47.   *The Halogenation of Phenolic Ethers and Anilides.   Part X.*
Substituted Tolyl Ethers.

By Brynmor Jones.

The kinetic study of the chlorination of ethers of the general formula $OR \cdot C_6H_4 \cdot X$ has now been extended to include several series of aromatic ethers which contain, in addition to the group X, one or more methyl substituents.   Analysis of the results obtained hitherto in terms of the equation $k = PZe^{-E/RT}$ has shown that the changes in velocity are to be attributed to variations in the energy of activation, and that in ethers of the type $p\text{-}OR \cdot C_6H_4 \cdot X$ the groups OR and X each contribute a characteristic quota to the activation energy of further substitution.   This has been found to be so when-

ever R is an alkyl, benzyl, or substituted benzyl group and X a deactivating substituent. For six new series of ethers the present results show that, when an activating group such as methyl is also present in the nucleus which undergoes chlorination, the simple additive relationships previously found are not strictly applicable in all cases. The significance of this is discussed.

AN earlier kinetic investigation of the chlorination of a few p-tolyl ethers of the type (I) revealed a definite tendency to departure from the simple additive relationships for the energies of activation found in several series of ethers of the type $p\text{-}OR\cdot C_6H_4X$. As this was the first departure from the additive rule to be observed, it was important to determine whether it was characteristic of all disubstituted ethers or whether the departure from

TABLE I.

Velocity coefficients for the chlorination of substances of the types $RO\text{-}C_6H_3(CH_3)$ *and* $RO\text{-}C_6H_3(X)(CH_3)$ *in 99% acetic acid, at 20°.*

Type $RO\text{-}C_6H_3(CH_3)$ with Br.
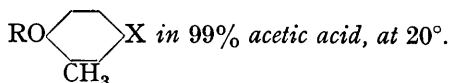
	$[Cl_2] = 0.0075$; $[HCl] = 0.0375$.		$[Cl_2] = 0.0050$; $[HCl] = 0.0250$.
Concn. of ether	0.0225	0.0375	0.0150
Mol. propn.	3	5	3
Group R.	$k.$		$k.$
CH_3	7.12	—	—
C_2H_5	13.2	—	—
CH_2Ph	3.92	3.77	3.88
$p\text{-}C_6H_4Me\cdot CH_2$	5.47	5.18	5.37
$p\text{-}C_6H_4Et\cdot CH_2$	5.45	5.21	5.43
$p\text{-}C_6H_4Cl\cdot CH_2$	—	—	2.23
$p\text{-}C_6H_4Br\cdot CH_2$	2.20	2.10	2.15
$p\text{-}C_6H_4(NO_2)\cdot CH_2$	0.807	—	—
$m\text{-}C_6H_4F\cdot CH_2$	1.90	—	1.89
$m\text{-}C_6H_4(NO_2)\cdot CH_2$	0.936	—	—
$o\text{-}C_6H_4Cl\cdot CH_2$	1.56	1.50	1.55
$o\text{-}C_6H_4(NO_2)\cdot CH_2$	0.76	—	0.76

Type $RO\text{-}C_6H_3(CH_3)$ with NO_2.
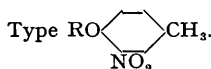
$[Cl_2] = 0.04$; $[ether] = 0.12$; $[HCl] = 0.05$.

Group R	CH_3	C_2H_5	$C_3H_7\beta$	$C_4H_9{}^a$
k	0.022	0.042	0.075	0.046

Type $RO\text{-}C_6H_3(CH_3)$ with Br.
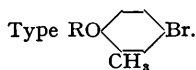
$[Cl_2] = 0.0075$; $[HCl] = 0.0375$.

Concn. of ether	0.0225	0.0075	Concn. of ether	0.0225	0.0075
Mol. propn.	3	1	Mol. propn.	3	1
Group R.	$k.$		Group R.	$k.$	
CH_3	4.36	4.60	$p\text{-}C_6H_4Bu^\gamma\cdot CH_2$	3.08	—
C_2H_5	8.63	9.04	$p\text{-}C_6H_4Cl\cdot CH_2$	1.38	1.53
$C_3H_7{}^a$	9.14	9.71	$p\text{-}C_6H_4Br\cdot CH_2$	1.34	—
$C_3H_7\beta$	14.16	—	$p\text{-}C_6H_4(NO_2)\cdot CH_2$	—	0.528
$C_5H_{11}{}^a$	9.25	—	$m\text{-}C_6H_4F\cdot CH_2$	1.09	—
CH_2Ph	2.28	2.52	$m\text{-}C_6H_4Cl\cdot CH_2$	1.03	—
$p\text{-}C_6H_4Me\cdot CH_2$	3.18	3.47	$o\text{-}C_6H_4Cl\cdot CH_2$	0.915	—
$p\text{-}C_6H_4Et\cdot CH_2$	3.18	—	$o\text{-}C_6H_4(NO_2)\cdot CH_2$	0.383	—

$[Cl_2] = 0.0075$; $[ether] = 0.0150$; $[HCl] = 0.0375$.

