

Studies in Light Absorption. Part XIII. Steric Effects in ortho-Substituted Styryl and Related Derivatives.*

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The effects of *ortho*-substituents on the ultraviolet spectra of styrene, benzylideneacetone, and related derivatives of the type Ph·CH=CHX are analysed in terms of the principles outlined in Part XI.*

THE discussion given in the two preceding papers of steric effects in ultraviolet spectra of conjugated aromatic and ethylenic ketones led to the conclusion, amongst others, that marked hindrance to planarity is caused by interference between the groups attached to the carbonyl function, rather than between such groups and the carbonyl function itself. Since valency angles at a doubly bonded carbon tend to be about the same (120°) whatever the other ligands, it might be expected that conjugated systems involving C=C in place of C=O groups might exhibit similar effects. That this is indeed the case is qualitatively apparent from the spectra of substituted styrenes, stilbenes, etc. (*inter al.*, Ley, *Ber.*, 1917, 50, 243; 1918, 51, 1808; 1923, 56, 771; Ramart-Lucas and Hoch, *Bull. Soc. chim. France*, 1935, 327; 1938, 848; R. N. Jones, *J. Amer. Chem. Soc.*, 1941, 63, 1658; 1943, 65, 1815, 1818; Rodebush and Feldmann, *ibid.*, 1946, 68, 896; Murray and Gallaway, *ibid.*, 1948, 70, 3867; Beale and Roe, *ibid.*, 1952, 74, 2302; Braude, Jones, and Stern, *J.*, 1947, 1087; Bryant, Kennedy, and Tanner, *J.*, 1949, 2389; Bharucha and Weedon, *J.*, 1953, 1571), and the present paper is concerned with a semiquantitative evaluation of these phenomena in terms of the principles outlined in Part XI (*loc. cit.*).

Data concerning *o*-alkylated styrenes and styryl derivatives are summarised in Table I. Most of the data have been taken from the literature, but those relating to 2-methyl- and 2:6-dimethyl-benzylideneacetone and their derivatives are new; the synthesis of these

TABLE I. *Ultraviolet absorption of o-alkylated styrene derivatives (main bands only).*

	X = H	CH=CH ₃	CHMe·OH	COMe	CMe=N·NH·CO·NH ₂
Ph·CH=CHX λ _{max.} (Å)	2440 ¹	2800 ³	2510 ³	2860 ⁵	3050 ⁵
ε	14,000	28,300	19,500	22,200	38,600
2-Me·C ₆ H ₄ ·CH=CHX λ _{max.} (Å)	2450 ¹	2810 ³	2550 ³	2900 ⁵	3040 ⁵
ε	12,600	25,000	16,000	17,000	32,500
ε/ε ₀	0.78	0.83	0.74	0.71	0.84
θ	28	24	30	33	23
2:6-Me ₂ C ₆ H ₃ ·CH=CHX λ _{max.} (Å)	—	—	—	2910 ⁵	2820 ⁵
ε	—	—	—	10,500	23,300
ε/ε ₀	—	—	—	0.40	0.60
θ	—	—	—	50	39
2:4:6-Me ₃ C ₆ H ₃ ·CH=CHX λ _{max.} (Å)	2450 ²	—	2510 ⁴	2930 ⁴	—
ε	7000	—	7500	14,000	—
ε/ε ₀	0.35	—	0.29	0.50	—
θ	54	—	57	44	—

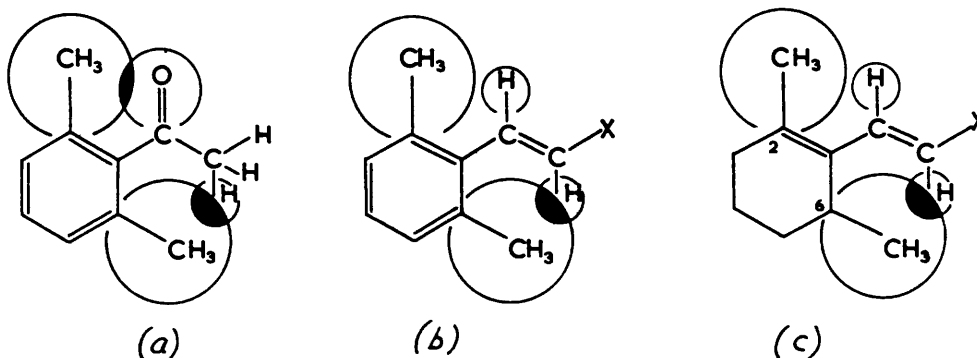
¹ Ramart-Lucas and Hoch, *loc. cit.* (in ethanol). The data to be found in the literature for styrene and substituted styrenes are extremely variable, probably owing to the presence of polymeric materials in some of the specimens used. The ε values cited are amongst the highest recorded. ² Bryant *et al.*, *loc. cit.* (in octane). ³ Braude, Jones, and Stern, *loc. cit.* (in ethanol). ⁴ Bharucha and Weedon, *loc. cit.* (in ethanol). ⁵ This paper.

