

# ULTRAVIOLET SPECTRA OF $\alpha$ -CARBOXYSTILBENES

## II. $\alpha$ -*o*-Carboxyphenylcinnamic Acids

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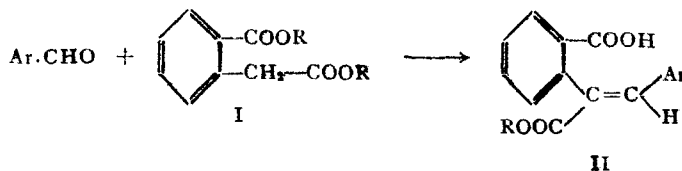
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### ABSTRACT

The ultraviolet spectra of methyl- $\alpha$ -*o*-carboxyphenyl cinnamates and  $\alpha$ -*o*-carboxyphenylcinnamic acids is reported. These compounds possess the characteristic *cis* stilbene spectral curve, thereby supporting Loewenthal and Pappo's suggestion that these compounds have *cis* Ph/Ph-COOR configuration. Formation of this isomer in the Stobbe reaction of dimethyl homophthalate and aryl aldehydes has been rationalized as proceeding *via* the erythro conformer of the oxyanion.

NUCLEAR substituted methyl- $\alpha$ -*o*-carboxyphenylcinnamates (II, R = CH<sub>3</sub>), and  $\alpha$ -*o*-carboxyphenylcinnamic acids, (II, R = H) were prepared by the Stobbe condensation of dimethyl homophthalate and aryl aldehydes (I); which gave the acid-esters (II, R = CH<sub>3</sub>) and these were hydrolysed to the corresponding diacids<sup>2</sup> (II, R = H).



A study of their ultraviolet spectra, showed that they all possessed the characteristic *cis* stilbene spectral curves.<sup>1</sup> The electronic effects of the substituents in the acids (II, R = H) showed their characteristic bathochromic shifts (Fig. 1), the shift for the diacids was based on an arbitrary 260 nm., calculated on 270 nm. for the *p*-chloro compound less 10 nm. as the shift of substituent,<sup>3</sup> as in the earlier paper<sup>1</sup> (see Table I).

The similarity of the UV curves of these compounds with *cis* stilbene curves corroborates Loewenthal and Pappo's<sup>2</sup> suggestion that these compounds have phenyl group *trans* to COOR.

TABLE I

*UV spectra of  $\alpha$ -o-carboxyphenylcinnamic acids/methyl- $\alpha$ -o-carboxyphenylcinnamates*

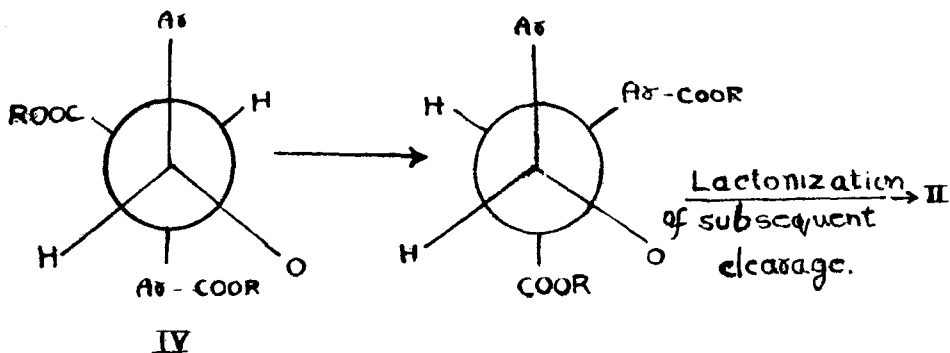
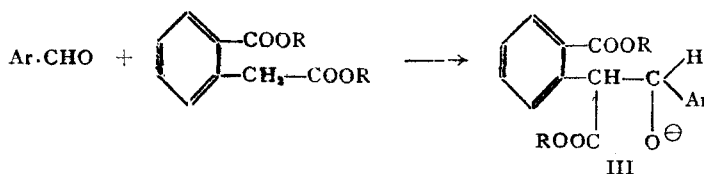
No.	Ar	Diacids II, R=H			Half-esters II, R=CH <sub>3</sub>	
		$\lambda_{\text{max.}}^{\text{EtOH}}$ nm.	$\Delta\lambda^*$ nm.	$\Delta\lambda$ Scott <sup>5</sup> nm.	$\lambda_{\text{max.}}^{\text{EtOH}}$ nm.	$\Delta\lambda_2$ nm.
1.	<i>p</i> . Cl. Ph	270	(-10)	+10	289	+19
2.	<i>p</i> . OCH <sub>3</sub> . Ph	289	+29	+25	304	+15
3.	3:4 (OCH <sub>3</sub> ) <sub>2</sub> . Ph#	293	+33	..	304	+11
		306			320	+14
4.	3:4 (O·CH <sub>2</sub> ·O). Ph#	291	+31	..	299	+8
		313			324	+11
5.	O.Cl.Ph	264	+4	+5	277	+13
					285	
6.	<i>p</i> .CH <sub>3</sub> .Ph	271	+11	+10	291	+20
7.	Ph	267	..		284	+17

