

ULTRAVIOLET SPECTRA OF α -CARBOXYSTILBENES—I

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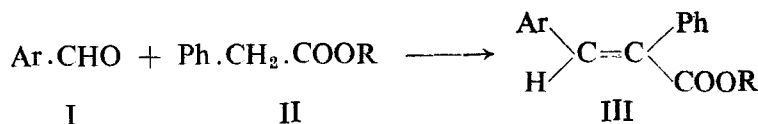
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ABSTRACT

The ultraviolet spectra of α -carboxy and α -carbomethoxystilbenes obtained in the Claisen/Stobbe reaction of methyl phenyl acetate and aromatic aldehydes is reported. All these compounds possess the characteristic *cis* stilbene spectral curve. Electronic effects of substituents in the acid show characteristic bathochromic shifts. A few *trans* α -carboxystilbenes have been prepared and their spectra have the characteristic *trans* stilbene pattern.

NUCLEAR substituted *cis* α -carboxystilbenes (III, R = H) and their esters (III, R = CH₃) were prepared by the alkoxide catalysed condensation of methyl phenyl acetate (II R = CH₃) and aryl aldehydes (I).¹



A study of their ultraviolet spectra (Figs. 1, 2) showed that they all possessed the characteristic *cis* stilbene spectral curves,^{2,3} where the E.T. band has an extinction coefficient less than the absorption of 220 nm (*see* Fig. 3 for *trans* stilbenes) (except for III, Ar = furyl) further the electronic effects of the substituents in the acids, (III, R = H) showed characteristic bathochromic shifts^{4a}; (as the compound Ar = Ph showed abnormality, the shift was based on an arbitrary 266 nm. calculated on 276 nm. for the *p*-chloro compound less 10 nm. as shift of substituent^{4a}).

The compound (III Ar = Ph, R = H) had the characteristic pattern, but had $\lambda_{\text{max}}^{\text{EtOH}}$ 279 nm., $\log \epsilon = 4.21$, but by independent evidence, the *cis* structure has been established unequivocally for it.¹

All the methyl esters also showed the characteristic spectral curves (Fig. 2), and a distinct shift of about 10–15 nm. over the acid value to the longer wavelength, though Scott^{4b} states that the difference is not usually greater than 2 nm.

