322. β-Aroylpropionic Acids. Part VIII.* The Effect of Substituents on the Absorption Spectra of Tetra-arylbutadienes. Tetra-aryltetrahydrofurans, 3 : 3-Diarylprop-2-ene-1-carboxylic Acids, and γγ-Diarylbutyrolactones.

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The structures of some more 2 : 2 : 5 : 5-tetra-aryltetrahydrofurans and 1 : 1 : 4 : 4-tetra-arylbuta-1 : 3-dienes are confirmed by comparing their absorption spectra with those of the most similar γγ-diarylbutyrolactones and 3 : 3-diarylprop-2-ene-1-carboxylic acids, respectively, and with those of the tetra-aryltetrahydrofurans and tetra-arylbutadienes studied by Baddar and Sawires.[1]

The effect of substituents on the absorption spectra of these compounds is also investigated.

The structures of the tetra-aryltetrahydrofurans and the tetra-arylbuta-1 : 3-dienes which were obtained by the action of arylmagnesium halides on succinic anhydride, methylsuccinic anhydride, and β-aroyl- and β-aroyl-α-methyl-propionic acids and their esters,[2] have been established by comparing their absorption spectra with those of the compounds studied previously,[1] and with those of the corresponding lactones and carboxylic acids, respectively. The study revealed also the effect of substituents and their position on these spectra.

The spectra were measured with a Beckman DU Quartz spectrophotometer, the tetra-aryltetrahydrofurans and the tetra-arylbutadienes being dissolved in "AnalaR" acetic acid–95% alcohol (1 : 3 v/v), the lactones and unsaturated carboxylic acids in 95% ethyl alcohol. The results are summarised in the Table.

Lactones and Tetrahydrofurans.—The absorption spectra of the lactones were similar in their general features to those studied by Baddar and Sawires.[1] Thus, the absorption of γγ-diphenyl- (I*a*) and γγ-di-*o*-methoxyphenyl-α-methylbutyrolactone (I*b*) were identical with those of γγ-diphenyl- and γγ-di-*o*-methoxyphenyl-butyrolactone, respectively.[1]

The close relationship between the absorption curves for γ-(2-methoxy-5-methylphenyl)-γ-*o*-methoxyphenyl- (I*c*) and γ-(5-chloro-2-methoxyphenyl)-γ-*o*-methoxyphenyl-butyrolactone (I*d*) on one hand, and that of (I*b*) on the other, gives evidence for their similarity in structure.

The curves for γγ-di-2 : 5-dimethoxyphenyl- (I*e*) and γγ-di-2 : 5-dimethoxyphenyl-α-methyl-butyrolactone (I*f*) are identical. They agree with the absorption of quinol ($\lambda_{max.}$ 294 mμ; ε 3100)[3] with nearly twice the intensity. The bathochromic shift and the large increase in intensity of absorption of these compounds, compared with results for γγ-di-*o*-methoxyphenylbutyrolactone[1] and compound (I*b*), respectively, are associated with the introduction of the second methoxyl group (cf. phenol[3] and quinol). The replacement of the *o*-methoxyphenyl group by the 4-methoxy-3-diphenylyl and 4 : 4'-dimethoxy-3-diphenylyl group (I*g* and *h*, respectively) causes a ten-fold increase in intensity of absorption.

* Part VII, preceding paper.

[1] Baddar and Sawires, *J.*, 1955, 4469.
[2] Baddar, El-Assal, and Habashi, preceding paper.
[3] Morton and Stubbs, *J.*, 1940, 1347; Morton and Sawires, *ibid.*, p. 1052.

