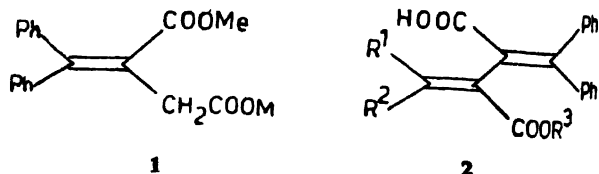
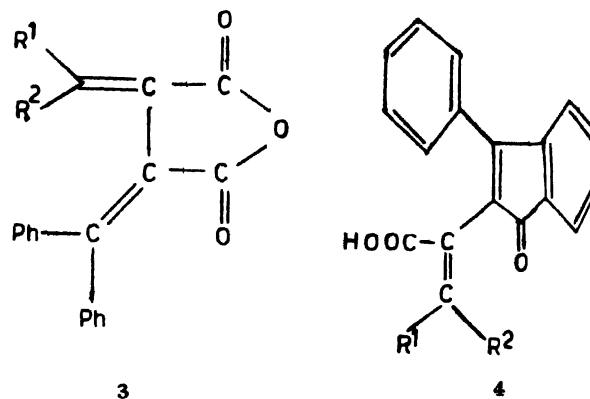


rotation is possible at C—C single bond between two double bonds giving possibility of *s-cis*-orientation too. Based on these concepts, molecular structures are fixed for the products obtained by cyclisation reactions with their anhydrides.



- 2a ; R¹R²=cyclo-C₆H₁₀, R³=Me
 b ; R¹R²=cyclo-C₆H₈, R³=Me
 c ; R¹R²=PhMe, R³=Me
 d ; R¹R²=Me₂, R³=Me
 e ; R¹R²=cyclo-C₆H₁₀, R³=H
 f ; R¹R²=cyclo-C₆H₈, R³=H
 g ; R¹R²=PhMe, R³=H
 h ; R¹R²=Me₂, R³=H



- 3a ; R¹R²=cyclo-C₆H₁₀
 b ; R¹R²=cyclo-C₆H₈
 c ; R¹R²=PhMe
 d ; R¹R²=Me₂
 4a ; R¹R²=cyclo-C₆H₁₀
 b ; R¹R²=cyclo-C₆H₈
 c ; R¹R²=PhMe
 d ; R¹R²=Me₂

Fulgides are of interest for their photochromic properties². Highly conjugated anhydrides (3a–d) were synthesised as intensely coloured compounds when the diacids (2e–h) were refluxed with acetyl chloride under anhydrous conditions. The five-ring cyclic anhydrides were identified on the basis of the presence of double absorption bands near 1 800 cm⁻¹ (C=O)³ and their hydrolysis to the corresponding diacids (2a–h) by boiling with aqueous alkali.

Internal Friedel Crafts cyclisation of the anhydrides (3a–d) with anhydrous AlCl₃ gave α-alkylidene-α-(2-inden-1-one)acetic acids (4a–d), the structures of which were supported by the following facts: The products were highly coloured and their uv spectra were very similar to the compounds having indenone structure⁴; the facile cyclisation occurring with anhydrides, as is generally the case with indenones; ir spectra showed absorptions at ~1 680 (C=O acid) and ~1 710 cm⁻¹ (C=O ketone) for five-membered ring indenones; pmr spectra depicted aromatic multiplet pattern for 1,2-substituted benzene systems

Cyclisation of Stobbe Condensation Products

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Manuscript received 10 April 1990, revised 10 October 1990,
accepted 14 January 1991

STOBBE condensation of benzhydrylidene succinate with ketones gave methyl 2-benzhydrylidene-3-carboxy-3-alkylidene butenoate which on saponification yielded 2-benzhydrylidene-3-carboxy-3-alkylidene butenoic acids (2e–h). In general, *E-s-trans*-structure was fixed for these acids¹. However, a free