R = CH_2Ph; $k = 2.31$ R = $p\text{-}C_6H_4(NO_2)\cdot CH_2$; $k = 0.491$

$[Cl_2] = 0.0050$; $[ether] = 0.0150$; $[HCl] = 0.0250$.

R = CH_3; $k = 4.35$ R = C_2H_5; $k = 8.56$ R = $C_3H_7{}^a$; $k = 9.08$.

additivity occurs only when activating groups are present in the molecule. The three series of disubstituted ethers investigated have the general formulæ (I), (II), and (III).

$$RO\langle\bigcirc\rangle CH_3 \qquad RO\langle\bigcirc\rangle Br \qquad RO\langle\bigcirc\rangle Cl$$
$$\quad\; X \qquad\qquad\qquad CH_3 \qquad\qquad\qquad Cl$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad\qquad \text{(III.)}$$
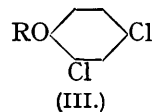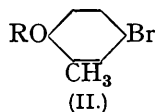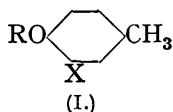
Such ethers have the advantage that one position only is available for chlorination, and the velocity coefficients relate to reaction at a single nuclear position. This is true also of the disubstituted ethers of s.-m-xylenol examined.

The mean values of the bimolecular velocity coefficients now reported are given in Tables I and II. As in earlier papers, the medium is " 99% acetic acid " (1 c.c. of water per 100 c.c. of solution), the concentrations are in g.-mols./l., and the time in minutes. The relative directive powers of the OR groups are again given in the form $100k_X^{OR}/k_X^{OMe}$; $k_{p\cdot X}^{OR}$ represents the velocity coefficient for the chlorination of $p\text{-}OR\cdot C_6H_4X$.

TABLE II.

Velocity coefficients of chlorination in 99% *acetic acid, at* 20°.

	Type RO⟨⟩Cl (Cl, Cl)	Type RO⟨⟩Cl (Cl CH₃ / CH₃)		Type RO⟨⟩Cl (O₂N CH₃ / CH₃)
	[Cl₂] = 0·04; [HCl] = 0·0475.	[Cl₂] = 0·0075; [HCl] = 0·0375.		[Cl₂] = 0·02; [HCl] = 0·0475.
Concn. of ether	0·12	0·0225	0·0075	0·04
Mol. propn.	3	3	1	2
	k.	*k.*		*k.*
R = CH₃	0·00321	14·1	14·5	0·0386
C₂H₅	0·00641	—	27·0	0·0690
C₃H₇[a]	0·00697	—	28·3	0·0748
C₆H₁₃[a]	—	—	—	—
CH₂Ph	0·00223	8·05	8·16	0·0728
p-C₆H₄Cl·CH₂	—	4·89	—	—
p-C₆H₄Br·CH₂	—	4·71	—	—
m-C₆H₄F·CH₂	—	3·85	—	—
m-C₆H₄Cl·CH₂	0·0010	3·75	—	—
o-C₆H₄Cl·CH₂	—	3·20	—	—

DISCUSSION.

The current practice, first introduced by Bradfield and Jones (J., 1928, 1006), of analysing data relating to reaction rates in solution in terms of the equation $k = PZe^{-E/RT}$ has led to a clearer understanding of the way in which constitutional changes affect chemical reactivity by focusing attention on the fact that the changes in velocity may be due to variations in P, in E, or in both P and E. Among the several reactions studied, two main groups can be distinguished : (1) reactions in which the differences in velocity can be accounted for, almost entirely at least, by variations in the energy of activation, changes in the value of P in comparison being almost negligible ; (2) reactions in which simultaneous variations in E and in P are found. Characteristic of these two groups of reactions is the circumstance that, in the first, the variable substituent is well removed from the point of reaction, when disturbances of a local nature are reduced to a minimum, while in the second group the variable substituent is usually near to the reactive centre (for references, cf. Watson, *Ann. Reports*, 1938, **35**, 236).

The nuclear chlorination of phenolic ethers of the general type $p\text{-}OR\cdot C_6H_4X$ has been shown to be a reaction of the first type. Although the nature of the reactants and of the medium imposes severe limitations on the temperature range over which measurements can be made, yet a careful study of the velocity coefficients of closely related series of ethers over a range of 15° has shown that, to the degree of exactness that can be expected over this limited range, P is constant. Small changes in P are not unexpected, but for

ethers of the above type these are only of minor importance and the differences in reaction rates are attributed, mainly at least, to variations in the energy of activation.

