

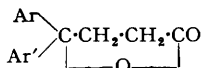
β -Aroylpropionic Acids. Part VI. Absorption Spectra as a Tool for confirming the Structure of Some Tetra-arylbutadienes and Tetra-aryltetrahydrofurans.*

By F. G. BADDAR and Z. SAWIRES.

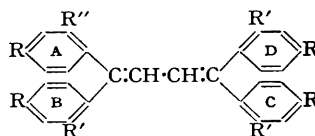
[Reprint Order No. 6567.]

The structures of some 1:1:4:4-tetra-arylbuta-1:3-dienes and 2:2:5:5-tetra-aryltetrahydrofurans are confirmed by comparing absorption spectra of the former with those of 1:1:4:4-tetra-*p*-methoxyphenylbuta-1:3-diene and the corresponding 3:3-diarylprop-2-ene-1-carboxylic acids, and those of the latter with those of the corresponding $\gamma\gamma$ -diarylbutyrolactones and tolyl ethers.

THIS investigation was designed to confirm the structure of some tetra-arylbutadienes (II) and tetra-aryltetrahydrofurans (III), which were obtained from the action of aryl-magnesium halides on succinic anhydride and β -aroylpropionic acids (cf. Baddar, El-Assal, and Habashi, *J.*, 1955, 456). Elucidation of the structure of these compounds by chemical means is practically impossible owing to the low yields and the non-reactivity. The investigation was extended to cover the relation between the tetra-arylbutadienes (II) and the corresponding 3:3-diarylprop-2-ene-1-carboxylic acids (IV), and between the tetra-aryltetrahydrofurans (III) and the corresponding lactones (I).

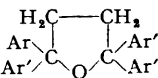


- (Ia) Ar = Ar' = Ph
 (Ib) Ar = Ar' = C₆H₄·OMe-*o*
 (Ic) Ar = Ar' = C₆H₄·OMe-*p*
 (Id) Ar = C₆H₄·OMe-*o*, Ar' = C₆H₄·OEt-*o*



- (IIa) R = R' = R'' = H
 (IIb) R = OMe, R' = R'' = H
 (IIc) R = H, R' = OMe, R'' = OEt
 (IId) R = H, R' = OEt, R'' = OMe

- (IIIa) Ar = Ar' = Ph
 (IIIb) Ar = Ar' = C₆H₄·OMe-*o*
 (IIIc) Ar = Ar' = C₆H₄·OEt-*o*
 (III d) Ar = Ph, Ar' = C₆H₄·OMe-*o*



- (IVa) Ar = Ph
 (IVb) Ar = C₆H₄·OMe-*o*
 (IVc) Ar = C₆H₄·OMe-*p*

Absorption spectra were measured with a Beckman DU Quartz Spectrophotometer. The compounds were dissolved in glacial acetic acid ("AnalaR") (25 ml.) and then diluted with 95% ethyl alcohol to 100 ml., except that the acids were dissolved in 95% ethyl alcohol. The results are summarised in the Table.

* Part V, *J.*, 1955, 2199.

Com- pound	$\lambda_{\max.}$ (m μ) †	ϵ	$\lambda_{\min.}$ (m μ)	ϵ	Com- pound	$\lambda_{\max.}$ (m μ) †	ϵ	$\lambda_{\min.}$ (m μ)	ϵ
IIb	363	36,900	302	12,050	IIIa	259	960	—	—
	~346	30,000				~256	850		
	266	28,540				277	9200		
IIc	335	26,410	269	12,140	IIIb *	~262	6250	—	—
	~301	18,000				279	8470		
	~290	16,600				274	8490		
II d	334	24,710	270	11,360	III d	279	9280	277	9190
	~295	15,800				273	9620		
	249	14,750				263	360		
IVa	~236	13,730	239	13,470	Ia	258.5	450	—	—
	282	6060				~254	370		
IVb	~235	13,740	270	4810	Ib	278	4650	276	4550
	~291	4350				273	4740		
IVc	~260	19,460	225	12,300	Ic	282	2415	280	2370
	~247.5	22,050				275	3030		
	246	22,260				278	4770		
	~241	19,800				273	4870		

* In "AnalaR" CCl₄.

