570. *Interdependence of Molecular Conformation and Conjugation in Aromatic Ethers. Part II.*[1]

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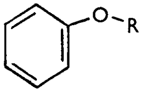
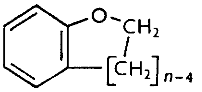
Chroman- and homochroman-2-carboxylic acid have been prepared. The method involved the action of perbenzoic acid on 2-bromo-1-tetralone and 6-bromo-1 : 2-benzosuberone respectively, and the hydrolysis of the resulting bromo-lactones by titration with cold alkali in the presence of hydrogen peroxide.

The ultraviolet absorption spectrum, the rate of bromination, and the acid dissociation constant of homochroman-2-carboxylic acid afford evidence for steric hindrance of conjugation in this compound.

PART I[1] was concerned with conjugation of the oxygen atom and the benzene ring in aromatic ethers mainly of types (I) and (II). The extinction coefficients of the ultraviolet absorption spectra of *tert.*-butoxybenzene and homochroman (II; $n = 7$), the rates of bromination of these ethers, and the rates of solvolysis of their chloromethyl derivatives were shown to be comparatively small. The data were interpreted in terms



(I)



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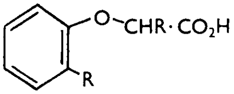

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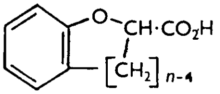

(IV)

of the interplanar angle of the ether group and the benzene ring, and the height of the energy barrier to be overcome if coplanarity, the condition for maximum resonance interaction of the ether group and the benzene ring, is to be attained. This paper is concerned

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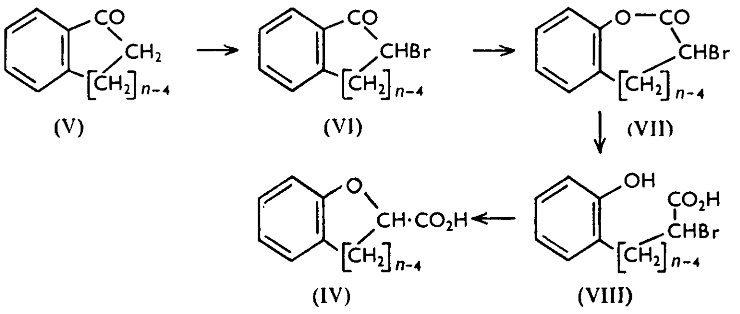
[1] Part I, Baddeley, Smith ,and Vickars ,*J.*, 1956, 476.

mainly with the corresponding carboxylic acids (IV; $n = 5$, 6, and 7); the acids (III; $R = R' = Me$; $R = R' = H$; and $R = Et$, $R' = Me$) are included for comparison. The dissociation constants of the acids in water at 25°, the rates of bromination in glacial acetic acid at 20°, and the wavelengths and extinction coefficients of the ultraviolet absorption bands of the acids in hexane are listed in the Table.

Comparison of the ultraviolet absorption spectra, acid dissociation constants, and rates of bromination of the acids.

		Bromination in AcOH		Absorption spectra			
				Max. (Å)		$\varepsilon_{\text{max.}}$	
	pK_a	$t_{20\%}$ (min.)	$k_{\text{rel.}}$				
Coumaran-2-carboxylic acid	3·25	14·2	30	2850	2790	2375	2670
Chroman-2-carboxylic acid	3·38	26·4	16	2810	2735	1860	1800
Homochroman-2-carboxylic acid	3·63	1920	0·22	2700	2650	555	570
α-*o*-Tolyloxybutyric acid	3·43	33·6	12·5	2775	2710	1170	1300
α-*o*-Tolyloxypropionic acid	3·37	20·8	20	2775	2710	1440	1620
Phenoxyacetic acid	3·35	420	1·0	2760	2700	1140	1275

Comparison of the absorption spectra and rates of bromination of the acids (IV) with those for the ethers (II) (see Part I) shows that the inductive withdrawal of electrons by the carboxyl group from the ether-oxygen atom displaces the absorption bands to shorter wavelengths and lower coefficients of absorption, and decreases the rate of bromination. Increase in the size of the heterocycle from five to seven members affects the ultraviolet absorption spectra of the acids (IV) and ethers (II) similarly, and causes a decrease in the rate of bromination which is somewhat greater in the case of the acids. The results afford evidence for steric hindrance of conjugation in homochroman-2-carboxylic acid similar to that in homochroman. The dissociation constants of the acids provide further evidence of this steric hindrance. Conjugation of the ether-oxygen atom and the benzene ring in the acids involves a displacement of electrons from the oxygen atom to the benzene ring which, by increasing the inductive effect of the oxygen atom, facilitates acid dissociation of the neighbouring carboxyl group. Thus the hindrance of conjugation in homochroman-2-carboxylic acid accounts for the comparatively low acid dissociation constant *i.e.*, high value of pK_a, of this compound.