On the assumption that P is constant for closely related series of ethers, it has been shown in earlier papers (1) that variations in E alone are sufficient to account for the differences in the velocity of chlorination, and (2) that the two substituents OR and X contribute additively to the energy of activation. This relationship has been found to hold for several series of ethers of the above type where X is a deactivating halogen atom (F, Cl, or Br) or a meta-directing group such as NO_2, CO_2H, COPh, or SO_2Ph.

The possibility of an extension of this limited generalisation was naturally visualised at the outset, and several new series of ethers which contain activating as well as deactivating substituents in the nucleus which undergoes substitution have been investigated.

In the chlorination of ethers of the types (I, X = Br), (II), and (III) the critical energy increment relating to the single point of entry will presumably be governed by the influence of all three substituents; *i.e.*, for the tolyl ethers, $E = E_0 + E_{OR} + E_{CH_3} + E_{Br}$, where E_0 is the critical increment in the unsubstituted compound, E_{OR} the energy contribution of the group OR to the point of attack, and E_{CH_3} and E_{Br} the modifying influence of the substituents CH_3 and Br.

Consequently, by analogy with the expressions developed in previous papers the following expression may be set up for (I, X = Br) :

$$k(\text{obs.}) = k\underset{\diagdown CH_3 \,(1)}{\overset{\diagup OR\,(4)}{\underset{}{\text{—Br}\,(3)}}} = PZe^{-(E_0 + E_{OR} + E_{Br} + E_{CH_3})/RT}$$

and a similar expression obtains when R′ is substituted for R in this ether. If the small variations due to differences in molecular weight are neglected, and as in the earlier papers P is assumed to be constant for a closely related series of ethers, then

$$k\underset{\diagdown CH_3\,(1)}{\overset{\diagup OR'\,(4)}{\underset{}{\text{—Br}\,(3)}}} \Big/ k\underset{\diagdown CH_3\,(1)}{\overset{\diagup OR\,(4)}{\underset{}{\text{—Br}\,(3)}}} = e^{(E_{OR} - E_{OR'})/RT}$$

Further, change of the alkyl group R to R′ in the series (II) and (III) leads to an identical expression; *i.e.*, in all three series the same expression is obtained as for the simpler ethers of the type p-OR·C_6H_4X.
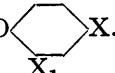
From this result two conclusions follow : (1) the relative directive powers of the OR groups in the three series of ethers should be independent of the nature of the other substituents present in the nucleus, and, in the tolyl ethers, of the actual positions of the methyl and bromine substituents; (2) the velocity ratios for the three series should be the same as those already found for the simple p-substituted phenyl ethers.

Examination of the velocity ratios given in Table III shows that these expectations, based on the assumption of the constancy of P, are only partly realised and the following points emerge : (1) In the tolyl ethers the relative directive powers of OR groups are found to be independent of the actual positions in the nucleus of the methyl and bromine substituents; (2) in the 2 : 4-dichlorophenyl ethers only are the same velocity ratios observed as in the ethers of the type p-OR·C_6H_4X. In both series of tolyl ethers they differ by approximately 15%, showing that the relative directive powers of the OR groups are not independent of the polar nature of the other groups present in the benzene nucleus.

This modification of the relative directive powers of OR groups as a result of the introduction of a methyl group into the nucleus which undergoes substitution occurs also in other series of ethers. Thus the presence of two methyl groups in 2 : 4-dichloro-3 : 5-dimethyl phenyl ethers modifies the velocity ratios found for the 2 : 4-dichlorophenyl ethers so that they no longer correspond with those for the monosubstituted ethers but instead show good agreement with the values obtaining in the tolyl series.

This effect of methyl groups is thus seen to be quite regular. At present its explanation can be approached only in a tentative way. Recent studies of reaction kinetics by Hinshelwood, Watson, and others (cf. Hinshelwood and Legard, J., 1935, 587 ; Hinshelwood and Winkler, J., 1936, 371 ; Watson, *Ann. Reports*, 1938, **35**, 238) have shown that, when the
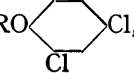
TABLE III.

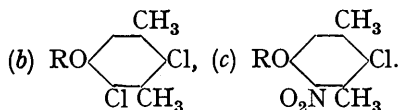Relative directive powers of the groups OR in compounds of the type RO⬡X, X_1.

Values of $100 k^{OR}_{XX_1}/k^{OMe}_{XX_1}$.

	R = CH₃.	C₂H₅.	C₃H₇ᵃ.	C₃H₇ᵝ.	C₄H₉ᵃ.	C₅H₁₁ᵃ.
X = CH₃, X₁ = Br	100	185	—	—	—	—
,, X₁ = NO₂	100	195	—	348	211	—
X = Br, X₁ = CH₃	100	197	210	325	—	212
X = Cl, X₁ = Cl	100	199	217	—	—	—
Phenyl ethers (mean)	100	199	223	440	223	221

R = C₆H₄A·CH₂.

