The Cleavage of Diaryl Ethers by Grignard Reagents in the Presence of Cobaltous Chloride. Part II.* Disubstituted Diphenyl Ethers.

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From relative molar yields of $R'·C_6H_4·OH$ against $R''·C_6H_4·OH$, obtained during cleavage of eleven disubstituted diphenyl ethers $R'·C_6H_4·O·C_6H_4·R''$, a scale of relative stabilising influence of various substituent groups R on the intermediate aryloxy-radical $R·C_6H_4O·$ has been worked out. This scale deviates from the electropositivity usually known for R in heterolytic reactions and is explained by the postulation that the stability of the aryloxy-radical is not directly measured by the electropositivity of R but to a large extent depends also on whether R offers opportunity for resonance within the radical.

In Part I * the cleavage of monosubstituted diphenyl ethers $R·C_6H_4·O·C_6H_5$ by the method indicated in the title was studied, and the results were explained in terms of the stablising effect of R on the intermediate aryloxy-radical $R·C_6H_4·O·$ by which the cleavage was considered to proceed. The relative stabilising effect of R was shown to be in general agreement with Ingold's theory (*Trans. Faraday Soc.*, 1934, **30**, 52) relating the electropositivity of R to the stability of such radicals. The ratio of the amount of substituted phenol $R·C_6H_4·OH$ to that of phenol obtained during cleavage, which afforded a comparison of R with hydrogen in each case, should also be applicable to a comparison among the substituent groups themselves. Such a direct reference to the hydrogen of phenol, however, is practicable only in the case of the chlorodiphenyl ethers, since with all the other ethers the corresponding substituted phenols are all formed to the practical exclusion of phenol (*i.e.*, in a ratio greater than 4 : 1) and a direct comparison of such values has little quantitative significance. For such a study, competitive cleavage which leads to substantial quantities of each phenol is indicated. The present paper describes such cleavage of eleven disubstituted diphenyl ethers $R'·C_6H_4·O·C_6H_4·R''$.

Experimental.—The ethers were prepared as described previously (see Table 1 for new), *ethers* except for the ether (R′ = *m*-OMe, R″ = *p*-Cl), for which a lower reaction temperature (200°) and a longer time (4 hr.) were employed. Cleavage was effected in the usual way, except for the following ethers: (i) R′ = *p*-Cl, R″ = *m*-OMe; (ii) R′ = *p*-OMe, R″ = *p*-Bu^t; (iii) R′ = *p*-Me, R″ = *p*-C_6H_5; and (iv) R′ = *m*-Me, R″ = *p*-C_6H_5, for which in order to obtain fair

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* Part I, preceding paper.

yields of the cleavage products it was necessary to use a 5-molar excess of the Grignard reagent and a 3-molar excess of cobaltous chloride.

TABLE 1. *Synthesis of disubstituted diphenyl ethers,* $R'\cdot C_6H_4\cdot O\cdot C_6H_4\cdot R''$.

R′	R″	Phenol, starting material	Yield (%)	B. p./mm. (or m. p.)	n_D^{22}	Found (%) C	Found (%) H	Found (%) Cl	Formula	Required (%) C	Required (%) H	Required (%) Cl
p-Cl	*m*-Me	*p*-Chlorophenol	43	106—107°/1	1·5776	—	—	16·4	$C_{13}H_{11}OCl$	—	—	16·2
,,	*p*-Me	,,	37	(56)	—	—	—	16·3	,,	—	—	16·2
,,	*m*-OMe	*m*-Methoxyphenol	43	119/1	1·5860	66·4	5·1	15·2	$C_{13}H_{11}O_2Cl$	66·5	4·7	15·1
,,	*p*-OMe	*p*-Chlorophenol	41	(54)	—	—	—	15·0	,,	—	—	15·1
p-OMe	*o*-Me	*o*-Cresol	49	140/1	1·5713	78·6	6·7	—	$C_{14}H_{14}O_2$	78·5	6·5	—
,,	*p*-Bu^t	*p*-*tert*.-Butylphenol	50	147—151/1	1·5545	79·9	7·8	—	$C_{17}H_{20}O_2$	79·7	7·8	—
p-Me	*p*-C_6H_5	*p*-Cresol	69	(94—96)	—	87·3	6·2	—	$C_{19}H_{16}O$	87·7	6·2	—
,,	*o*-OMe	,,	42	(51—52)	—	78·6	6·5	—	$C_{14}H_{14}O_2$	78·5	6·5	—
m-Me	*p*-C_6H_5	*m*-Cresol	76	(66—67)	—	86·8	6·2	—	$C_{19}H_{16}O$	86·7	6·2	—

Cleavage mixtures containing chlorophenols or methoxyphenols were analysed for chlorine and methoxyl, respectively; mixtures containing phenol and *p*-phenylphenol were fractionally distilled; and the mixture of *m*- and *p*-cresol was estimated iodometrically.