$\Delta\lambda^*$  = With respect to 270 nm. for *p*-chloro compound *minus* 10 nm.

$\Delta\lambda_2$  =  $\lambda_{\text{max.}}^{\text{EtOH}}$  Ester-  $\lambda_{\text{max.}}^{\text{EtOH}}$  acid.

# = These compounds show 2 speaks in the E.T. band.

Formation of a *cis* Ph/Ph-COOR isomer, predominantly in these reactions, could be rationalized through an argument similar to the one pro-



pounded earlier<sup>4</sup> that the anion (III) will be more stable in the erythro conformation (IV) (mesolike structure, the bulkiest groups opposing one another) rather than the threo one and that the erythro structure would lead to the *cis* Ph/Ph-COOR isomer (II), after lactonization and subsequent cleavage.

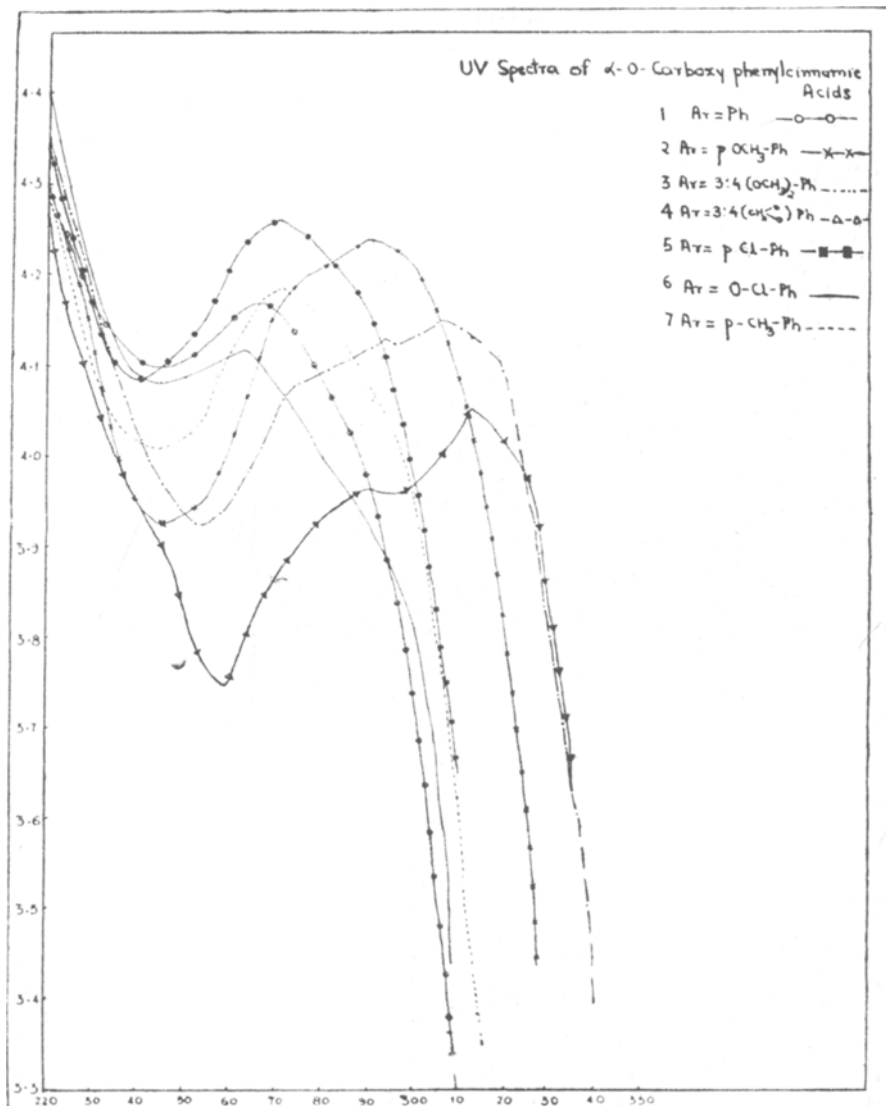


FIG. 1

All the acid-esters (II, R = CH<sub>3</sub>) also showed the characteristic spectral curves (Fig. 2), and a distinct shift of about 10–20 nm. over the acid value to the longer wavelength as in the earlier series.<sup>1</sup>

### EXPERIMENTAL

The ultraviolet spectra were recorded on Beckmann DU 2 spectrophotometer with ethanol as solvent.

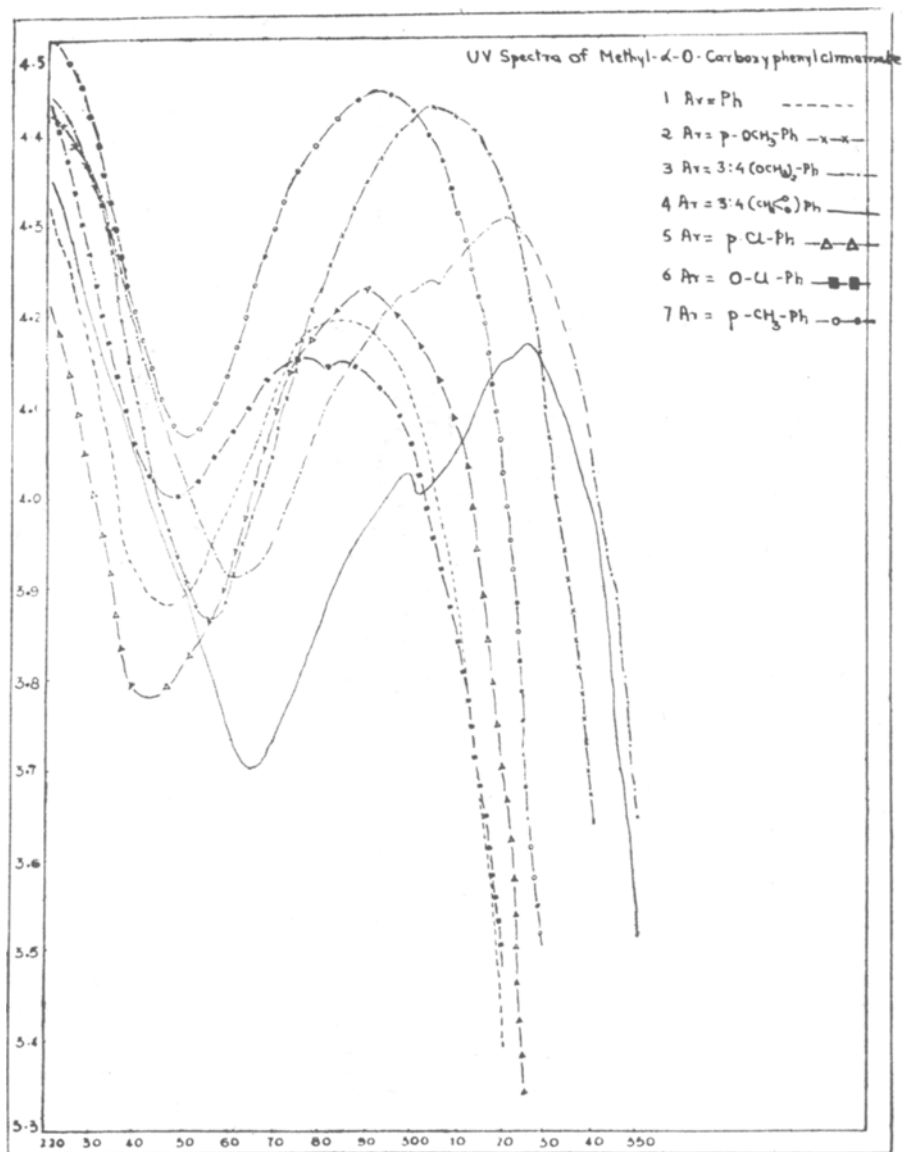


FIG. 2

TABLE II  
 Stobbe condensation of dimethyl homophthalate with aromatic aldehydes