	A = H.	p-Me.	p-Et.	p-Buᵞ.	p-Cl.	p-Br.	p-NO₂.	m-F.	m-Cl.	m-NO₂.	o-Cl.
X = CH₃, X₁ = Br	55	77	77	—	—	31	11·3	27	—	13	22
X = Br, X₁ = CH₃	54	74	73	71	33	31	11·5	25	24	—	21
X = Cl, X₁ = Cl	69	—	—	—	—	—	—	—	32	—	—
Phenyl ethers (mean)	68	95	95	95	42	41	14·1	34	33	16	28

TABLE IV.

Relative directive powers of the groups OR in compounds of the type (a) RO⬡Cl, Cl,

(b) RO⬡Cl with CH₃ (top), Cl CH₃ (bottom), (c) RO⬡Cl with CH₃ (top), O₂N CH₃ (bottom).

Values of $100 k^{OR}_{X}/k^{OMe}_{X}$.

	R = CH₃.	C₂H₅.	C₃H₇ᵃ.	C₆H₁₃ᵃ.	A = H.	p-Cl.	p-Br.	m-F.	m-Cl.	o-Cl.
Series (a)	100	199	217	—	69	—	—	—	32	—
,, (b)	100	185	195	—	57	35	34	27	27	23
,, (c)	100	179	194	189	—	—	—	—	—	—
Phenyl ethers (mean)	100	199	223	221	68	42	41	34	33	28
Tolyl ethers (mean)	100	192	210	—	55	33	31	26	24	22

(header for the last five data columns: R = C₆H₄A·CH₂.)

variable group is comparatively near to the point of reaction, the changes in velocity are in many cases to be attributed very largely to variations in E but that the factor P also undergoes appreciable changes. A somewhat similar state of affairs may occur when methyl groups are present in the above ethers. The presence of a group such as methyl, which raises the general reactivity of the nucleus to which it is attached, at no great distance from other groups or from the point of reaction may possibly cause larger variations in P than occur in compounds of the simpler type p-OR·C₆H₄X and also, perhaps, some departure from the additive energy relationships. These may result from direct interaction of some kind with other groups and by other " local disturbances." It is noteworthy that the variations from the expected velocity ratios are found mainly when the group R which is varied is a simple alkyl group (cf. Tables III and IV).

When, on the other hand, comparison is restricted to the substituted benzyl ethers, where the variable substituent is in the m- or the p-position of the aromatic nucleus and therefore at some distance from the reactive centre, then all three series phenyl, tolyl, and xylyl give velocity ratios which show satisfactory agreement. This suggests that for substituted benzyl ethers the conclusions drawn in earlier papers from the study of phenyl ethers apply also to the tolyl and xylyl ethers.

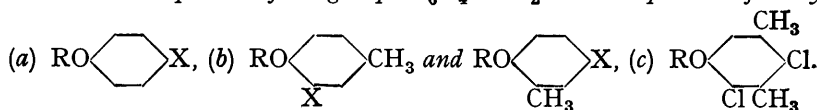It is significant in this connexion that, when a strongly polar substituent such as a nitro-group is situated in the ortho-position of the benzyl group, differences in velocity ratios appear. The relative directive power of the o-nitrobenzyloxy-group in the 3-bromo-p-tolyl series is 19·5 and in the isomeric 5-bromo-o-tolyl series 16·8, whereas the mean value found in the simple phenyl ethers is 21.

TABLE V.

Relative directive powers of the groups $C_6H_4A \cdot CH_2 \cdot O$ *in compounds of the type*

$$C_6H_4A \cdot CH_2 \cdot O \langle \rangle X.$$
$$\overline{X_1}$$
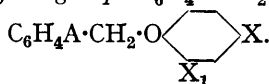
Values of $100k_{XX_1}^{O \cdot CH_2 \cdot C_6H_4A}/k_{XX_1}^{O \cdot CH_2Ph}$.

	A = H.	*p*-Me.	*p*-Et.	*p*-Bu$^\gamma$.	*p*-Cl.	*p*-Br.	*p*-NO$_2$.	*m*-F.	*m*-Cl.	*m*-NO$_2$.	*o*-Cl.
X = CH$_3$, X$_1$ = Br	100	138	139	—	58	56	21	49	—	24	40
X = Br, X$_1$ = CH$_3$	100	139	139	135	61	59	21	48	45	—	40
Phenyl ethers (mean)	100	139	139	139	60	58	21	49	47	24	41

TABLE VI.