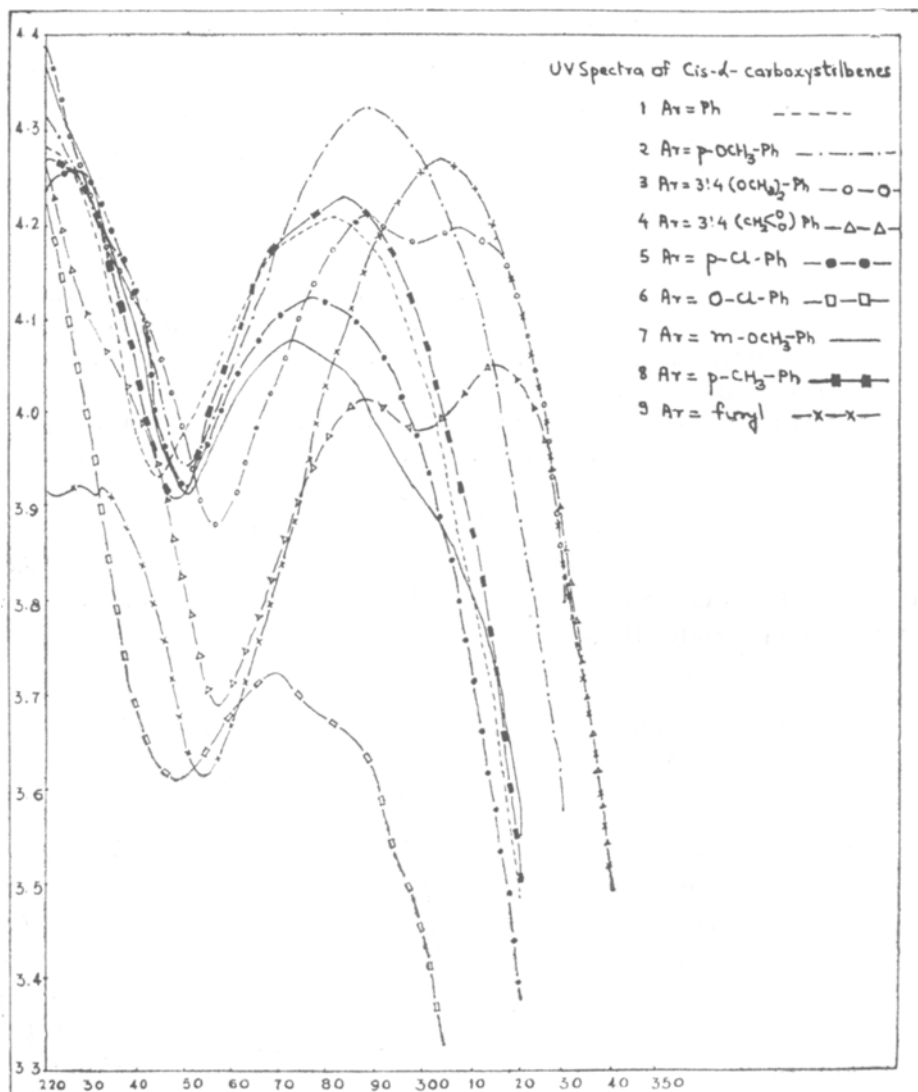


FIG. 1

The IR spectra of these compounds (III, R = H), e.g., Ar = *p*-Cl-C₆H₄, *m*-OCH₃-C₆H₄ and Ar = *p*-CH₃-C₆H₄ showed a broad peak of OH stretch

at 2925 cm^{-1} , a phenyl conjugated α, β -unsaturated acid peak at 1670 cm^{-1} a $\text{C}=\text{C}$ conjugated peak at 1600 cm^{-1} and the $\text{C}-\text{O}$ stretch peak at 1260 cm^{-1} ,⁵