compounds is detailed in the Experimental section. It will be seen that *ortho*-methyl substituents without exception cause what have been labelled type (1) steric effects, *i.e.*, reductions in the intensities of the characteristic *K*-bands without accompanying hypsochromic wavelength displacements. Published data for styrenes, methylstyrylcarbinols, and phenylbutadienes (Bryant *et al.*, *loc. cit.*; Braude, Jones, and Stern, *loc. cit.*) show that *p*-methyl substituents generally cause a small increase in ε ($\Delta\epsilon \sim +2000$) and it may be assumed that, in the absence of steric hindrance, *o*-methyl substituents would have similar effects. The ratios ε/ε₀ of the values of observed extinction coefficients to those expected

* Parts XI and XII, preceding papers.

on this basis in the systems $\text{Ph}\cdot\text{CH}=\text{CHX}$ vary appreciably with X but are of the order of 0.7—0.8 for one, and 0.3—0.5 for two *o*-methyl substituents. The interplanar angles θ between the phenyl and the $\text{CH}=\text{CHX}$ group calculated from these ratios by the equation $\cos^2 \theta = \epsilon/\epsilon_0$ (assuming $\theta = 0^\circ$ for the unsubstituted compounds) range from *ca.* 20° to 30° for one, and from *ca.* 40° to 60° for two *o*-methyl substituents.

The values of θ in Table I are, not unexpectedly, similar to those for *o*-substituted acetophenones (Part XI, *loc. cit.*). All the compounds in this Table are known to possess, or may be assumed from their methods of preparation to possess, *trans*-configurations at the ethylenic double bond, and significant overlap will therefore occur only between an *o*-methyl substituent and the $\text{C}=\text{CH}$ moiety (Fig. *b*). Such overlap will not differ very



greatly from that between an *o*-methyl substituent and the $\text{C}-\text{CH}_3$ moiety in acetophenones (Fig. *a*); $\text{C}=\text{CH}$ is more rigid and the interfering hydrogen atom lies exactly in the plane of the chromophoric group, but this will be compensated to some extent by the fact that although none of the hydrogen atoms in $\text{C}-\text{CH}_3$ need lie in the plane of the chromophoric group, two hydrogen atoms instead of one will, then, by necessity, be within the repulsion radius of the *o*-methyl substituent.

Since the β -substituent X is not, according to the Figure, involved in steric hindrance to uniplanarity, the nature of the substituent should, as a first approximation, have no significant influence on θ . The second-order variation of θ with X which is actually observed may have several causes. One is that when X is itself a strongly conjugating group such as $\text{CH}=\text{CH}_2$, COMe , or CO_2H , it will affect the electronic forces which oppose non-planarity throughout the whole conjugated system. Another factor which has been neglected in the semiquantitative treatment given in this and the two preceding papers is that an accurate measure of transition probabilities is represented by integrated band areas rather than by ϵ_{max} . The use of ϵ_{max} will cause little error as long as the band shapes in a series of spectra remain closely comparable, but may no longer be justified when the spectra show appreciable vibrational structure, as is the case with some of the triconjugated systems in Table I.

It is of interest that, unlike 2 : 6-dimethylstyryl derivatives, 9-vinylanthracene derivatives show steric effects of type (2) and exhibit practically no conjugation between the anthryl group and the $\text{CH}=\text{CHX}$ side chain (Braude, Fawcett, and Newman, *J.*, 1950, 793). Steric interference with the 1 : 8-hydrogen atoms of the anthryl groups is evidently much more severe than with the hydrogen atoms of *o*-methyl groups, presumably owing to the greater rigidity of the polycyclic system (cf. Jones, *J. Amer. Chem. Soc.*, 1945, 67, 2127; *Chem. Rev.*, 1947, 41, 353).

We now turn to a comparison of styryl and diene derivatives. As in the case of aromatic and alicyclic ethylenic ketones (Part XII, *loc. cit.*), steric effects in the two series might be expected to be very similar. The only examples for which comparative data are available are the benzylideneacetones and the previously studied (Part VI, *J.*, 1949, 1890) alicyclic dienones of the ionone-type, and for these compounds the values of ϵ/ϵ_0 and θ are, in fact, in remarkably close agreement (Table 2).

It will be noted that the spectral properties of the 6 : 6-dimethylcyclohexene derivative, rather than the 2-methylcyclohexene derivative which shows hardly any steric hindrance, are comparable to those of 2-methylbenzylideneacetone. This is in agreement with the conclusion (Part VI, *loc. cit.*; cf. Braude, Bruun, Weedon, and Woods, *J.*, 1952, 1419;

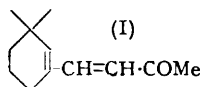
TABLE 2. Comparison of steric effects in benzylideneacetones and alicyclic dienones
(R = CH=CH·COMe).

	λ_{\max} (Å)	ϵ	ϵ/ϵ_0^*	θ^*		λ_{\max} (Å)	ϵ	ϵ/ϵ_0^*	θ^*
	2860	22,000	1.0	0		2810	20,800	1.0	0
	2230 2910	11,000 17,000	— 0.71	— 33		2280 2810 2900	4,100 13,000 13,500	— — 0.65	— — 36
	2220 2810 2910	10,000 11,000 10,500	— 0.40 —	— 50 —		2230 2960	6,500 10,700	— 0.46	— 47

* Based on long-wavelength bands.