RESULTS AND DISCUSSION

The results of cleavage experiments are given in Table 2. By combining these with those obtained in Part I (*loc. cit.*) it is possible to prepare a list of the relative stabilising influence of various substituents R on the aryloxy-free radical $R\cdot C_6H_4\cdot O\cdot$ in terms of a stabilisation index *S* relative to hydrogen as unity (Table 3). Thus in Part I, 3·0 parts of *p*-chlorophenol to one part of phenol were obtained from *p*-chlorodiphenyl ether; hence for the *p*-chlorine atom, $S = 3\cdot0$ (first row). With *p*-chloro-*p*′-methoxydiphenyl ether, the yield of *p*-cresol is 61%, and hence for *p*-methoxy-, $S = 61/39 \times 3\cdot0 = 4\cdot7$. Similarly for *p*-methyl, $S = 80/20 \times 3\cdot0 = 12$ (second row). With these subsidiary standards the figures for the other substituents in the third and the fourth row are calculated. The *m*-methyl group was further checked against *p*-phenyl (fifth row). It is seen that, where more than one standard was used for a particular substituent, the values obtained checked well with each other (*m*- and *p*-methyl and *p*-methoxy-).

TABLE 2. *Cleavage of ethers,* $R'\cdot C_6H_4\cdot O\cdot C_6H_4R''$.

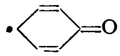
R′	R″	Cleavage (%)	OMe (%) in phenolic mixture	$R'\cdot C_6H_4\cdot OH$ (moles %)	R′	R″	Cleavage (%)	OMe (%) in phenolic mixture	$R'\cdot C_6H_4\cdot OH$ (moles %)
p-Cl	*m*-Me	39	8·1, 8·1 *	26	*p*-OMe	*o*-Me	23	13·8	51
,,	*p*-Me	50	6·5, 6·4 *	20	,,	*p*-Me	35	8·5	31
,,	*m*-OMe	20	17·0	31	,,	*p*-Bu^t	13	9·0, 8·9	40
,,	*p*-OMe	18	14·9	39	*p*-Me	*m*-Me	14	—	62
m-Me	*p*-C_6H_5	15	—	51	,,	*o*-OMe	52	18·4, 18·1	30
					,,	*p*-C_6H_5	13	—	58

* Cl, %.

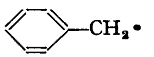
TABLE 3. *Stabilisation index* (*S*) *of substituent groups,* R.

R, reference standard		Me			OMe			Cl			Bu^t	C_6H_5
		o	*m*	*p*	*o*	*m*	*p*	*o*	*m*	*p*	*p*	*p*
H	(1·0)	—	—	—	—	—	—	0·1	0·3	3·0	—	—
p-Cl	(3·0)	—	8·6	12	—	6·7	4·7	—	—	—	—	—
p-OMe	(4·7)	4·5	—	11	—	—	—	—	—	—	7·1	—
p-Me	(12)	—	7·3	—	28	—	5·4	—	—	—	—	8·7
p-C_6H_5	(8·7)	—	8·8	—	—	—	—	—	—	—	—	—

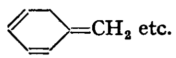
Although considerable chemical evidence existed, and was advanced in Part I, to support the postulate that free aryloxy-radicals $R\cdot C_6H_4\cdot O\cdot$ are relatively more stable than aryl radicals $R\cdot C_6H_4\cdot$, and that consequently cleavage should proceed *via* the former rather than the latter, it seems desirable, in view of the fact that this postulate forms the basis of the proposed cleavage mechanism, to find further support from a consideration of the relative energies of such radicals. In the equilibrium $C_6H_5{\cdot}O{\cdot} + C_6H_5{\cdot}H \rightleftharpoons C_6H_5{\cdot}OH + C_6H_5{\cdot}$, the left- or right-hand side is favoured according to whether the phenoxy- or the phenyl radical, respectively, is the more stable. A consideration of bond energies alone would lead to the conclusion that the right-hand side is favoured, since the bond energy of the O–H linkage is 110 kcal. and that of the C–H linkage is only 87 kcal. However, resonance between structures such as (I) as well as the Kekulé structures should, by analogy with the free benzyl radical, stabilise the phenoxy-radical by about 20 kcal.