Relative directive powers of the groups $C_6H_4A \cdot CH_2 \cdot O$ *in compounds of the type*

$$(a)\ RO\langle \rangle X,\ (b)\ RO\langle \rangle CH_3\ and\ RO\langle \rangle X,\ (c)\ RO\langle \rangle^{CH_3}_{Cl}Cl.$$
$$\overline{X}\overline{CH_3}\overline{Cl\ CH_3}$$

Values of $100k_X^{O \cdot CH_2 \cdot C_6H_4A}/k_X^{O \cdot CH_2Ph}$.

	A = H.	*p*-Cl.	*p*-Bγ.	*p*-NO$_2$.	*m*-F.	*m*-Cl.	*o*-Cl.
(a) Phenyl ethers (mean)	100	60	58	21	49	47	41
(b) Tolyl ethers (mean)	100	59·5	57·5	21	48·5	45	40
(c) Xylyl ethers	100	61	58·5	—	48	46·5	40

In view of the scope provided for the possible operation of complicating factors in polysubstituted ethers of the type of the 2 : 4-dichloro-3 : 5-dimethylphenyl ethers it is a matter of particular interest that the relative directive powers of OR groups observed in this series differ by only 15% from those found in the simpler ethers of the type *p*-OR·C$_6$H$_4$X.

A more complete understanding of the influence of nuclear-situated methyl groups in these several series requires the determination of velocity coefficients over as wide a range of temperature as possible and the analysis of these in terms of the two parameters of the Arrhenius equation.

Two interesting examples of the well-known effect of methyl in raising the general level of reactivity of the nucleus to which it is attached are provided by the comparison of the velocity coefficients for the two pairs of ethers (*a*) *p*-bromophenyl ethers and the 5-bromo-*o*-tolyl ethers, and (*b*) the 2 : 4-dichlorophenyl and the corresponding 2 : 4-dichloro-3 : 5-dimethylphenyl ethers. The presence of a single methyl group in the 5-bromo-*o*-tolyl ethers increases the rate of chlorination as compared with the *p*-bromophenyl ethers 2·7 times although there is only one of the two ortho-positions free for substitution. In the second pair the effect is more striking, for the introduction of two methyl groups into the 2 : 4-dichlorophenyl ethers increases the velocity of chlorination over 4000 times.

The ethers investigated in this series of papers are now sufficiently varied to make it possible, by employing the above velocity ratios, to predict the actual velocity of chlorination of individual ethers under standard conditions provided the velocity coefficient of one member of the series be known accurately.

The main conclusions of this investigation may be summarised as follows : (1) For a series of 2 : 4-dichlorophenyl ethers the same relative directive powers of OR groups are found as for the simpler ethers of the type *p*-OR·C$_6$H$_4$X investigated in earlier papers. (2) When a methyl group is present in the nucleus which undergoes substitution, as in the tolyl ethers, or when two methyl groups are present as in the 2 : 4-dichloro-3 : 5-dimethylphenyl ethers, there is a divergence of approximately 15% from the mean values found for the monosubstituted phenyl ethers. When, however, comparison is restricted to a range of substituted benzyloxy-groups where the variable substituent is situated in the *m*- or *p*-positions of the aromatic nucleus and is therefore well removed from the point of reaction, the same velocity ratios are observed in the phenyl, tolyl, and xylyl series. (3) The
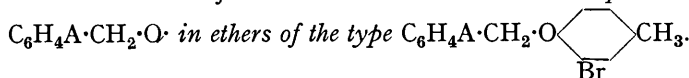
discovery for polysubstituted compounds such as the 2 : 4-dichloro-3 : 5-dimethylphenyl ethers of relative directive powers of OR groups which differ so little from the values obtaining in the simple monosubstituted ethers is a significant feature of the present work. (4) Comparison of the velocity coefficients of analogous 2 : 4-dichlorophenyl and 2 : 4-dichloro-3 : 5-dimethylphenyl ethers shows that the presence of the two methyl groups increases the rate of chlorination more than 4000 times.

EXPERIMENTAL.

Velocity Measurements.—The method of determining the velocity coefficients was the same as in the author's previous work and satisfactory values were obtained in all cases. With the 3-bromo-*p*-tolyl ethers, however, it was reported in Part III, and now confirmed, that when measurements are made with equal initial concentrations of reactants the velocity coefficients show a steady rise of approximately 10%. When, on the other hand, the molecular ratio of ether to chlorine is increased to 3 : 1, the drift in the values of the velocity coefficients is no longer detectable and satisfactory constants are obtained. Nevertheless, the existence of a secondary reaction of this magnitude makes the figures recorded in Table I for this series of ethers a little less trustworthy than those given for other series, but so far as the relative directive powers of groups are concerned, it is clear from Table VII that the above discrepancy has no noticeable effect, since ratios of velocity coefficients remain unaltered by a further increase in the ether : chlorine ratio to 5 : 1.

TABLE VII.

