 (s, 3H, Me), 3.25 (s, 2H, CH_2), 3.65 (s.3H, OMe), 7.15 (s, 5H, Ar)
1i	70	96^a	211 (212)	—	—	1712, 1690	1.63 (s, 6H, alicy), 2.27 (s, 2H, alicy), 2.67 (s, 2H, alicy), 3.42 (s, 2H, CH_2), 3.72 (s, 3H, OMe)
1j	60	—	197 (198)	—	—	—	—
1k	60	—	174 (172)	—	—	1710, 1690	1.86, 2.19 (s, 3H each, 2XMe), 3.44 (s, 2H, CH_2), 3.74 (s, 3H, OMe)
1*l*	65	105^a	188 (186)	—	—	1720, 1692	1.82 (s, 3H, Me), 0.9-1.2 (t, J = 7, 3, Me), 2.0–2.70 (q.2H, CH_2), 3.35 (s, 2H, CH_2), 3.70 (s, 3H, OMe)

2a	—	165^{a}	104 (104)	5.6** 9.0	225 (3.60)	1695	3.44 (s, 2H, CH_2), 7.23 (s, 5H, Ar), 7.70 (s, 1H, CH)
2b	—	192^{d}	179 (180)	5.55 9.10	291 (3.87)	1682	3.73 (s, 3H, OMe), 3.41 (s, 2H, CH_2), 6.57–7.37 (m, 4H, Ar), 7.63 (s. 1H, CH)
2c	—	130^{a}	146 (148)	7.00 10.9	299 (3.43) 308 (3.36) 318 (3.37)	1680	3.66, 3.70, 3.80 (s, 2H each, 2x Ome), 3.41 (s, 2H, CH_2), 6.51–7.31 (m, 2H, Ar), 7.64 (s, 1H, CH)
2d	—	183^{c}	127 (128)	5.0 9.0 —	227 (2.59) 333 (3.25) 290 (3.54)	1690	3.57 (s, 2H, CH_2), 7.22–7.92 (m, 7H, Ar), 7.98 (s, 1H, CH)
2e	—	187^{a}	97 (98)	6.03 10.75	320 (3.53) 402 (4.12) 420 (3.57)	1683	3.75 (s, 2H, CH_2), 6.20–7.50 (m, 3H, Ar) 7.88 (s, 1H, CH)
2f	—	166^{a}	141 (141)	5.15 6.27	—	1690	3.33 (s, 2H, CH_2), 7.16 (s, 10H, Ar)
2g	—	176^{a} &183^{a}	158 (158)		—	—	**
2h	—	164^{b}	112 (110)	5.45 9.50	232 (4.19) 276 (4.03)	1695	2, 39 (s, 3H, Me), 3.20 (s, 2H, CH_2), 7.37 (m, 5H, Ar)
2iΠ	—	183^{a}	100 (99)	5.63	—	1689	1.48 (s, 6H, alicy), 2.13 (s, 2H, alicy), 2.57 (s, 2H, alicy), 3.23 (s, 2H, CH_2), 8.46 (s, 2H, COOH)
2jΠ	—	φ	92 (93)	—	—	1698	1.07–2.48 (m, 8H, alicy), 3.2 (s, 2H, CH_2), 9.57 (s, 2H, COOH)
2kΠ	—	172^{a}	81 (80)	—	—	1696	1.83, 2.1 (2, 3H, 2XMe), 3.27 (s, 2H, CH_2)
2*l*Π	—	149^{a}	85 (86)	—	—	1695	1.88 (s, 3H, Me), 0.94–1.24 (t, J = 7, 3H, Me), 2.04–2.38 (q, 2H, CH_2), 3.36 (s, 2H, CH_2), 9.3 (s, 2H, COOH)
2mΠ	—	145^{a}	99 (99)	—	—	—	1.60 (s, 4H, alicy), 2.04 (s, 4H, slivy), 2.45 (q, 1H, CH_2), 2.94 (q, 1H, CH_2), 3.44 (q, 1H, CH), 10.99 (s, 2H, COOH)