(I)



(II)



(III)

(Szwarc, *J. Chem. Phys.*, 1948, **16**, 128). Moreover, Pullman (*Discuss. Faraday Soc.*, 1947, **2**, 26) has calculated that in the free benzyl radical, (II) makes a 62·8% contribution and (III) 37·2%. If these proportions hold for the phenoxy-radical, then the replacement of the =C by the =O linkage should give a further 15 kcal. Hence in the reaction above the left-hand side is favoured to an extent of approximately 12 kcal., *i.e.*, the phenoxy-free radical is the more stable.

If it is accepted that aryloxy-radicals are the intermediates in the cleavage, and that substituents act mainly electropositively in stabilising such radicals (Ingold, *loc. cit.*), the values obtained in Table 3 might constitute a measure of the relative polarisation effects of R in the radicals. Thus from the data it would be concluded that: (*a*) the electronic effect of the *p*-chlorine atom is ($+M > -I$), and that $+M$ is considerable in magnitude, by comparison with the value obtained for the *m*-chlorine atom (factor of 10 : 1); (*b*) that in the *p*-phenyl group, the preponderance of the $+M$ effect over $-I$ is even more pronounced; (*c*) that the *p*-methyl group is more electron-releasing than either the *m*-methyl or the *p-tert.*-butyl group, in spite of the greater $+I$ effect which the last two groups possess (this result would have to be attributed solely to hyperconjugation of the *p*-methyl group); (*d*) that the *p*-methoxy-group has a greater tendency for electron-release than hydrogen ($+M > -I$), as is well known, but that this tendency in the radical is smaller than that of the *p*-methyl group; (*e*) that the value for the *o*-methoxy-substituent appears abnormally high, and that of the *o*-chloro- extremely low; (*f*) that the *m*-methoxy-group does not exhibit the effect usually attributed to this group, namely, $-I$.

These observations in many respects deviate from the results obtained by the well-known acid–base equilibria measurements, *e.g.*, in the thermodynamic dissociation constants of substituted acetic and benzoic acids (see Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons, 1953, pp. 722—750), from which it is known that (*a*) the electronic effect for the *p*-chlorine atom is ($-I > +M$), (*b*) that for *m*-methoxy is $-I$, and (*c*) that in electropositivity the *p*-methoxy-group is greater than the *p*-methyl group. The stabilising influence of R, if taken as a direct measure of the electropositivity, would also appear too large for (*a*) the *p*-methyl group, as compared with *m*-methyl and *p-tert.*-butyl, since the hyperconjugative effect is usually known to be relatively small, and (*b*) the *p*-phenyl substituent which recent measurements on the dissociation constant of diphenyl-4-carboxylic acid (Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479) show to be only weakly ($+M > -I$).

Most of these apparent irregularities can be explained if it is postulated that the stability of the free aryloxy-radical is not dependent on the electropositivity of R as measured in heterolytic reactions, but to a large extent depends also on whether R offers opportunity for resonance within the radical itself. Thus in cases where only the inductive effect $+I$ operates, the radical is stabilised, hence the observed values for the *m*-methyl and *p-tert.*-butyl groups; where both the inductive and the mesomeric mechanisms are operative, however, the latter would appear to play a more decisive rôle, hence the relatively large values for the *p*-methyl and *p*-phenyl groups, as well as the stabilising effect of the *p*-chlorine atom. When viewed in this light, the *o*-methyl group, which possesses a greater

$+I$ and a smaller $+M$ effect than *p*-methyl, also gives a value for S of the correct order, and suggests that the proximity factor responsible for the abnormal figures for the *o*-methoxy- and *o*-chloro-substituents is not entirely a steric one. No explanation can be offered for the greater S value of the *p*-methyl than of the *p*-methoxy-, and for the abnormally large one of the *m*-methoxy-group.

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