Effect of relative concentrations of ether to chlorine on the directive powers of the groups

$C_6H_4A \cdot CH_2 \cdot O \cdot$ *in ethers of the type* $C_6H_4A \cdot CH_2 \cdot O$⟨ ⟩$CH_3$, $\underset{Br}{}$.

Values of $100k_X^{O \cdot CH_2 \cdot C_6H_4A}/k_X^{O \cdot CH_2Ph}$.

Mol. propn. ether : chlorine.	A = H.	*p*-Me.	*p*-Et.	*p*-Cl.	*p*-Br.	*p*-NO₂.	*m*-F.	*m*-NO₂.	*o*-Cl.
3 : 1	100	139	139	—	56	21	49	24	40
5 : 1	100	137	138	—	56	—	—	—	40
3 : 1	100	138	140	58	55	—	49	—	40

The cause of the upward drift in the velocity coefficients is not clear, but it is significant that the isomeric 5-bromo-*o*-tolyl ethers give satisfactory constants at all concentrations. This suggests that, when it is in the *p*-position, the methyl group is itself attacked by chlorine—a view which is supported by the similar behaviour of ethers which have an ethyl or a *n*-propyl group, but not a *tert.*-butyl or -amyl group, in the *p*-position.

To ensure the purity of the specimens used in the velocity measurements, each ether was crystallised three times, usually from ethyl alcohol or glacial acetic acid, and only in exceptional cases was further purification essential. The following random selection of examples illustrates the constancy of the mean values of the velocity coefficients in individual experiments. (1) 5-Bromo-*o*-tolyl benzyl ether had k = 2·27, 2·29, 2·28, and 2·26 after three crystallisations from ethyl alcohol and one from glacial acetic acid, and k = 2·30 after a further crystallisation from benzene. (2) 2 : 4-Dichloro-3 : 5-dimethylphenyl *m*-chlorobenzyl ether, after two crystallisations from ethyl alcohol and one from glacial acetic acid, had k = 3·74, and after two further crystallisations from ethyl alcohol k = 3·76.

Materials.—The ethers were prepared by standard methods from the parent phenol and the appropriate benzyl chloride or bromide, the latter being themselves obtained according to the instructions given in Part IX and J., 1935, 1815.

3-Bromo-*p*-cresol was obtained by bromination of a commercially pure sample of *p*-cresol in ice-cold carbon tetrachloride, and the fraction of b. p. 214—216° employed for the preparation of the 3-bromo-*p*-tolyl ethers. The methyl and ethyl ethers had b. p.'s of 125°/20 mm. and 133°/24 mm. respectively, and the benzyl ether crystallises from alcohol in clusters of colourless prisms, m. p. 43·5° (Found :* C, 60·8; H, 4·9. Calc. : C, 60·6; H, 4·7%). The p-*methylbenzyl* and p-*ethylbenzyl ethers* crystallise from glacial acetic acid in colourless elongated prisms, m. p. 92° (Found : C, 62·1; H, 5·2. $C_{15}H_{15}OBr$ requires C, 61·9; H, 5·2%), and m. p. 67° (Found : C, 63·1; H, 5·7. $C_{16}H_{17}OBr$ requires C, 63·0; H, 5·6%), respectively. The p-*chloro*- and the p-*bromo-benzyl ethers*, the latter obtained from purified *p*-bromobenzyl bromide (cf. J., 1935, 1815), also crystallise from glacial acetic acid in clusters of colourless elongated

* All micro-determinations by Dr. Ing A. Schoeller.

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prisms, m. p. 67° (Found : C, 53·9; H, 4·1. $C_{14}H_{12}OClBr$ requires C, 54·0; H, 3·9%), and m. p. 85° (Found : C, 47·2; H, 3·4. $C_{14}H_{12}OBr_2$ requires C, 47·2; H, 3·4%), respectively. From glacial acetic acid the p-*nitrobenzyl ether* crystallises well in long, pale yellow prisms, m. p. 135° (Found : C, 52·2; H, 3·95. $C_{14}H_{12}O_3NBr$ requires C, 52·2; H, 3·8%), and the m-*fluoro-benzyl ether* separates from alcohol in large clusters of colourless prisms, m. p. 41° (Found : C, 56·95; H, 4·2. $C_{14}H_{12}OFBr$ requires C, 56·95; H, 4·1%). The o-*chlorobenzyl ether* melts at 54·5° and crystallises from glacial acetic acid in clusters of elongated prisms (Found : C, 54·1; H, 4·1%). The o-*nitrobenzyl ether* crystallises similarly, and after four crystallisations from glacial acetic acid had m. p. 110° (Found : C, 52·9; H, 3·5%).

