

## Stereochemistry in the Stobbe Condensation

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The diacids obtained from acid-esters 2-carbomethoxy-1- $\beta$ -naphthyl-4,4-diphenylbutadiene-3-carboxylic acid (**3a**) and 3-carbomethoxy-1- $\beta$ -naphthyl-4,4-diphenylbutadiene-2-carboxylic acid (**3b**) are identical. Also, the diacids obtained from 2-carbomethoxy-1- $\beta$ -naphthyl-4,4-methyl, phenylbutadiene-3-carboxylic acid (**3d**) and 3-carbomethoxy-1- $\beta$ -naphthyl-4,4-methyl, phenylbutadiene-3-carboxylic acid (**3e**) are identical. The physico-chemical properties along with the cyclization reactions‡ of the products clearly indicate that the Stobbe condensation of alkylidene succinic ester with arylaldehydes invariably leads to the product having *trans* Ar/COOMe groups.

**Key Words:** Stereochemistry, Stobbe, Condensation.

### INTRODUCTION

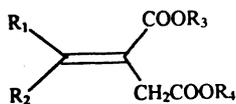
Stereoselectivity has been observed<sup>1,2</sup> in the Stobbe condensation of aromatic aldehydes with dimethyl alkylidene succinate (**1**,  $R_3 = R_4 = \text{Me}$ ,  $R_1R_2 = \text{Cyclo } C_6H_{10}$ ,  $\text{Ph}_2$ ,  $\text{Cyclo } C_5H_8$ ,  $\text{Me}_2$ ) and it was conclusively established that the oxyanion (**2**) leads to the acid-esters which have *trans*-Ar/COOMe groups. Further support to this *trans*-Ar/COOMe rule has been obtained in the present study on the Stobbe condensation of  $\beta$ -naphthaldehyde with alkylidenesuccinates which were prepared by the condensation of dimethylsuccinate with acetophenone and benzophenone.

1- $\beta$ -Naphthyl-4,4-diphenylbutadiene-2,3-dicarboxylic acid (**3c**) and 1- $\beta$ -naphthyl-4-phenylbutadiene-2,3-dicarboxylic acid (**3f**) prepared by saponification of the acid-esters (**3a**) and (**3d**) obtained as Stobbe condensation products of dimethyl  $\beta$ -naphthylitaconate with acetophenone and benzophenone respectively, were found to be structurally the same as the diacids prepared by the other possible route (involving Stobbe condensation of dimethyl alkylidenesuccinates (**1e** and **1g**) with  $\beta$ -naphthaldehyde followed by saponification of the resultant acid-esters (**3b** and **3e**).

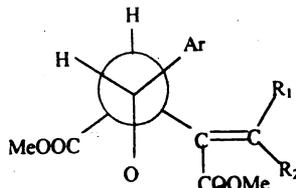
In addition to identification of diacids from the two different routes on the basis of m.m.p. determination and spectral data, their cyclizations were done with PPA and conc.  $H_2SO_4$  where indenones (**6**) were formed confirming the *trans*-Ar/COOMe geometry. (The indenonic structure was identified on the basis of IR (aryl five membered ring ketone absorptions at  $1720-1710 \text{ cm}^{-1}$ ) and PMR spectra (aromatic multiplet pattern shows the cyclizations occurring in benzene ring and also the undisturbed naphthalene peaks). These spectra have similarity with the spectra of earlier synthesised indenones.<sup>3,4</sup>

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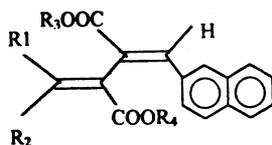
‡PPA, conc.  $H_2SO_4$  and internal Friedel-Crafts cyclisations.



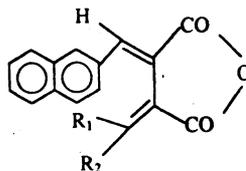
(1)



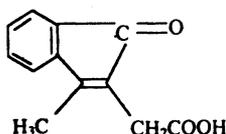
(2)



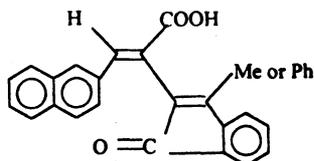
(3)



(4)

(a)  $R_1R_2=Ph_2$ ,  $R_3=Me$ ,  $R_4=H$ (b)  $R_1R_2=Ph_2$ ,  $R_3=R_4=H$ (c)  $R_1R_2=Ph_2$ ,  $R_3=R_4=Me$ (d)  $R_1=H$ ,  $R_2=2-C_{10}H_7$ ,  $R_3=R_4=Me$ (e)  $R_1R_2=PhMe$ ,  $R_3=Me$ ,  $R_4=H$ (f)  $R_1R_2=PhMe$ ,  $R_3=R_4=H$ (g)  $R_1R_2=PhMe$ ,  $R_3=R_4=Me$ (a)  $R_1R_2=Ph_2$ ,  $R_3=Me$ ,  $R_4=H$ (b)  $R_1R_2=Ph_2$ ,  $R_3=H$ ,  $R_4=Me$ (c)  $R_1R_2=Ph_2$ ,  $R_3=R_4=H$ (d)  $R_1R_2=PhMe$ ,  $R_3=Me$ ,  $R_4=H$ (e)  $R_1R_2=PhMe$ ,  $R_3=H$ ,  $R_4=Me$ (f)  $R_1R_2=PhMe$ ,  $R_3=R_4=H$ 