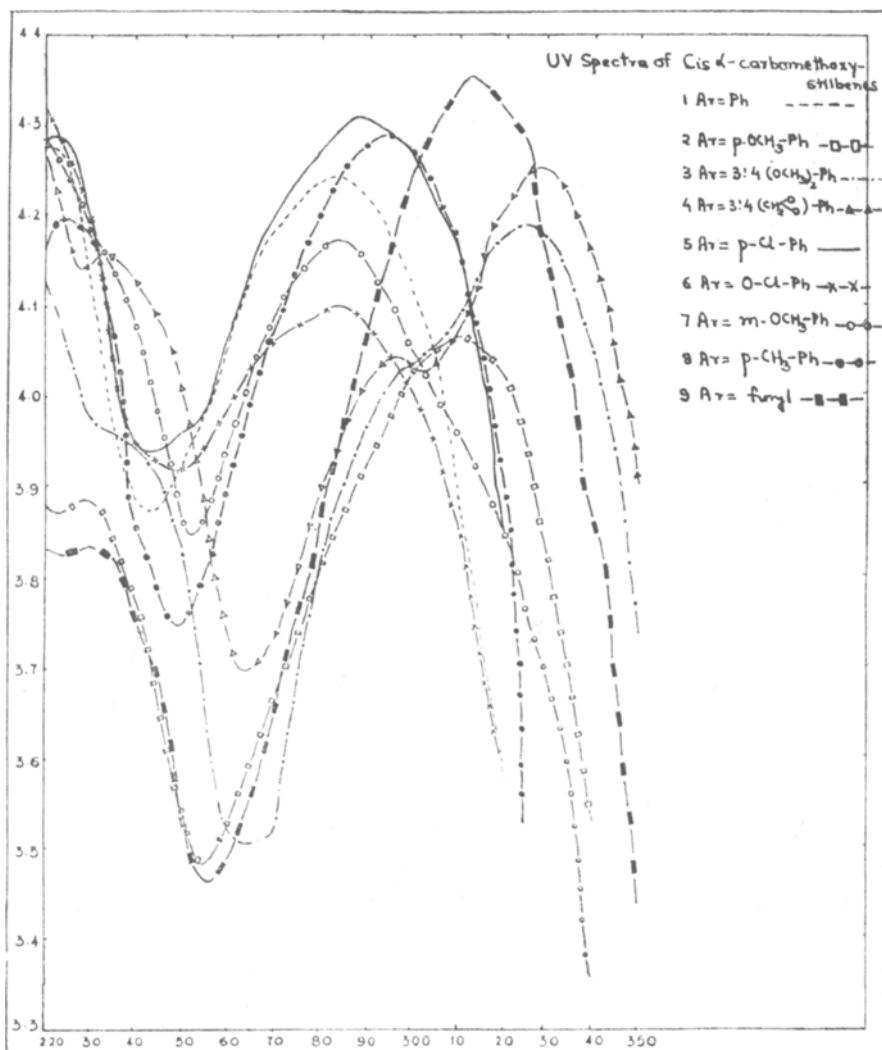


FIG. 2

Similarly the ester, (III, $\text{R} = \text{CH}_3$) showed a conjugated ester peak at 1720 cm^{-1} a $\text{C}=\text{C}$ conjugated peak at 1600 cm^{-1} and a $\text{C}-\text{O}$ stretch peak at 1255 cm^{-1} ,⁵

Some *trans* stilbene systems (IV) prepared by the Perkin reactions of aldehydes (I) and phenylacetic acid⁶ (II, $\text{R} = \text{H}$) showed the characteristic

trans stilbene curves with L.E. band at 225 nm. having a smaller extinction coefficient than the E.T. band (see Fig. 3).

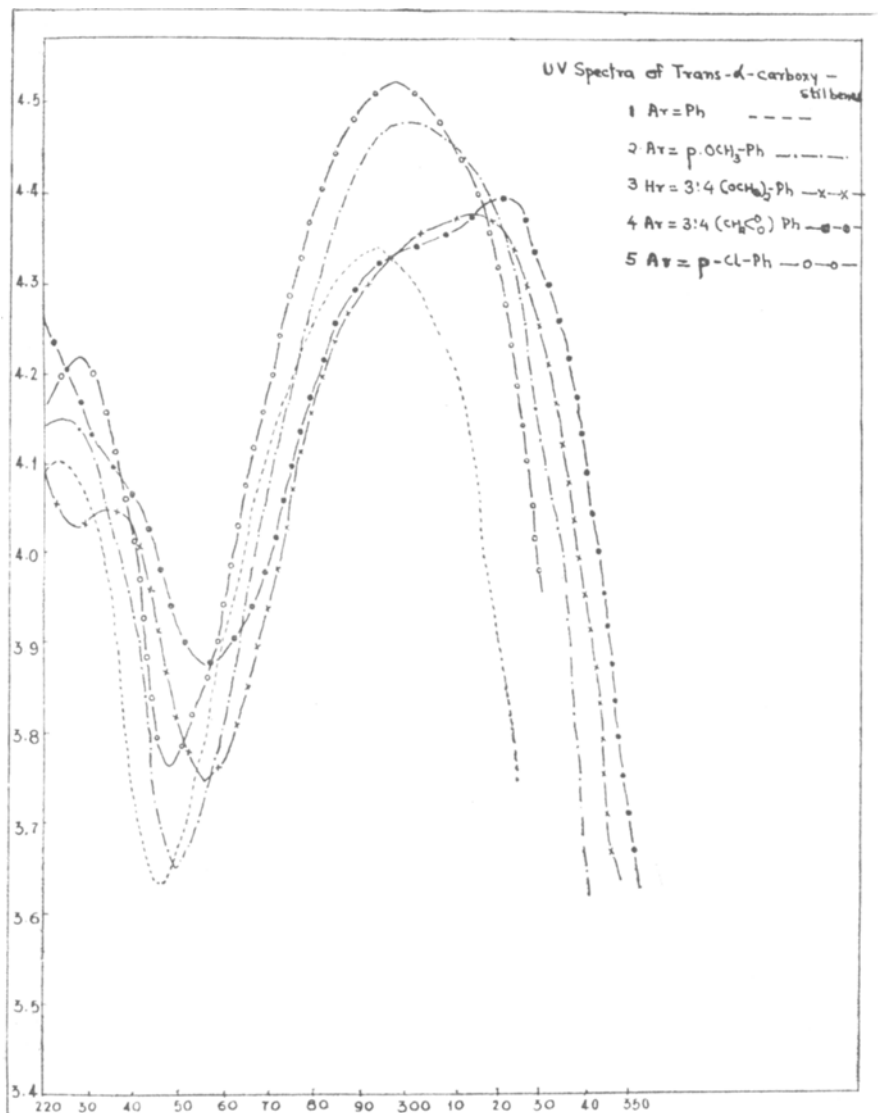
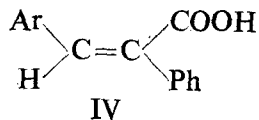