NOTES

TABLE 1—PHYSICAL AND SPECTRAL DATA OF COMPOUNDS*

Compd no.	M.p. °C	Eq. wt Found/(Calcd)	λ_{\max} (nm) (log ϵ)	$\nu_{C=O}$ (cm ⁻¹)	δ (ppm)	
					aliph/alicyc	ArH
2e	210 ^a	180.0 (181.2)	289 (4.23), 248 (4.50)	1 674 ^o	1.33 (6H, s), 2.09 (2H, s), 2.50 (2H, s)	7.16 (10H, s) ^o
2f	130 ^a	173.1 (174.2)	270 (4.24), 228 (4.53)	1 677 ^o	1.37 (4H, s), 2.10 (2H, s), 2.49 (2H, s)	6.90–7.40 (10H, m) ^o
2g	184 ^a	194.1 (192.2)	270 (4.07), 228 (4.29)	1 685	2.18 (3H, s)	6.40–7.45 (15H, m)
2h	199 ^a	159.4 (161.2)	268 (3.25), 225 (3.29)	1 660 ^o	1.64 (3H, s), 2.00 (3H, s)	7.21 (10H, s) ^o
3a	148 ^b	—	348 (5.17), 275 (5.43), 227 (5.60)	1 823, 1 774	0.80–3.10 (10H, m)	7.43 (10H, s)
3b	155 ^b	—	355 (5.32), 285 (5.45), 227 (5.63)	1 808, 1 765	0.70–2.90 (8H, m)	6.30–7.70 (10H, m)
3c	199 ^b	—	349 (4.66), 227 (5.21), 230 (5.48)	1 807, 1 770	2.46 (3H, s)	6.30–7.40 (15H, m)
3d	165 ^b	—	349 (5.21), 275 (5.44), 227 (5.71)	1 790, 1 747	1.25 (3H, s), 2.28 (3H, s)	7.10–7.40 (10H, m)
4a	185 ^b	342.40 (344.40)	352 (4.56), 272 (5.07), 237 (5.37)	1 715, 1 690	1.20–1.57 (6H, s), 1.9 (2H, s), 2.70 (2H, s)	7.20–8.30 (9H, m)
4b	195 ^b	328.97 (330.38)	311 (4.29), 275 (4.57), 235 (4.92)	1 712, 1 680	1.48 (4H, br s), 1.95 (2H, s), 2.76 (2H, s)	6.95–7.70 (9H, m)
4c	172 ^b	365.04 (366.42)	300 (4.80), 275 (5.00), 227 (5.16)	1 710, 1 695	2.21 (3H, s)	6.40–7.40 (14H, m)
4d	215 ^b	305.50 (304.34)	311 (4.36), 268 (4.68), 236 (5.01)	1 709, 1 685	1.54 (3H, s), 2.13 (3H, s)	7.00–7.50 (9H, m)

*All compounds gave satisfactory C and H analyses; 2e–h (yield 90–100%) colourless, 3a–d (80–90%) yellow, 4a–d (90–100%) deep yellow.

**Solvent for crystallisation: ^aethanol–water, ^bC₆H₆–n-hexane.

which showed cyclisation occurring in benzene ring; all products have similar pmr pattern.

Experimental

The uv spectra (EtOH) were recorded on a Varian DMS-80 spectrophotometer, ir spectra on a Varian (KBr) CFT-20 spectrophotometer and pmr spectra (CDCl₃) on a Perkin-Elmer R-32 instrument with TMS as internal standard.

Stobbe condensation of dimethyl benzhydrylidene-succinate⁵ (1) and ketones. General procedure: An equimolar mixture of 1 and ketone was added under inert and dry conditions to potassium t-butoxide and the reaction at room temperature for 1 h gave after usual workup methyl 2-benzhydrylidene-3-carboxy-3-alkylidenebutenoates (2a–d). Saponification of all the acid-esters (2a–d) with 8% alcoholic KOH for 8 h gave the corresponding diacids (2e–h; Table 1)⁶.

2-Benzhydrylidene-3-carboxy-3-alkylidenebutenoic acid anhydrides (3a–d): The diacids (2e–h; 1 g) were refluxed with acetyl chloride (10 ml) for 2 h on a water-bath under anhydrous condition and the excess acetyl chloride was removed with dry benzene

under reduced pressure. The residue was crystallised by addition of dry n-hexane to give the anhydrides 3a–d (Table 1).

All anhydrides on boiling with 8% aqueous KOH for 30 min and acidification gave the original diacids 2e–h.

α -Alkylidene- α -(2-inden-1-one)acetic acid (4a–d): An ice-cold suspension of powdered AlCl₃ in nitrobenzene was added dropwise under anhydrous ice-cold conditions to a solution of the anhydrides in nitrobenzene. After 24 h at 0° under anhydrous condition, the reaction mixture was poured in crushed ice, acidified with ice-cold 6N HCl and nitrobenzene distilled off. The residue was extracted with ice-cold ether and washed repeatedly with ice-cold Na₂CO₃ solution. Acidification of alkaline layer yielded the yellow coloured products (Table 1).

Acknowledgement

The authors are grateful to Sadtler Research Laboratories, Philadelphia, U.S.A. and to R.S.I.C., C.D.R.I., Lucknow, for ir and pmr spectra.

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