The acids (IV; $n = 6$ and 7) were afforded by the annexed novel procedure. The bromo-ketones (VI; $n = 6$ and 7), obtained from the ketones (V), reacted slowly with perbenzoic acid in chloroform, to give the bromo-lactones (VII). These were extensively decomposed by hot alkali but were conveniently converted into the bromo-acids (VIII) by addition of hydrogen peroxide and titration with cold sodium hydroxide solution. The cyclised acids (IV; $n = 6$ and 7) were obtained from the bromo-acid (VIII) by the action of hot alkali.

EXPERIMENTAL

Materials.—(i) Coumaran-2-carboxylic acid was prepared [2] from coumarin, and crystallised from light petroleum in needles, m. p. 117—119° (Found: C, 66·1; H, 5·0%; acid equiv., 165. Calc. for $C_9H_8O_3$: C, 66·0; H, 4·9%; equiv., 165).

(ii) *Chroman-2-carboxylic acid* was prepared from 2-bromo-1-tetralone.[3] The latter (15 g.) was allowed to react with perbenzoic acid (19 g.) in chloroform (340 c.c.) at room temperature for 10 days. The mixture was then washed, first, with an aqueous solution of potassium iodide (4 g.) containing 2N-hydrochloric acid (5 c.c.), then with an aqueous solution of sodium thiosulphate (2·5 g.) and, finally, several times with sodium hydrogen carbonate solution. The chloroform layer was separated and dried ($MgSO_4$), and the chloroform was removed by distillation. The residue, a pale yellow oil (11·7 g.), was dissolved in ethanol (40 c.c.) containing one drop of phenolphthalein solution, 90% hydrogen peroxide solution (5 c.c.) was carefully added, and the mixture was neutralised with 2N-sodium hydroxide (~20 c.c.). The mixture was poured into water (250 c.c.), the whole washed with ether, and the aqueous layer acidified and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue, a pale yellow oil (5 g.), was heated on a steam-bath for 45 min. with 2N-sodium hydroxide (20 c.c.). The mixture was cooled, washed with ether, acidified, and extracted with ether. This extract was dried ($MgSO_4$) and gave a pale brown solid (2·9 g.) by evaporation. The product was dissolved in the minimum amount of sodium hydrogen carbonate solution, and the equivalent amount of dilute hydrochloric acid was added in four parts with ether-extraction after each addition. The first three extracts gave the required acid (1·3 g.), m. p. 90—95°; the fourth gave resin. The acid was purified chromatographically in the manner described by Bhargava and Heidelberger [4] and crystallised from light petroleum in colourless needles, m. p. 98·5—100° (Found: C, 67·6; H, 5·2%; acid equiv., 176. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%; equiv., 178).

(iii) *Homochroman-2-carboxylic acid* was similarly prepared from 4-*bromo*-1 : 2-*benzo*cyclo*hepten*-3-*one*. This bromo-ketone (24 g.) was obtained in 90% yield from benzosuberone [5] by the procedure described [3] for the preparation of 2-bromo-1-tetralone; it is a colourless oil, b. p. 115·5—116°/0·3 mm. (Found: C, 55·2; H, 4·8; Br, 33·4. $C_{11}H_{11}OBr$ requires C, 55·2; H, 4·6; Br, 33·5%). The required acid (1·85 g.) separated from light petroleum in needles, m. p. 100—102·5° (Found: C, 68·9; H, 5·8%; acid equiv., 195. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·25%; equiv., 192).

(iv) Phenoxyacetic and α-*o*-tolyloxy-propionic and -butyric acid were prepared and purified as previously described.

Ultraviolet Absorption Spectra.—Solutions (0·0005M) of the acids in hexane [6] and a Hilger "Uvispek" photoelectric spectrophotometer were used.

Rates of Bromination.—The time intervals for 20% bromination of the acids in glacial acetic acid at 20°, the initial solutions being 0·001M with respect to bromine and 0·01M with respect to aromatic acid, were determined by the procedure described by de la Mare and Vernon.[7]

pK_a *Values for the Acids.*—These were determined for 0·005M-solutions in water at 25° by potentiometric titration, a Cambridge Portable Laboratory pH Meter of accuracy 0·01 pH unit being used.

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[2] *Org. Synth.*, 1944, **24**, 33; Fittig and Ebert, *Annalen*, 1883, **216**, 166; Stoermer and Konig, *Ber.*, 1906, **39**, 493.

[3] Wilds and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 87.

[4] Bhargava and Heidelberger, *ibid.*, 1955, **77**, 166.

[5] Aspinall and Baker, *J.*, 1950, 745.

[6] Graff, O'Connor, and Skau, *Ind. Eng. Chem. Analyt.*, 1944, **16**, 556.

[7] de la Mare and Vernon, *J.*, 1951, 1764.