† ~ Approximate wavelength for inflexion.

Analysis of Spectra and Discussion.—(a) *Dienes and acids.* The absorption spectrum of 1:1:4:4-tetra-*p*-methoxyphenylbuta-1:3-diene (IIb; Fig. 1) agrees well in general features with that of the related tetraphenylbutadiene (IIa) (cf. Alberman, Haszeldine, and Kipping, *J.*, 1952, 3284), with a slight shift (20 m μ) towards the red probably due to an increase in the effective conjugation in the former compound. The increase in the intensity of the short-wavelength band may be connected with the two, nearly independently absorbing, out-of-plane, *p*-methoxyphenyl groups, which absorb at much higher wavelengths than the non-substituted phenyl groups (cf. Burawoy and Chamberlain, *J.*, 1952, 2310).

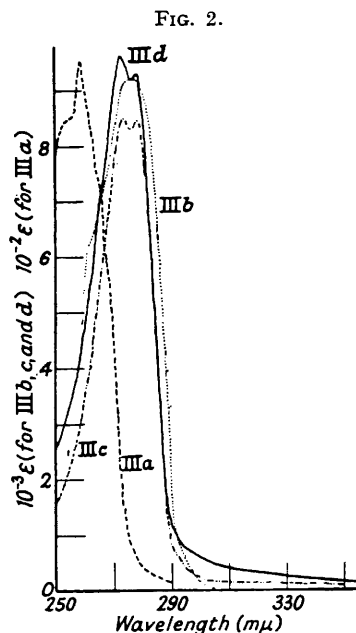
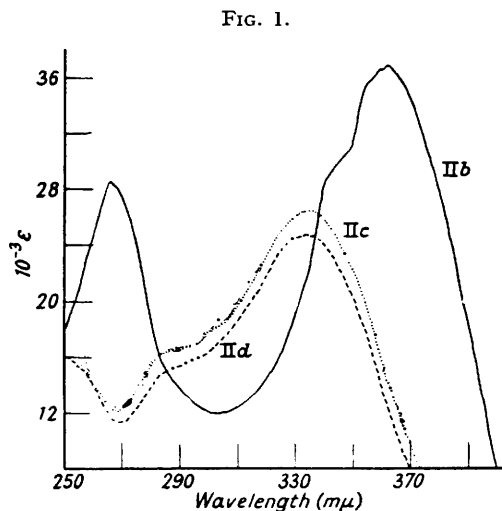
The curves for 4-*o*-ethoxyphenyl-1:1:4-tri-*o*-methoxyphenyl- (IIc; Fig. 1) and 1:1:4-tri-*o*-ethoxyphenyl-4-*o*-methoxyphenylbuta-1:3-diene (II d; Fig. 1) are very similar, so their structures must be chromophorically identical. They are very close to the displaced 1:4-diphenylbuta-1:3-diene absorption. In comparison with the known 1:1:4:4-tetra-*p*-methoxyphenylbuta-1:3-diene (IIb) (cf. Tadros and Aziz, *J.*, 1951, 2555), there is a shift in the absorption bands towards the violet. This may be due to the replacement of the *o*-hydrogen atom by the bulky methoxyl or ethoxyl group, which forces rings B and C (see II) out of the plane of the rest of the butadiene system, and causes a slight twist in rings A and D. Such a steric inhibition of resonance was noticed even for 1:1:4:4-tetraphenylbuta-1:3-diene (cf. Alberman *et al.*, *loc. cit.*).

The two tetra-arylbutadienes (IIc and d) differ also between themselves: the latter, with the more bulky ethoxyl groups, has a slightly lower $\lambda_{\max.}$ and $\epsilon_{\max.}$ than the former. The inflexion in the curves of these two compounds at *ca.* 295 m μ may be attributed to the independently non-interacting absorption of the two *o*-alkoxyphenyl groups B and C. This difference between *para*- and *ortho*-substituted tetraphenylbuta-1:3-dienes is similar to that between *p*- and *o*-methoxycinnamic acids (Morton and Sawires, *J.*, 1940, 1063), and was termed the *para*-effect by Morton and Stubbs (*J.*, 1940, 1347).

