939. *Interdependence of Conformation and Conjugation in Aromatic Ethers. Part III.*[1]

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The ultraviolet absorption spectra and rates of bromination of coumaran and its 2-methyl and 2 : 2-dimethyl derivatives and the rates of solvolysis of their chloromethyl derivatives in 90% aqueous ethanol have been determined and compared with the corresponding data for the ethers PhOR, where R is Et, Pr^i, and Bu^t. The comparison shows that, in the absence of steric interaction of the *tert.*-butyl group and the benzene ring, *tert.*-butoxybenzene and its chloromethyl derivative would react about three times faster than they do.

Reactivity decreases in the order 2-methyl- > 2 : 2-dimethyl-coumaran > coumaran.

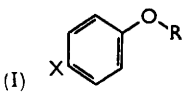
In Part I [1] and earlier communications [2] the effects of alkyl groups R and of the value of *n* on the ultraviolet absorption spectra and rates of bromination of the ethers (I) and (II) respectively (X = H) and on the rates of solvolysis of their chloromethyl derivatives (X = CH_2Cl) have been offered as evidence for a relation between conformation and conjugation of an ether-oxygen atom and a benzene ring. The extinction coefficients of *tert.*-butoxybenzene and homochroman (II; $n = 3$), the rates of bromination of these ethers, and the rates of solvolysis of their chloromethyl derivatives are all comparatively small, and these anomalies have been explained in terms of increase of steric interaction with decrease of the interplanar angle of the ether group and the benzene ring in these compounds. In the ethers (I; X = H) and their chloromethyl derivatives reactivity increases in the order $R = Bu^t < Me < Et < Pr^i$ which is compatible with the view that these alkyl groups have an inductive effect which increases in the order $Me < Et < Pr^i < Bu^t$, and that that of the *tert.*-butyl group is more than counterbalanced by steric interaction of this group and the benzene ring. This view requires that, should steric interaction be circumvented, R would affect the reactivity of these compounds only by induction; the work described in this paper was designed to achieve this simplification and thereby to measure the effect of steric interaction on the reactivity of *tert.*-butoxybenzene and its chloromethyl derivative.

The carbon atoms of the heterocyclic ring of coumaran (II; $n = 1$; X = H) are held

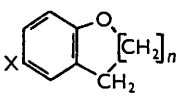
[1] Part I, Baddeley, Smith, and Vickars, *J.*, 1956, 2455; Part II, Baddeley and Cooke, *J.*, 1958, 2797.

[2] Baddeley and Smith, *Nature*, 1949, **164**, 1014; Baddeley, Holt, Smith, and Whittaker, *ibid.*, 1951, **168**, 386.

in, or close to, the plane of the benzene ring and conjugation of the oxygen atom and the benzene ring should not be altered by steric interaction when the hydrogen atoms of the



(I)



(II)

2-methylene group are replaced by bulky groups. Evidence for this view is provided by the ultraviolet absorption spectra of coumaran and its 2-methyl and 2 : 2-dimethyl derivatives; they are nearly identical. The compounds have three absorption peaks in the region 2500—2900 Å (see p. 4668); wavelengths and extinction coefficients for the middle peaks are listed in Table 1, together with those for the corresponding peaks of some related

TABLE 1. *Comparison of the ultraviolet absorption spectra of the ethers.*

	$C_6H_4\cdot O\cdot CRR'\cdot CH_2$		$C_6H_5\cdot O\cdot CRR'\cdot CH_3$	
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
R = R′ = H	2830	3095	2710	1938
R = Me, R′ = H	2820	3090	2730	1920
R = R′ = Me	2820	3070	2700	454
	Ethyl *o*-tolyl ether		2720	1744

alkyl phenyl ethers. Having thus demonstrated that steric hindrance of conjugation does not occur in 2-methyl- and 2 : 2-dimethyl-coumaran, it is reasonable to assume that such hindrance cannot affect the rates of bromination of these ethers and of solvolysis of their chloromethyl derivatives.