3-*Nitro*-p-*tolyl ethers.* The methyl, ethyl, *iso*propyl, and p-methylbenzyl ethers were prepared from a purchased specimen of m-nitro-p-cresol, and the butyl and benzyl ethers from a specimen prepared by the nitration of p-cresol in glacial acetic acid. The first two ethers were obtained in good yield by the action of the alkyl sulphate on a warm solution of the nitrocresol in sodium hydroxide. The other four were prepared from the appropriate benzyl chloride or alkyl bromide and the nitrocresol in an alcoholic solution of sodium ethoxide. The specimens used for the velocity measurements had the following constants : methyl ether, b. p. 149—150°/13 mm.; ethyl ether, b. p. 151°/13 mm.; *iso*propyl ether, b. p. 175°/33 mm.; *n*-butyl ether, b. p. 172°/13 mm. The benzyl ether melts at 55° and crystallises from alcohol in clusters of colourless prisms, and the p-*methylbenzyl ether* crystallises in pale yellow prisms, m. p. 69° (Found : C, 70·3; H, 5·9. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·9%).

5-Bromo-o-cresol, prepared by bromination of o-cresol in ice-cold carbon tetrachloride and crystallised from ligroin (b. p. 40—60°), had m. p. 62—64°. Five alkyl ethers prepared from this specimen had the following constants : the methyl ether had m. p. 67° and crystallised from ethyl alcohol in flat, colourless plates; the ethyl ether, b. p. 127°/19 mm.; *n*-propyl ether, b. p. 142°/20 mm.; *iso*propyl ether, b. p. 129°/19 mm. (Found : C, 52·8; H, 5·9. $C_{10}H_{13}OBr$ requires C, 52·4; H, 5·7%); the n-*amyl ether*, b. p. 166°/17 mm. (Found : C, 56·6; H, 6·7. $C_{12}H_{17}OBr$ requires C, 56·0; H, 6·7%). The benzyl ether and ten substituted benzyl ethers were also prepared, but even after the usual precautions to ensure pure specimens had been observed the velocity coefficients obtained in individual experiments showed a slight downward drift. This was probably due to the presence in the 5-bromo-o-cresol of a small percentage of the unreactive 3 : 5-dibromo-o-cresol which was difficult to remove. The ethers were therefore purified until constant values of k were obtained, and in several instances this necessitated five or six crystallisations. The *benzyl ether*, after three crystallisations from ethyl alcohol and two from glacial acetic acid, from which it crystallises in clusters of colourless prisms, melts at 62° (Found : C, 60·9; H, 4·65. $C_{14}H_{13}OBr$ requires C, 60·6; H, 4·7%). The p-*methylbenzyl ether* separates in colourless, elongated prisms, m. p. 83°, after three crystallisations from alcohol and three from glacial acetic acid (Found : C, 61·6; H, 5·1. $C_{15}H_{15}OBr$ requires C, 61·8; H, 5·2%), and the p-*ethylbenzyl ether*, after similar treatment, crystallises in stout, colourless prisms, m. p. 81° (Found : C, 63·0; H, 5·7. $C_{16}H_{17}OBr$ requires C, 63·0; H, 5·6%). The p-tert.-*butylbenzyl ether*, prepared from a pure specimen of p-*tert*.-butylbenzyl bromide, was crystallised in turn from alcohol, twice from benzene, once from glacial acetic acid, and finally from alcohol and had m. p. 99°. It crystallises from ethyl acetate in colourless, monoclinic prisms (Found : C, 64·9; H, 6·5. $C_{18}H_{21}OBr$ requires C, 64·9; H, 6·4%). The p-*chlorobenzyl ether*, after two crystallisations from alcohol and two from glacial acetic acid, separates from the latter solvent in colourless, matted clusters, m. p. 96° (Found : C, 54·2; H, 3·8%). In the preparation of the analogous p-*bromobenzyl ether*, purified p-bromobenzyl bromide was used, and the ether, after three crystallisations from glacial acetic acid in which it is not appreciably soluble at room temperature and from which it crystallises in colourless prisms, had m. p. 117° (Found : C, 47·3; H, 3·4%). The p-*nitrobenzyl ether* crystallises from glacial acetic acid in long, pale yellow prisms, m. p. 156° (Found : C, 52·4; H, 3·8%). Its maximum solubility in glacial acetic acid is 0·5 g./100 c.c. at 20°.

The m-*fluorobenzyl* and the m-*chlorobenzyl ethers*, m. p. 73° (Found : C, 57·1; H, 4·1%), and m. p. 63° (Found : C, 53·9; H, 3·95%), respectively, after three crystallisations from glacial acetic acid, separate in colourless elongated prisms. The m-*nitrobenzyl ether*, which crystallises from glacial acetic acid in pale yellow, elongated prisms, m. p. 98°, is sensitive to light, the colour changing gradually to dark brown.

The o-*chlorobenzyl ether* crystallises from glacial acetic acid in clusters of colourless, slender prisms, m. p. 50° (Found : C, 53·9; H, 3·8%), and the o-*nitrobenzyl ether* separates from the same solvent in colourless, long, narrow prisms, m. p. 109°, which darken a little on exposure to diffused light and on melting (Found : C, 52·65; H, 3·7%).