No.	Aldehyde I, Ar = <sup>a</sup> g.	Half-ester II, R = CH <sub>3</sub>	Diacid (Prepared by saponification of half-ester II, R = H)
1.	Ph (4.0 g.)	9 g., 84%, m.p. 151°, lit. <sup>2</sup> 152°, $\lambda_{\text{max}}^{\text{EtOH}}$ 284 nm., (4.19).	m.p. 207°, lit. <sup>2</sup> 200°, $\lambda_{\text{max}}^{\text{EtOH}}$ 267 nm., (4.17).
2.	<i>p</i> . OCH <sub>3</sub> .Ph (5.0 g.)	9.8 g., 83% <sub>or</sub> , m.p. 151°, $\lambda_{\text{max}}^{\text{EtOH}}$ 304 nm., (4.43); Found: eq. wt., 311, C, 69.5, H, 5.1; reqd. for C <sub>18</sub> H <sub>16</sub> O <sub>6</sub> : eq. wt., 312, C, 69.1, H, 5.1%.	m.p. 206–207°, lit. <sup>6a</sup> 208–209°, $\lambda_{\text{max}}^{\text{EtOH}}$ 289 nm., (4.23).
3.	3:4 (OCH <sub>3</sub> ) <sub>2</sub> .Ph (2.10 g.)	4 g., 93%, m.p. 180°, $\lambda_{\text{max}}^{\text{EtOH}}$ 304, 320 nm., (4.23, 4.30). Found: eq. wt., 341, C, 66.8, H, 4.92; reqd. for C <sub>19</sub> H <sub>18</sub> O <sub>6</sub> : eq. wt., 342, C, 66.6, H, 5.2%.	m.p. 193°, lit. <sup>6a</sup> 196°, $\lambda_{\text{max}}^{\text{EtOH}}$ 293, 306 nm., (4.12, 4.15).
4.	3:4 (O·CH <sub>2</sub> ·O).Ph (3.70 g.)	7.5 g., 92%, m.p. 170°, $\lambda_{\text{max}}^{\text{EtOH}}$ 299, 324 nm., (4.02, 4.17). Found: eq. wt., 325, C, 66.5, H, 4.1; reqd. for C <sub>18</sub> H <sub>14</sub> O <sub>6</sub> : eq. wt., 326, C, 66.2, H, 4.2%.	m.p. 232°, lit. <sup>6a</sup> 235°, $\lambda_{\text{max}}^{\text{EtOH}}$ 291, 313 nm., (3.96, 4.05).
5.	<i>p</i> . Cl.Ph (2.50 g.)	5 g., 85%, m.p. 108°, $\lambda_{\text{max}}^{\text{EtOH}}$ 289 nm., (4.23). Found: eq. wt., 317, C, 64.2, H, 4.0; reqd. for C <sub>17</sub> H <sub>13</sub> O <sub>4</sub> Cl: eq. wt., 316.5, C, 64.4, H, 4.1%.	m.p. 212°, $\lambda_{\text{max}}^{\text{EtOH}}$ 270 nm., (4.26). Found: eq. wt., 150, C, 63.1, H, 3.6; reqd. for C <sub>18</sub> H <sub>13</sub> O <sub>4</sub> Cl, eq. wt., 151.2, C, 63.4, H, 3.6%.
6.	<i>o</i> . Cl.Ph (3.0 g.)	6.5 g., 92%, m.p. 143°, $\lambda_{\text{max}}^{\text{EtOH}}$ 277, 285 nm., (4.15, 4.15). Found: eq. wt., 316, C, 64.05, H, 3.97; reqd. for C <sub>17</sub> H <sub>13</sub> O <sub>4</sub> Cl, eq. wt., 316.5, C, 64.4, H, 4.1%.	m.p. 233°, lit. <sup>6b</sup> 240°, $\lambda_{\text{max}}^{\text{EtOH}}$ 264 nm., (4.11).
7.	<i>p</i> . CH <sub>3</sub> .Ph (3.0 g.)	6.5 g., 86%, m.p. 134°, $\lambda_{\text{max}}^{\text{EtOH}}$ 291 nm., (4.45). Found: eq. wt., 295, C, 73.02, H, 5.18, reqd. for C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> : eq. wt., 296, C, 72.98, H, 5.4%.	m.p. 233°, $\lambda_{\text{max}}^{\text{EtOH}}$ 271 nm., (4.18). Found: eq. wt., 140, C, 72.5, H, 4.6; reqd. for C <sub>17</sub> H <sub>14</sub> O <sub>4</sub> : eq. wt., 141, C, 72.3, H, 4.96%.