3a	85	155a	—	—	221 (3.97) 267 (4.27)	1838, 1865	3.82 (s, 2H, CH_2), 7.73 (s, 5H, Ar), 7.71 (s, 1H, CH)
3b	90	121a	—	—	—	1839, 1768	3.68 (s, 2H, CH_2), 3.83 (s, 3H, OMe), 6.25–7.71 (m, 4H, Ar), 7.81 (s, 1H, CH)
3c	82	165a	—	—	—	1840, 1785	3.52 (s, 2H, CH_2), 3.65, 3.69, 3.80 (s, 3H each, 3X OMe), 6.05–7.35 (m, 2H, Ar), 7.65 (s, 1H, CH)
3d	88	206a	—	—	220 (3.45) 268 (3.59) 305 (3.54)	1845, 1780	3.82 (s, 2H, CH_2), 7.23–7.98 (m, 7H, Ar), 8.03 (s, 1H, OH)
3e	80	152a	—	—	227 (3.62) 402 (4.12) 387 (4.12)	1810, 1762	3.86 (s, 2H, CH_2), 6.44–7.34 (m, 3H, Ar), 7.54 (s, 1H, CH)
3f	82	146a	—	—	274 (3.44)	1832, 1765	3.62 (s, 2H, CH_2, 7.27 (m, 10H, Ar)
3g	80	128 & 1329, a	—	—	215 (4.53) 239 (4.51)	η_0	3.67 (s, 2H, CH_2), 6.8–7.36 (m, 9H, Ar) for E isomer
3h	85		—	—	232 (4.91) 278 (3.91)	1830, 1765	2.61 (s, 3H, Me), 3.43 (s, 2H, CH_2), 7.00–7.47 (m, 5H, Ar)

* All the compounds gave satisfactory C and H analyses.

♣ All anhydrides yielded the corresponding diacids on refluxion with 8% alc. KOH.

Π All these diacids fail to produce the respective anhydrides with AcCl.

•• pKa_1 and pKa_2 values for diacids.

Z and E isomer

φ Chars at 230.

** Z isomer: δ 63.37 (s, 2H, CH_2), 6.67–8.07 (m, 9H, Ar).

E isomer: δ 3.00 (s, 2H, CH_2), 6.53–7.86 (m, 9H, Ar).

♦ Z isomer: 4.50, 8.20; E isomer : 4.75, 8.80.

η_0 1850, 1770 cm^{-1} for Z and 1840, 1765 cm^{-1} for E isomer.

\+ Solvents for crystallisation : (a) C_6H_6-n-hexane (50 : 50 v/v); (b) C_6H_6-pet.ether (40–60) (50 : 50 v/v); (c) C_2H_5—O—C_2H_5-n-hexane (50 : 50 v/v).

$ Calculated values are given in parentheses.

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 was determined by titrimetric method[3] as their equivalent weights.

General procedures for Stobbe condensation and saponification of Stobbe condensation products were similar to those described earlier[3–5]. The anhydrides were synthesised[6] by refluxing corresponding acids with acetyl chloride under anhydrous conditions for 2 h.

RESULTS AND DISCUSSION

The acid-esters[1], 1-alkylidene (or arylidene) methyl succinates **(1)** were synthesised by Stobbe condensation of dimethylsuccinate with carbonyl compounds. With unsymmetrical ketones, *e.g.*, ethylmethyl ketone and acetophenone, a mixture of geometrical isomers was obtained as the reaction products whereas *p*-chlorobenzophenone* formed both *cis*-and *trans*- products. The products **(1)** and **(2)** did not show migration of the double bond† where *trans*-Ph/COOMe structure was maintained. No changes occurred during the saponification step. However, the anhydrides **(3)**‡ were easily produced by treatment of the acids with acetyl chloride.

All the products were characterized by their pKa, UV, IR and ^{1}H NMR data (Table-1) where remarkable similarities in values wre observed with previously synthesised system[3, 4].

ACKNOWLEDGEMENT

The authors are grateful to RSIC, CDRI, Lucknow for IR and ^{1}H NMR spectra.

REFERENCES

1. S. Jabbar, Studies in the synthesis and structure of Indenones, Ph. D. Thesis, Nagpur University (1994).
2. S. Deshmukh, Cyclization reactions, Ph. D. Thesis, Nagpur University (1992).
3. S. Banerjee and G. Bhagavant, *Indian J. Chem.*, **20B**, 362 (1981).
4. G. Gupta and S. Bhanerjee, *Indian J. Chem.*, **29B**, 787 (1990).
5. G. Bhagavant and S. Banerjee, *Curr. Sci. (India)*, **44**, 846 (1975).
6. S. Banerjee, *Indian J. Chem.*, **16B**, 487 (1977).

(*Received:* 26 March 2002; *Accepted*: 27 May 2002) AJC–2744

---

*This experiment was repeated several times and the ratio of the (Z) : (E) isomers noted which was found to be 2 : 3 the (E) isomer was formed in high concentration.

†The cyclohexenyl product (2m) was obtained by Stobbe reaction in sodium ethoxide at reflux temperature.

‡The anhydrides wre studied for their photochromic properties in a photochemical reactor. All the anhydrides yielded the original diacids when hydrolysed with 8% alc. KOH.