2 : 4-*Dichlorophenyl ethers.* The methyl ether, m. p. 28—29°, the ethyl ether, b. p. 120°/8 mm. (after standing for several years this specimen solidified, m. p. 30—31°), and the benzyl ether, which crystallises from alcohol in clusters of colourless cubes, m. p. 63° (Found : C, 62·1; H, 3·9. Calc.: C, 61·7, H, 4·0%), were prepared from a specimen of 2 : 4-dichlorophenol obtained from *p*-chlorophenol by Orton and King's method of chlorination (J., 1911, **99**, 1185). In the preparation of the other ethers of this series a commercially pure sample of the dichlorophenol was used.

The *n*-propyl ether distils as a colourless liquid, b. p. 127°/13 mm., and the *iso*propyl ether at 118°/13 mm. The p-*methylbenzyl ether* separates from alcohol in clusters of colourless, elongated prisms, m. p. 92° (Found : C, 63·1; H, 4·8. $C_{14}H_{12}OCl_2$ requires C, 62·9, H, 4·5%). From alcohol the m-*chlorobenzyl ether* separates in clusters of colourless, slender prisms, m. p. 51° (Found : C, 54·35; H, 3·15. $C_{13}H_9OCl_3$ requires C, 54·3; H, 3·15%), and the o-*chlorobenzyl ether* crystallises in clusters of elongated prisms, m. p. 65° (Found : C, 54·3; H, 3·05%).

2 : 4-Dichloro-3 : 5-dimethylphenol was obtained from a purchased specimen of 2-chloro-5-*m*-xylenol by Orton and King's method of chlorination, freshly-prepared chloroacetamide being used as the source of chlorine. When the reaction was complete the acetamide was removed by treatment with water and the 2 : 4-dichloro-3 : 5-dimethylphenol, after being dried and crystallised from ligroin, had m. p. 83°. From this the following thirteen ethers were prepared.

The *methyl ether* crystallises from ethyl alcohol in colourless prisms, m. p. 82° (Found : C, 52·65; H, 4·85. $C_9H_{10}OCl_2$ requires C, 52·65; H, 4·9%). The *ethyl*, n-*propyl*, and *octyl ethers* crystallise from alcohol in clusters of elongated prisms : ethyl ether, m. p. 53° (Found : C, 54·85; H, 5·4. $C_{10}H_{12}OCl_2$ requires C, 54·8; H, 5·5%); *n*-propyl ether, m. p. 31° (Found : C, 56·7; H, 6·0. $C_{11}H_{14}OCl_2$ requires C, 56·65; H, 6·0%); octyl ether, m. p. 35° (Found : C, 63·3; H, 7·8. $C_{16}H_{24}OCl_2$ requires C, 63·35; H, 8·0%).

The *benzyl ether* after three crystallisations from ethyl alcohol, from which it separates in colourless prisms, melts at 89° (Found : C, 64·0; H, 4·8. $C_{15}H_{14}OCl_2$ requires C, 64·1; H, 5·0%). The p-*methylbenzyl ether* crystallises similarly and melts at 74° (Found : C, 64·4; H, 5·4. $C_{16}H_{16}OCl_2$ requires C, 65·1, H, 5·5%). The p-*chloro*- and p-*bromo-benzyl ethers* crystallise in colourless, elongated prisms, m. p. 99° (Found : C, 57·0; H, 3·95. $C_{15}H_{13}OCl_3$ requires C, 57·0; H, 4·15%), and m. p. 110° (Found : C, 50·2; H, 3·7. $C_{15}H_{13}OCl_2Br$ requires C, 50·0; H, 3·6%), respectively. Both the m-*fluoro*- and the m-*chloro-benzyl ether* crystallise from ethyl alcohol in colourless, elongated prisms of m. p. 88° (Found : C, 60·4, H, 4·4. $C_{15}H_{13}OFCl_2$ requires C, 60·2; H, 4·4% Found : C, 56·5; H, 4·2%, respectively). The o-*chloro*-isomeride separates from glacial acetic acid in very slender, colourless prisms, m. p. 101° (Found : C, 57·1; H, 4·1%). The p-*nitrobenzyl ether* crystallises from glacial acetic acid in white, elongated prisms, m. p. 157° (Found : C, 55·3; H, 4·3. $C_{15}H_{13}O_3NCl_2$ requires C, 55·2; H, 4·0%), and the m-*isomeride* separates in pale yellow elongated prisms of m. p. 163° (Found : C, 55·5; H, 4·1%). Both these ethers have a low solubility in cold glacial acetic acid : that of the *m*-isomeride is less than 0·25 g./100 c.c. at 20°.