(5)



(6)

## EXPERIMENTAL

PMR spectra were recorded in  $CDCl_3$  using TMS as an internal standard and UV spectra in spectroscopic ethanol on a DMS-80 (Varian) spectrophotometer. The pH-metric titrations were done in aq. ethanol (50 : 50, v/v) on a direct reading ECIL pH-meter (model pH having a glass-calomel electrode assembly).

General procedures for Stobbe condensation and saponification of Stobbe condensation products and their cyclizations were similar as reported earlier<sup>1,2</sup>. Molecular weights of the acid products were determined by titrimetric method as their equivalent weights (Table-1).

TABLE-1  
 PHYSICAL AND SPECTRAL DATA OF ACID-ESTER (3a, 3b, 3d, 3e), DIACIDS (3c, 3f) AND INDENONES (6)\*

Compd	Yield† (%)	m.p.‡ (°C)	Eq. wt.††	pKa	$\lambda_{\max}$ (nm) (log $\epsilon$ )	IR (cm <sup>-1</sup> )	PMR ( $\delta$ , ppm)			
							Me	-OMe	Ar-H	-CH=
3a	85	173	433 (434)	9.00	234(4.73)	1715 1690	—	3.40	6.72-7.46 (17H)	8.01 (1H)
3b	80	186	432 (434)	8.30	225 (3.98) 270 (4.12)	1710 1695	—	3.95	7.00-7.9 (18H)	7.83 (1H)
3c	—	192	209 (210)	—	240 (4.20) 252 (4.00) 309 (3.85)	— 1690	—	—	6.3-7.8 (18H)	—
3d	87	180	374 (372)	8.75	270 (4.22) 308 (4.23)	1708 1675	2.46 (3H)	3.78	6.06-7.86 (12H)	8.00 (1H)
3e	85	—**	373 (372)	7.90	220 (3.22) 270 (3.00)	1717 1696	2.52 (3H)	3.89	7.09-7.92 (12H)	7.99 (1H)
3f	—	145	180 (179)	—	240 (4.01) 318 (3.00)	— 1690	2.49 (3H)	—	6.9-7.5 (12H)	7.77 (1H)
6 $\phi$	—	160	341 (340)	—	215 (4.52) 249 (4.55)	1720 1695	2.44 (3H)	—	6.45-8.15 (13H)	—
6 $\delta$	—	155	401 (402)	—	220 (4.58) 250 (4.50)	1710 1690	—	—	6.92-7.8 (17H)	8.11 (1H)

\* All the compounds gave satisfactory C and H analyses.

† Diacids were obtained in 90-100% and indenones in 80-100% yields.

‡ Solvents for crystallisation, benzene-n-hexane.

\*\* obtained as non-crystallisable oil.

†† Calculated values are given in parentheses.

$\phi$  with Me;  $\delta$  with Ph.

## RESULTS AND DISCUSSIONS

The UV, IR and NMR spectral data and the pKa values (Table-1) of all the compounds showed close similarity with those of the corresponding systems reported earlier which support the *trans*-Ar/COOMe orientation. The problem of geometrical isomerism existed in the Stobbe condensations with acetophenone<sup>4</sup>. The diacids (**1f** and **3f** with *cis*-Ph/COOH) identified by their cyclization\* and spectral data could be isolated by fractional crystallizations. In all these isolated products a *trans*- $\beta$ -naphthyl/COOH (or COOMe) orientation is detected.

## ACKNOWLEDGEMENT

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\*Stobbe condensation of acetophenone with dimethylsuccinate yielded oily acid-ester (**1e**) which on saponification and fractional crystallisation yielded diacid (**1f**) with *trans* Ph/CH<sub>2</sub>COOH groups. Internal Friedel-Crafts cyclizations of the corresponding anhydride, and PPA or conc. H<sub>2</sub>SO<sub>4</sub> cyclisation of the diacid (**1f**) gave indenone (**5**) in quantitative yields, m.p. 170°C, eq. wt. 201.65 (Calc. 202.20), UV: 235 (4, 76), 276 (4, 62); IR : 1712 (CO ring ketone), 1670 (CO acid), 1630, 1600 (C=C), 1220 (C—O); PMR: 2.49 (3H, s, Me), 3.26 (2H, s, CH<sub>2</sub>), 6.94–7.50 (4H, m-Ar).