(1) *Dimethyl homophthalate*.—Homophthalic acid was prepared by potassium dichromate-sulphuric acid oxidation of indene,<sup>5</sup> and dimethyl homophthalate was obtained by diazomethane esterification of the acid.

(2) *Methyl- $\alpha$ -*o*-carboxyphenyl-3'-4'-methylenedioxy*cinnamate ( $R = CH_3$ ,  $Ar = 3:4$  methylenedioxyphenyl).—Piperonal (3.7 g.) and dimethyl homophthalate (5.2 g.) was added to butanolic potassium tert. butoxide (from 1 g. potassium in 30 ml. tert. butanol), and stirred magnetically for 30 minutes under inert anhydrous conditions at room temperature. The reaction mixture was acidified to Congo red with 6 N hydrochloric acid and tert. butanol was removed under reduced pressure. The residue was taken up in ether and was repeatedly extracted with ice-cold sodium carbonate solution. The resulting alkaline layer on acidification with 6 N hydrochloric acid gave methyl- $\alpha$ -*o*-carboxyphenyl-3'-4'-methylenedioxycinnamate (II,  $R = CH_3$ ,  $Ar = 3:4$  methylenedioxyphenyl) 7.5 g., yield 92%, crystallized from benzene, m.p.  $170^\circ$   $\lambda_{\text{max.}}^{\text{EtOH}}$  299 nm.,  $\log \epsilon = 4.02$ , 324 nm.,  $\log \epsilon = 4.17$ . Found: eq. wt., 325, C, 66.5, H, 4.1; reqd. for  $C_{18}H_{14}O_6$ , eq. wt., 326, C, 66.2; H, 4.2%.

(3)  *$\alpha$ -*o*-Carboxyphenyl-3'-4'-methylenedioxy*cinnamic acid.—Methyl- $\alpha$ -*o*-carboxyphenyl-3'-4'-methylenedioxycinnamate (II,  $R = CH_3$ ,  $Ar = 3:4$  methylenedioxyphenyl) (1 g.) was refluxed with 8% aqueous sodium hydroxide (25 ml.) for 5 hours. On acidification it gave  $\alpha$ -*o*-carboxyphenyl-3'-4'-methylenedioxycinnamic acid (0.9 g.) (II,  $R = H$ ,  $Ar = 3:4$  methylenedioxyphenyl), crystallized from rectified spirit, m.p.  $232^\circ$ , lit. 6a,  $235^\circ$ ,  $\lambda_{\text{max.}}^{\text{EtOH}}$  291 nm.,  $\log \epsilon = 3.96$ , 313 nm.,  $\log \epsilon = 4.05$ . Found: eq.wt. 155; reqd. for  $C_{17}H_{12}O_6$ : eq.wt., 156.

Similarly other aldehydes were condensed with dimethyl homophthalate and corresponding products isolated (see Table II).

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. Bagavant, G. and Patwardhan, B. H. .. Previous paper.

2. Loewenthal, H. J. E. and Pappo, R. .. *J. Chem. Soc.*, 1952, p. 4799.
3. Scott, A. I. .. *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, 1964, p. 109.
4. Patwardhan, B. H. and Bagavant, G. .. *Curr. Sci.*, 1971, **40**, 350; *Ind. J. Chem.*, 1972, **10**, 59.
5. Horning, E. C. .. *Organic Synthesis*, John Wiley & Sons, New York, Coll. Vol. 1955, **3**, 449.
6. (a) Buu Hoi .. *Compt. Rend.*, 1944, **211**, 643; *Chem. Abstr.*, 1942, **36**, 758.  
(b) ————— .. *Ibid.*, 1944, **218**, 942; *Chem. Abstr.*, 1946, **40**, 4046.