Further support for the structure of these butadienes is the existence of a similar relation between the above cinnamic acids and the corresponding 3:3-diarylprop-2-ene-1-carboxylic acids (IV) (Table). The absorption of 3:3-diphenylprop-2-ene-1-carboxylic acid (IVa) is shifted to a shorter wavelength and is less intense than that of cinnamic acid ($\lambda_{\max.}$ 269 m μ ; ϵ 18,200). This may similarly be attributed to steric inhibition of resonance known in systems containing the $-\text{CH}:\text{CPh}_2$ group (Jones, *J. Amer. Chem. Soc.*, 1943, 65, 1820). When the propene acid (IVa) is compared with the *o*-methoxy-substituted acid (IVb), it reflects the same relation between cinnamic acid and *o*-methoxycinnamic acid. Thus the band at 249 m μ for the propene acid (IVa) is shifted to longer wavelength (282 m μ) with marked decrease in intensity, while the inflexion at 236 m μ persists. The *p*-methoxy-substituted propene acid (IVc) bears similar relations to the parent acid (IVa) and the *o*-methoxy-acid (IVb) as those existing between the corresponding cinnamic acids, with

the high-intensity characteristic of *para*-substitution. Further confirmation for the structure of these three butadienes arises in that their solutions exhibited sky-blue fluorescence under ultraviolet irradiation (mercury-arc quartz lamp), while the tetrahydrofurans did not fluoresce (cf. Alberman *et al.*, *loc. cit.*).

(b) *Lactones and tetrahydrofurans.* $\gamma\gamma$ -Diphenylbutyrolactone (Ia) has an absorption (Table) very near to that of diphenylmethane (λ_{\max} . ca. 262 $m\mu$, ϵ 490) (Orndorff, Gibbs, McNulty, and Shapiro, *J. Amer. Chem. Soc.*, 1927, **49**, 1541) or nearly twice that of toluene (λ_{\max} . 262.5 $m\mu$, ϵ 270). This is an agreement with expectation in that the replacement of the CH_2 group by the five-membered lactone ring will not cause major deviation from the spectrum of diphenylmethane. The substituted lactones (Ib, c, and d) should be chromophorically equivalent to the similarly substituted diphenylmethanes or very near to the corresponding tolyl ethers (Burawoy and Chamberlain, *loc. cit.*). Although the general



features are the same, the quantitative relations hold only roughly. This is natural, since it cannot be maintained that one carbon atom effects complete insulation of the two methoxyphenyl chromophores, resulting in ϵ_{\max} , which is higher than twice that of the corresponding cresol [*e.g.*, ϵ_{\max} for the lactone (Ib) = 4650, and for *o*-cresol = 1725].

Since the lactones (I) possess structures which were verified chemically (Baddar, El-Assal, and Habashi, *loc. cit.*), it was planned to support the structure of the tetra-aryltetrahydrofurans (IIIb, c, and d) by comparing their absorptions with those of tetrahydro-2 : 2 : 5 : 5-tetraphenylfuran (IIIa) (Baddar *et al.*, *loc. cit.*; Komppa and Rohrmann, *Annalen*, 1934, **509**, 259; Valeur, *Compt. rend.*, 1903, **136**, 695), and of the nearest corresponding lactones (I). The results showed that the tetrahydrofuran (IIIa) has nearly twice ϵ_{\max} for the lactone (Ia) (Table) or nearly 4 times that for toluene. Similarly, the tetrahydrofurans (IIIb, c, and d) had the same relation to the nearest corresponding lactones (Ib, c, and b, respectively) (Table) and to the tolyl ethers. This similarity, as well as the non-fluorescence of these compounds in ultraviolet light, afford good support for the furan structures.

The authors express their gratitude to the U.S. Naval Medical Research Unit No. 3, Cairo, Egypt, for facilities to use their Beckman Spectrophotometer in this investigation.