MacGillivray, Kreuger, and Eichhorn, *Proc. k. ned. Akad. Wetenschap.*, 1951, **54**, B, 449) that the β -ionone and its analogues have *s-trans*-configurations (Fig. c), so that 6-methyl substituents cause much more interference than 2-methyl substituents. It is of interest that the parallelism between the phenyl and cyclohexenyl derivatives extends, at least qualitatively, to the appearance, in the hindered compounds, of bands near 2230 Å probably associated with the partial "enone" [CH:CH-COMe] chromophores. The rather high intensities of these bands in the case of the substituted benzylideneacetones is probably due to overlap with short-wavelength absorption due to the benzene ring.

One apparent anomaly reported in the literature concerns 4-(3 : 3-dimethylcyclohex-1-enyl)but-3-en-2-one (I) for which Schinz and Seifert (*Helv. Chim. Acta*, 1951, **34**, 728) recorded λ_{\max} 2850 Å (ϵ 12,500). Since the conjugated dienone system in (I) should not be subject to steric hindrance to planarity, the recorded ϵ value is surprisingly low. Through the kindness of Dr. Schinz, to whom we offer our cordial thanks for his co-operation, we have been able to re-determine the light absorption of a freshly purified sample of this ketone and of its 2 : 4-dinitrophenylhydrazone. The new values obtained for the ketone (λ_{\max} 2800 Å, ϵ 25,000 in EtOH) and its derivative (λ_{\max} 4000 Å, ϵ 35,000 in CHCl₃) are those expected for a normal, unhindered dienone.



(I)

EXPERIMENTAL

(For general methods, see Part XI, *loc. cit.*)

Benzylideneacetone (4-phenylbut-3-en-2-one), crystallised from pentane, had m. p. 42°, and gave a semicarbazone, m. p. 187—188°, and 2 : 4-dinitrophenylhydrazone, m. p. 226°.

2-Methylbenzylideneacetone (4-*o*-Tolylbut-3-en-2-one).—Aqueous sodium hydroxide (10% ; 0.5 ml.) was added, with external cooling, to *o*-tolualdehyde (2.2 g.), acetone (5 ml. ; "AnalaR"), and water (2 ml.). The mixture was shaken for 2 hr. at room temperature under nitrogen, and then acidified with dilute sulphuric acid and extracted with ether. Distillation of the ether extract afforded a mixture (1.9 g.) of aldol and unsaturated ketone, b. p. 89—110°/0.15 mm., n_D^{18} 1.5720—1.5550 (cf. Meerwein, *Annalen*, 1908, **358**, 89; Bharucha and Weedon, *J.*, 1953, 1571).

This product was heated with oxalic acid (4.0 g.) for 2 hr. on the steam-bath, under nitrogen. Water was added and the neutral products were isolated by extraction with ether, giving *o*-methylbenzylideneacetone, b. p. 84°/0.1 mm., n_D^{15} 1.5906. The *semicarbazone* crystallised from 2-methoxyethanol in hexagonal plates, m. p. 206—207° which became yellow in light (Found : C, 66.75; H, 7.0; N, 19.15. C₁₂H₁₅ON₃ requires C, 66.35; H, 6.95; N, 19.35%). The 2 : 4-dinitrophenylhydrazone crystallised from a large volume of ethyl acetate as dark red

prisms, m. p. 231° (Found : C, 60.5; H, 4.85; N, 16.6. $C_{17}H_{16}O_4N_4$ requires C, 60.0; H, 4.75; N, 16.45%).

2 : 6-Dimethylbenzylideneacetone [4-(2 : 6-Xylyl)but-3-en-2-one].—Condensation of 2 : 6-dimethylbenzaldehyde (1.4 g.) (Braude and Sondheimer, *J.*, 1955, 3754) and acetone (4 ml.), and dehydration of the product, as above, gave 2 : 6-dimethylbenzylideneacetone (0.6 g.), b. p. 94°/0.1 mm., n_D^{25} 1.5764 (Found : C, 83.0; H, 8.4. $C_{12}H_{14}O$ requires C, 82.75; H, 8.1%). The semicarbazone crystallised from aqueous methanol in plates, m. p. 171° (Found : C, 68.0; H, 7.5; N, 18.4. $C_{13}H_{17}ON_3$ requires C, 67.5; H, 7.4; N, 18.15%). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in dark red prisms, m. p. 212—214° (Found : N, 16.2. $C_{18}H_{18}O_4N_4$ requires N, 15.8%).

When the initial period of shaking with sodium hydroxide was reduced to 2 hr., the yield of ketone was much lower, mainly unchanged aldehyde being recovered. A low yield of ketone was also obtained from a condensation in ethanol and sodium ethoxide (cf. Prelog, Führer, Hagenbach, and Frick, *Helv. Chim. Acta*, 1947, 30, 113).

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