The Arrhenius parameters for solvolysis of the chloromethyl derivatives in 90% aqueous ethanol are listed in Table 2, and in Table 3 the reactivities of these chlorides are compared with those of the chloromethyl derivatives of the corresponding alkyl aryl ethers. The corresponding comparison for the bromination of the ethers in acetic acid is provided by Table 4; the time intervals for 20% consumption of bromine and therefrom the calculated relative rates of bromination are listed. As was expected, there is an overall resemblance between the two comparisons. They show that in the absence of steric interaction of the

TABLE 2. *Arrhenius parameters for the solvolysis of the chlorides in* 90% *aqueous ethanol.*

$CH_2Cl\cdot C_6H_3\cdot O\cdot CRR'\cdot CH_2$	$10^3k_{0.0}$ (min.$^{-1}$)	$10^3k_{10.0}$ (min.$^{-1}$)	$10^3k_{15.0}$ (min.$^{-1}$)	$10^3k_{25.0}$ (min.$^{-1}$)	E (kcal./mole)	$10^{-11}A$ (min.$^{-1}$)
R = R′ = H	25·4	77·8	132	—	17·3	15
R = Me, R′ = H	47·9	146	248	—	17·2	24
R = R′ = Me	36·0	109	184	—	17·1	15
4 : 3-MeO·C_6H_3Me·CH_2Cl	2·50	8·91	16·3	51·1	19·7	107
4 : 3-EtO·C_6H_3Me·CH_2Cl	4·76	16·6	29·9	91·9	19·3	110

TABLE 3. *Comparison of energies of activation and rates of solvolysis of the chlorides.*

	$CH_2Cl\cdot C_6H_3\cdot O\cdot CRR'\cdot CH_2$ in 90% aq. EtOH			$CH_2Cl\cdot C_6H_4\cdot O\cdot CRR'\cdot CH_3$ in 90% aq. EtOH			$C_6H_4\cdot CHCl\cdot CRR'\cdot CH_2$ in EtOH (ref. 3)	
	$10^3k_{0.0}$ (min.$^{-1}$)	$k_{rel.}$	E (kcal./mole)	$10^3k_{25.0}$ (min.$^{-1}$)	$k_{rel.}$	E (kcal./mole)	$k_{rel.}$	E (kcal./mole)
R = R′ = H ...	25·4	100	17·3	18·5	100	20·3	100	21·6
R = Me, R′ = H	47·9	189	17·2	32·5	176	18·8	12	22·8
R = R′ = Me ...	36·0	142	17·1	8·20	44	20·8	2	23·0

tert.-butyl group and the benzene ring the rates of reaction of *tert.*-butoxybenzene and of its chloromethyl derivative would both be about three times faster than they are. It is noteworthy that the coefficients of ultraviolet absorption by this ether are about a quarter of what they would be in the absence of steric hindrance of conjugation (see Table 1).

The comparisons provided by Tables 1, 3, and 4 confirm our previous conclusion that doubtless as a consequence of the imposed coplanarity of the ether group and the benzene

TABLE 4. *Comparison of the rates of interaction of the ethers* (M/200) *and bromine* (M/1000) *in acetic acid at* 20°.

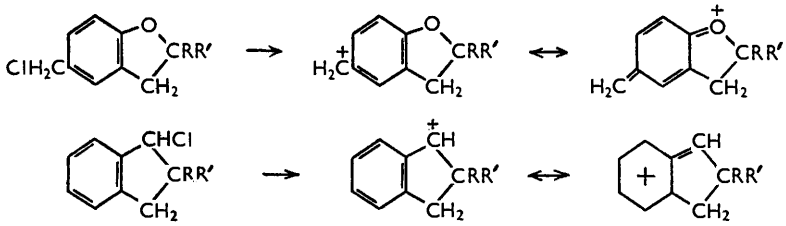
	$C_6H_4\cdot O\cdot CRR'\cdot CH_2$		$C_6H_5\cdot O\cdot CRR'\cdot CH_3$		$o\text{-}C_6H_4Me\cdot O\cdot CRR'\cdot CH_3$
	$t_{20\%}$ (sec.)	$k_{rel.}$	$t_{20\%}$ (sec.)	$k_{rel.}$	$t_{20\%}$ (sec.)
R = R′ = H	15·5	100	342 *	100	78
R = Me, R′ = H	9·0	170	270	127	—
R = R′ = Me	11·5	140	786	44	—
			o-$C_6H_4Me\cdot OMe$		186

* In Part I, $t_{20\%}$ for PhOEt (M/100) was wrongly given as 1·44 min.; the correct value is 2·80 min.

ring, the five-membered heterocyclic ring of coumaran and its derivatives enhances conjugation.