No.	R	Ar	Ar′	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ mμ)	$\varepsilon_{min.}$
(I)	*Lactones* Ar′ArC(O)·CH$_2$·CHR·CO						
a	Me	Ph	Ph	248 i	347	243·5	288
				255 i	436		
				258·5	521		
				263 i	419		
b	Me	*o*-MeO·C$_6$H$_4$	*o*-MeO·C$_6$H$_4$	272	4740	242	278
				278	4620	275·5	4560
c	H	2-MeO-5-Me·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	278	4820	244	327
d	H	2-MeO-5-Cl·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	279	4630	248	441
e	H	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MOe)$_2$C$_6$H$_3$	294	7980	254	455
f	Me	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MeO)$_2$C$_6$H$_3$	294	7940	253	378
g	H	2-MeO-5-Ph·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	263·5	20,850	235	6680
h	H	2-MeO-5-(C$_6$H$_4$·OMe-*p*)·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	267·5	25,460	263·5	6100
(II)	*Tetrahydrofurans* Ar′ArC(O)·CH$_2$·CHR·CAr′$_2$						
a	Me	*o*-MeO·C$_6$H$_4$	*o*-MeO·C$_6$H$_4$	274	8240		
				277 i	7925		
b	H	2-MeO-5-Me·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	276 i	7970		
				278	8160		
c	H	2-MeO-5-Cl·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	274 i	7740		
				278·5	8040		
d	H	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MeO)$_2$C$_6$H$_3$	289 i	13,100		
				292	13,520		
e	Me	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MeO)$_2$C$_6$H$_3$	289 i	13,370		
				292	13,900		
f	H	2-MeO-5-(C$_6$H$_4$·OMe-*p*)·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	269 i	27,650		
				271	27,860		
				272 i	27,650		
(III)	*Butadienes* Ar′ArC:CH·CH:CAr′$_2$						
a	—	2-MeO-5-Me·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	292·5 i	17,750	267·5	13,390
				337·5	25,800		
				339 i	25,750		
b	—	2-MeO·C$_{10}$H$_6$ (1)	*o*-MeO·C$_6$H$_4$	292·5 i	19,350	267	15,520
				336 i	26,670		
				339	26,740		
(IV)	*Acids* Ar′ArC:CH·CHR·CO$_2$H						
a	Me	*o*-MeO·C$_6$H$_4$	*o*-MeO·C$_6$H$_4$	281	6190	270	5500
b	H	2-MeO-5-Me·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	284	4950	271·5	4470
c	H	2-MeO-5-Cl·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	285·5	5970	271	4910
d	H	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MeO)$_2$C$_6$H$_3$	300	8000	273	2850
e	Me	2 : 5-(MeO)$_2$C$_6$H$_3$	2 : 5-(MeO)$_2$C$_6$H$_3$	299	8350	273	3390
f	H	2-MeO-5-Ph·C$_6$H$_3$	*o*-MeO·C$_6$H$_4$	248 i	25,980	230·5	22,020
				250 *	26,080	251	26,040
				252 *	26,080		
				255 i	25,940		
	(*o*-MeO·C$_6$H$_4$)$_2$CH·OH			273	4990	244	361
				277 i	4680		
	1-(2 : 5-Dimethoxyphenyl)-1 : 4 : 4-tri-*o*-methoxyphenylbutane-1 : 4-diol (VII*a*)			272 i	7430	247	831
				279	8210		
				290 i	3900		

i = Inflexion (approx.). * Poor persistence.

A similar relation stands for anisole ($\lambda_{max.}$ 265 mμ; ε 2300),[4] 4-methoxydiphenyl ($\lambda_{max.}$ 261 mμ; ε 21,000),[5] and 4 : 4′-dimethoxydiphenyl ($\lambda_{max.}$ 264 mμ; ε 24,610; in EtOH)[6] (Williamson and Rodebush[7] gave for the last compound $\lambda_{max.}$ 263 mμ; ε 21,700; in *n*-hexane).

The curves for the tetrahydrofuran derivatives (II*a*—*e*) are identical with those of the related lactones (I*b*—*f*, respectively) with nearly twice the absorption intensity.

[4] Wolf and Herold, *Z. phys. Chem.*, 1931, **12**, *B*, 201; Wolf and Strasser, *ibid.*, 1933, **21**, *B*, 389.
[5] Burawoy and Chamberlain, *J.*, 1952, 2310.
[6] Baddar and Sawires, unpublished work.
[7] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.

The absorption intensity of 5-(4 : 4′-dimethoxy-3-diphenylyl)tetrahydro-2 : 2 : 5-tri-*o*-methoxyphenylfuran (II*f*) is roughly equal to the sum of the intensities for γγ-di-*o*-methoxyphenylbutyrolactone [1] and 5-(4 : 4′-dimethoxy-3-diphenylyl)-γ-*o*-methoxyphenylbutyrolactone (I*h*).

The close relation between the absorption of the above-mentioned furans and the related lactones, as well as of the furans studied by Baddar and Sawires,[1] is strong evidence for the structure assigned to these compounds.

Dienes and Acids.—The curves for the tetra-arylbutadienes (III*a* and *b*) agree closely with those for 4-*o*-ethoxyphenyl-1 : 1 : 4-tri-*o*-methoxyphenyl- and 1 : 1 : 4-tri-*o*-ethoxyphenyl-4-*o*-methoxyphenyl-buta-1 : 3-diene.[1] This, as well as the fluorescence under ultraviolet irradiation (mercury-arc quartz lamp),[1] is strong evidence for the structure assigned to these compounds.

The intensity of absorption of 3 : 3-di-*o*-methoxyphenyl-1-methylprop-2-ene-1-carboxylic acid (IV*a*) is identical with that of 3 : 3-di-*o*-methoxyphenylprop-2-ene-1-carboxylic acid,[1] and much lower than those of 3 : 3-diphenyl- and 3 : 3-di-*p*-methoxyphenylprop-2-ene-1-carboxylic acid.[1] This is attributed to the steric inhibition of resonance of the *o*-methoxyphenyl group with the ethylenic linkage,[1] a phenomenon even more pronounced with the acids (IV*b*—*e*), in which the substituent in position 5′ exerts an additional steric effect. As a result the acids have spectra very close to those of the corresponding lactones (I*c*—*f*, respectively), with a slight bathochromic shift (*ca.* 6 mμ), indicating very strong inhibition of resonance between the disubstituted phenyl groups and the ethylenic linkage.

The butane-1 : 4-diol structure assigned to the compound (VII*a*) of the preceding paper was supported by its absorption spectrum, which is nearly equivalent to the summation of those for di-*o*-methoxyphenylmethanol and the mean values for γγ-di-*o*-methoxyphenylbutyrolactone and (I*e*).

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