FIG. 3

EXPERIMENTAL

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

The *cis* acids and esters (III) were prepared by the Claisen/Stobbe condensation of the aldehyde and methyl phenyl acetate, as described earlier¹ (see Table II).

TABLE I
UV Spectra of Cis α carboxy/ α -carbomethoxystilbenes

No.	Ar	Acid			Ester	
		$\lambda_{\max}^{\text{EtOH}}$ nm.	$\Delta\lambda^*$ nm.	$\Delta\lambda$ Scott ^{4a} , for Ar Co.R. nm.	$\lambda_{\max}^{\text{EtOH}}$ nm.	$\Delta\lambda_2$ nm.
1.	<i>p</i> -Cl. Ph	276	(-10) Std.	+10	287	+11
2.	<i>p</i> -OCH ₃ . Ph	287	+21	+25	309	+22
3.	3 : 4 (OCH ₃) ₂ . Ph†	287 315	+21		300 325	+13 +10
4.	3 : 4 (O.CH ₂ O). Ph†	287 315	+21		295 325	+8 +10
5.	<i>m</i> . (OCH ₃). Ph	272	+6	+7	284	+12
6.	<i>o</i> . Cl.Ph	270	+4	+5	284	+14
7.	<i>p</i> . CH ₃ . Ph	283	+17	+10	295	+12
8.	Ph	279			284	

$\Delta\lambda^*$ With respect to 276 nm. for $\lambda_{\max}^{\text{EtOH}}$ *p*-chloro compound minus 10 nm.

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

† These compounds show 2 peaks in the E.T. band.

The *trans* α -carboxystilbenes were prepared by Perkin reaction of aldehydes with phenylacetic acid.^{6,7}

TABLE II
Claisen/Stobbe condensation of aromatic aldehydes with methyl phenyl acetate

No.	Aldehyde I	Acid product III, R = H	Neutral product III, R = CH ₃
1.	Ar = Ph (5.3 g.)	5.5 g., 48%, m.p. 170-2°, lit. ^{3, 7, 8} 170° λ _{max} ^{EtOH} . 220, 279 nm., (4.28, 4.20).	6.1 g., 52%, m.p. 75-76°, lit. ^{8, 9} 76° λ _{max} ^{EtOH} 284 nm., (4.23).
2.	Ar = <i>p</i> -OCH ₃ .Ph (7.0 g.)	3 g., 23%, m.p. 189° lit. ^{7, 8, 9} 189° λ _{max} ^{EtOH} 287 nm. (4.33).	7 g., 51%, m.p. 90°, lit. ⁸ 90°, λ _{max} ^{EtOH} 310 nm., (4.07).
3.	Ar = 3:4 (OCH ₃) ₂ .Ph (8.5 g.)	4.4 g., 30%, m.p. 224°, λ _{max} ^{EtOH} 287, 307 nm., (4.21, 4.20). Found: eq. wt. 284, C, 71.3, H, 5.2; reqd. for C ₁₇ H ₁₆ O ₄ ; eq. wt. 284; C, 71.8, H, 5.6%.	6 g., 40%, m.p. 106-107°, λ _{max} ^{EtOH} 325 nm., (4.19) Found: C, 72.1, H, 5.9; reqd. for C ₁₈ H ₁₈ O ₄ : C, 72.49; H, 6.04%.
4.	Ar = 3:4 (O.CH ₂ .O).Ph (6.5 g.)	3 g., 26%, m.p. 232°, lit. ^{8, 9} 233°, λ _{max} ^{EtOH} 287, 315 nm., (4.01, 4.05).	7 g., 57%, m.p. 106-107°, lit. ⁸ 106° λ _{max} ^{EtOH} 296, 328 nm., (4.04, 4.24).
5.	Ar = <i>p</i> -Cl.Ph (7.0 g.)	4.7 g., 38%, m.p. 198-199°, λ _{max} ^{EtOH} 227, 276 nm., (4.25, 4.12). Found: eq. wt. 258, C, 69.7, H, 4.3; reqd. for C ₁₈ H ₁₁ O ₃ Cl: eq. wt. 258.5; C, 69.6, H, 4.4%.	7.2 g., 53%, m.p. 100°, λ _{max} ^{EtOH} 222, 287 nm., (4.29, 4.30). Found: C, 70.4, H, 4.7; reqd. for C ₁₉ H ₁₃ O ₂ Cl: C, 70.4, H, 4.7%.