As to the effect of 2-methyl substituents on the rate of reaction of coumaran and its chloromethyl derivative, the data show that whereas one methyl group, doubtless by its inductive effect, increases the rate, the increase is nearly halved by the second methyl group. This anomaly indicates that together the two methyl groups may hinder solvation, which is especially important in the polar transition states of bromination and solvolysis, or provide a positively charged envelope of hydrogen atoms which opposes those electronic displacements which give the neighbouring oxygen atom a positive charge. These possibilities must also be borne in mind when interpreting the behaviour of *tert.*-butoxybenzene and its chloromethyl derivative.

In conclusion we wish to indicate that the ionisation processes (III) and (IV) are sufficiently closely related to make it likely that the factors which make the rate of the former decrease in the order R = Me, R′ = H > R = R′ = Me will contribute to the corresponding decrease in the latter [3] (see Table 3).



EXPERIMENTAL

Materials.—Ethers. Coumaran,[1] b. p. 78—81°/15 mm., n_D^{20} 1·5524 (picrate, m. p. 75—76°), 2-methylcoumaran,[4] b. p. 80°/17 mm., n_D^{17} 1·531 (Found: C, 80·9; H, 7·4. Calc. for $C_9H_{10}O$: C, 80·6; H, 7·5%), 2 : 2-dimethylcoumaran,[5] b. p. 76—77°/15 mm., n_D^{20} 1·517 (Found: C, 81·0; H, H, 7·9. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1%), and ethyl *o*-tolyl ether,[6] b. p. 181—182°, n_D^{20} 1·5051, were prepared as described in the literature cited.

Hydroxymethyl Derivatives from the Ethers.—5-Hydroxymethylcoumaran. A solution of acetyl chloride (2 mol.) and aluminium chloride (1 mol.) in ethylene dichloride at −10° was added with stirring to a cooled solution of coumaran in diethylene chloride. The temperature of the mixture was not allowed to exceed −6° and after 5 min. the mixture was poured on ice and hydrochloric acid. The organic layer was separated and, together with the ethylene dichloride extracts of the aqueous layer, was washed successively with water, dilute alkali, and water, and dried (K_2CO_3). Removal of the solvent gave *5-acetylcoumaran*, which separated from light petroleum in needles, m. p. 61—63° (Found: C, 74·1; H, 6·1. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2%). Hypochlorite oxidation [7] of the ketone gave *coumaran-5-carboxylic acid* which separated from ethanol in slender needles, m. p. 188—190° (Found: C, 65·8; H, 4·9%; equiv., 162.

[3] Baddeley, Rasburn, and Rose, *J.*, 1958, 3168.
[4] von Auwers, *Annalen*, 1918, **415**, 150; Adams and Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 656.
[5] Adams, Bartz, and Miller, *ibid.*, 1935, **57**, 371.
[6] Staedel, *Annalen*, 1883, **217**, 41.
[7] Newman and Holmes, *Org. Synth.*, Coll. Vol. II, 1943, p. 428.

$C_9H_8O_3$ requires C, 65·9; H, 4·9%; equiv., 164). Reduction of the ethyl ester by lithium aluminium hydride gave the required alcohol,[1] b. p. 158—160°/11 mm., n_D^{18} 1·5776 (phenylurethane,[1] m. p. 88—89°).

5-Hydroxymethyl-2-methylcoumaran. The experimental procedure was similar to that in the preparation of 5-hydroxymethylcoumaran. 5-Acetyl-2-methylcoumaran,[8] b. p. 163—164°/20 mm. (oxime,[8] m. p. 84—85°), melted at 8—9°, and gave *2-methylcoumaran-5-carboxylic acid* which separated from ligroin in short needles, m. p. 149—150° (Found: C, 67·6; H, 5·5%; equiv., 174. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%; equiv., 178). The required *alcohol*, b. p. 155—158°/14 mm. (Found: C, 73·0; H, 7·3. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%), gave a *phenylurethane* which separated from light petroleum in short needles, m. p. 106—107° (Found: C, 72·5; H, 6·1; N, 4·8. $C_{17}H_{17}O_3N$ requires C, 72·1; H, 6·0; N, 5·0%).

5-Hydroxymethyl-2 : 2-dimethylcoumaran. *5-Acetyl-2 : 2-dimethylcoumaran* separated from light petroleum in highly refractive prisms, m. p. 84—85° (Found: C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·5%). *2 : 2-Dimethylcoumaran-5-carboxylic acid* separated from aqueous ethanol in flat needles, m. p. 174—176° (Found: C, 69·0; H, 6·3%; equiv., 191. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%; equiv., 192). The required *alcohol*, b. p. 158—160°/14 mm., n_D^{18} 1·5575 (Found: C, 73·9; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%), gave a *phenylurethane* which separated from light petroleum in needles, m. p. 69—70° (Found: C, 72·4; H, 6·2; N, 4·9. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4; N, 4·7%).

4-Ethoxy-3-methylbenzyl alcohol, b. p. 141—143°/10 mm., m. p. 81—82° (Found: C, 72·5; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%) [*phenylurethane*, m. p. 85—86° (Found: C, 71·7; H, 6·6; N, 5·0. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%)], was afforded by reduction of 4-ethoxy-3-methylbenzaldehyde,[9] m. p. 31—32°.

Chloromethyl Derivatives from the Ethers.—These were prepared from the hydroxymethyl compounds: Solutions of these alcohols (*ca.* 3 g.) in light petroleum (b. p. 60—80°; 500 c.c.) at 0° were saturated with dry hydrogen chloride; the solutions were dried ($CaCl_2$), solvent was volatilised at 40° under reduced pressure, and the residues were extracted with light petroleum (b. p. <40°). Removal of solvent afforded the required chloromethyl derivatives which were flash-distilled in nitrogen at reduced pressure. This general procedure minimised formation of resins and gave the following chlorides: 5-chloromethylcoumaran,[1] m. p. 41—42° (Found: Cl, 20·5. Calc. for C_9H_9OCl: Cl, 21·0%); *5-chloromethyl-2-methylcoumaran*, b. p. 95°/0·7 mm. (Found: Cl, 19·0. $C_{10}H_{11}OCl$ requires Cl, 19·4%); *5-chloromethyl-2 : 2-dimethylcoumaran*, b. p. 93°/0·7 mm. (Found: Cl, 17·9. $C_{11}H_{13}OCl$ requires Cl, 18·1%); 4-ethoxy-3-methylbenzyl chloride, b. p. 87°/0·2 mm. (Found: Cl, 18·8. Calc. for $C_{10}H_{13}OCl$: Cl, 19·0%).

Rates of Solvolysis of the Chloromethyl Derivatives.—The solvent was 90% aqueous ethanol and the procedure was that previously described.[1] Each rate determination was repeated two or three times and at more than one temperature. The average rate coefficients and other Arrhenius parameters are listed in Table 2. The rate constants are accurate to ±1·5%, and the values of E to ±0·3 kcal./mole.

Rates of Bromination of the Ethers in Acetic Acid.—These rates were measured by the technique used by Robertson, de la Mare, and Johnston;[10] the times for 20% reaction with the ether (0·005M) and bromine (0·001M) in acetic acid at 20·0° and the relative rates are listed in Table 4.

Ultraviolet Absorption Spectra of the Ethers in Hexane.—These were measured by means of a Hilger "Uvispek" photoelectric spectrophotometer. The solvent was purified in the manner previously described.[1] The values of $\lambda_{max.}$ and ε are listed in Table 5.

TABLE 5. *Ultraviolet absorption spectra of the ethers in hexane.*

	$\lambda_{max.}$			ε		
Coumaran	2890	2830	2740 *	3055	3095	2250
2-Methylcoumaran	2890	2820	2750 *	2790	3090	2460
2 : 2-Dimethylcoumaran	2890	2820	2740 *	2770	3070	2335
Ethyl *o*-tolyl ether	2780	2720	2600 *	1666	1744	800

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[8] Arnold and McCool, *J. Amer. Chem. Soc.*, 1942, **64**, 1316.
[9] Gattermann, *Annalen*, 1907, **357**, 355.
[10] Robertson, de la Mare, and Johnston, *J.*, 1943, 276.