6. Ar = *o*.Cl.Ph (7.0 g.) .. 7.4 g., 49%, m.p. 127°, $\lambda_{\text{max}}^{\text{EtOH}}$, 267, 270 nm., (3.71, 3.72). Found: eq. wt. 257, C, 69.2, H, 4.5; reqd. for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Cl}$: eq. wt. 258.5, C, 69.6, H, 4.4%.
7. Ar = *p*-CH₃.Ph (6.0 g.) .. 4 g., 35%, m.p. 168°, lit.⁹ 168°, $\lambda_{\text{max}}^{\text{EtOH}}$, 283 nm., (4.22).
8. Ar = *m*-OCH₃.Ph (7.0 g.) .. 6.3 g., 47%, m.p. 188°, lit.^{9, 10} 188° $\lambda_{\text{max}}^{\text{EtOH}}$, 272 nm., (4.07).
9. Ar = furyl (5 g.) .. 2 g., 20%, m.p. 146°, $\lambda_{\text{max}}^{\text{EtOH}}$, 228, 232, 302 nm., (3.92, 3.92, 4.27). Found: eq. wt. 213, C, 73.2, H, 4.9; reqd. for $\text{C}_{18}\text{H}_{10}\text{O}_3$: eq. wt. 214, C, 72.9, H, 4.6%.
- 6.7 g., 44%, m.p. 72°, $\lambda_{\text{max}}^{\text{EtOH}}$, 284 nm., (4.10). Found: C, 70.2, H, 4.7; reqd. for $\text{C}_{16}\text{H}_{13}\text{O}_2\text{Cl}$: C, 70.4, H, 4.7%.
- 8 g., 60%, m.p. 83°, $\lambda_{\text{max}}^{\text{EtOH}}$, 224, 295 nm. (4.19, 4.28). Found: C, 80.6, H, 6.17; reqd. for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.5, H, 6.37%.
- 6.8 g., 51%, m.p. 56°, $\lambda_{\text{max}}^{\text{EtOH}}$, 284 nm., (4.16). Found: C, 76.1, H, 5.7; reqd. for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.12, H, 5.97%.
- 5.4 g., 47%, m.p. 85°, $\lambda_{\text{max}}^{\text{EtOH}}$, 230, 313 nm., (3.83, 4.35). Found: C, 73.6, H, 5.2; reqd. for $\text{C}_{14}\text{H}_{12}\text{O}_3$: C, 73.6, H, 5.26%.

TABLE III
Perkin reaction of phenylacetic acid and aromatic aldehydes

No.	Aldehyde I	III, R = H	IV
1.	Ar = Ph (30 g.)	29 g., 60%, m.p. 170-2°, lit. ^{3,7,8} 172°, $\lambda_{\text{max}}^{\text{EtOH}}$ 220, 279 nm. (4.28, 4.21).	3.1 g., 6%, m.p. 137° lit. ^{3,7} 137°, $\lambda_{\text{max}}^{\text{EtOH}}$ 224, 294 nm., (4.10, 4.34).
2.	Ar = <i>p</i> -OCH ₃ .Ph (13.6 g.)	17 g., 68%, m.p. 189°, lit. ^{7,8,9} 189°, $\lambda_{\text{max}}^{\text{EtOH}}$ 287 nm., (4.33).	1.7 g., 6.8%, m.p. 119-120°, lit. ⁷ 120°, $\lambda_{\text{max}}^{\text{EtOH}}$ 303 nm. (4.48).
3.	Ar = 3:4(OCH ₃) ₂ .Ph (16.6 g.)	21 g., 73%, m.p. 224°, $\lambda_{\text{max}}^{\text{EtOH}}$ 287, 307 nm. (4.21, 4.20). Found: eq. wt., 284, C, 71.5, H, 5.3; reqd. for C ₁₇ H ₁₆ O ₄ , eq. wt., 284, C, 71.8, H, 5.6%	2 g., 7%, m.p. 162-163°, $\lambda_{\text{max}}^{\text{EtOH}}$ 314 nm. (4.37). Found: eq. wt., 283, C, 71.4, H, 5.4; reqd. for C ₁₇ H ₁₆ O ₄ , eq. wt., 284, C, 71.8, H, 5.6%.
4.	Ar = 3:4(O.CH ₂ .O).Ph (15 g.)	20 g., 74%, m.p. 232°, lit. ^{8,9} 232° $\lambda_{\text{max}}^{\text{EtOH}}$ 287, 315 nm., (4.01, 4.05).	2.7 g., 10%, m.p. 106°, $\lambda_{\text{max}}^{\text{EtOH}}$ 319 nm., (4.39). Found: eq. wt., 267, C, 71.7 H, 4.5; reqd. for C ₁₆ H ₁₂ O ₄ , wt., 268 C, 71.6 H, 4.4%.
5.	Ar = <i>p</i> -Cl.Ph (13 g.)	20 g., 70%, m.p. 198-199°, $\lambda_{\text{max}}^{\text{EtOH}}$ 227, 276 nm., (4.25, 4.12). Found: eq. wt., 258, C, 69.8, H, 4.4; reqd. for C ₁₅ H ₁₁ O ₂ Cl, eq. wt., 258.5, C, 69.6, H, 4.4%.	2 g., 7%, m.p. 132-133°, $\lambda_{\text{max}}^{\text{EtOH}}$ 228, 298 nm., (4.21, 4.52). Found: eq. wt., 257, C, 69.6, H, 4.7; reqd. for C ₁₅ H ₁₁ O ₂ Cl, eq. wt., 258.5, C, 69.6, H, 4.4%.

Cis and trans α -carboxy-4'-chlorostilbene.—*p*-Chlorobenzaldehyde (13 g.) and phenylacetic acid (13.6 g.) were refluxed for 35 minutes in presence of 20 ml. acetic anhydride and 20 ml. triethylamine. The reaction mixture was cooled, and acidified with concentrated hydrochloric acid. The precipitated solid was filtered, and repeatedly extracted with 2% sodium hydroxide solution. The resulting alkaline suspension was filtered and the filtrate acidified with acetic acid to pH 6 using universal indicator paper. The precipitated solid was filtered, dried and crystallized from aqueous ethanol, when it yielded, *cis* α -carboxy-4'-chloro-stilbene (III; Ar = *p*-Cl-C₆H₄), 20 g., yield 70%, m.p. 198–199°, $\lambda_{\text{max}}^{\text{EtOH}}$ 227 nm., log ϵ = 4.25, 276 nm., log ϵ = 4.12. Found: eq. wt., 258; C, 69.8, H, 4.4; reqd. for C₁₅H₁₁O₂Cl: eq. wt., 258.5, C, 69.6, H, 4.4%.

The filtrate on acidification with concentrated hydrochloric acid and chilling overnight gave *trans* α -carboxy-4'-chlorostilbene (IV, Ar = *p*-Cl-C₆H₄). Crystallized from benzene, 2 g., yield 7%, m.p. 132–133°. $\lambda_{\text{max}}^{\text{EtOH}}$ 228 nm., log ϵ = 4.21, 298 nm., log ϵ = 4.52. Found: eq. wt., 257; C, 69.6, H, 4.7; reqd. for C₁₅H₁₁O₂Cl: eq. wt. 258.5, C, 69.6, H, 4.4%.

Similarly other *trans* α -carboxystilbenes were obtained (see Table III).

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