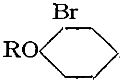
69. *The Halogenation of Phenolic Ethers and Anilides. Part XI. Substituted Benzyl Ethers of some Alkylphenols.*

By BRYNMOR JONES.

An extension of the kinetic study of the chlorination of aromatic ethers of the general type ROAlkyl has been made, and in all cases the relative directive powers of benzyloxy-groups are found to be the same as in the simpler ethers of the type *p*-OR·C_6H_4X. For analogous ethers with varying alkyl groups the relative velocities of substitution are $CH_3 : C_2H_5 : n\text{-}C_3H_7 : CMe_3 : CMe_2Et = 100 : 121 : 92{\cdot}5 : 48{\cdot}5 : 40{\cdot}5$. This series provides another example of the departure of alkyl groups from the theoretical sequence required by the operation of their general inductive effects.

Velocity coefficients for several 6-halogenothymyl ethers are also recorded. As expected, these display high reactivity: their rates of chlorination are compared with those of the simpler *p*-halogenophenyl ethers.

IN Part X (this vol., p. 267) the velocity coefficients of chlorination of three series of substituted tolyl ethers were recorded, and the influence of methyl groups on the reactivity of the nucleus which undergoes substitution was discussed. Measurements are now recorded for four similar series of ethers where the alkyl group situated in the *p*-position to the OR group is ethyl, *n*-propyl, *tert.*-butyl or *tert.*-amyl. In compounds of this type substitution occurs in the *o*-position to the OR group, and the velocity coefficients relate to reaction at a single nuclear position. With the 3-bromo-*p*-tolyl ethers, however, evidence was obtained of a secondary reaction which had a disturbing effect on the velocity coefficient. This was apparent when equal initial concentrations of reactants were employed, since a steady rise of approximately 10% over the range 35—70% change was observed. In order to minimise the effect of this disturbance the primary reaction had to be isolated, and this was achieved by increasing the molecular ratio of ether to chlorine to 3 : 1, whereby satisfactory velocity coefficients were obtained. The 3-bromo-*p*-ethylphenyl and the 3-bromo-*p*-*n*-propylphenyl ethers were found to behave similarly, with the secondary reaction displaying, if anything, a slightly greater prominence. For this reason only a few ethers in these two series were examined. The 3-bromo-*p*-*tert.*-butylphenyl and 3-bromo-*p*-*tert.*-amylphenyl benzyl ethers, on the other hand, gave satisfactory values at all concentrations examined (cf. experimental section). Similar behaviour has been observed during the bromination of the alkylphenols (Sprung, *Ind. Eng. Chem. Anal.*, **1941**, **13**, 3538; *Amer. Chem. Abs.*, **1941**, **35**, 1774). When a primary alkyl group occupies the *o*- or the *p*-position, partial bromination of the alkyl group occurs in addition to the usual nuclear substitution, and, as a result, more bromine is absorbed at room temperature than is required by theory. With *sec.*- and *tert.*-alkyl substituents, on the other hand, normal results are obtained. Brominated at 5°, all the alkylphenols examined, with the exception of the 2 : 6-dimethylphenol, behave normally.

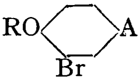
As a result of their high reactivity the velocity coefficients for the benzyl and substituted benzyl ethers of 6-chloro- and 6-bromo-thymol are less trustworthy than those recorded for less reactive ethers.

As in all other series, the measurements were made in 99% acetic acid (1 c.c. of water per 100 c.c. of solution) at 20°, but since the rate of nuclear chlorination decreases with a decrease in the water content of the medium, an attempt to get more accurate velocity coefficients was made by adopting conditions in which chlorination occurs less rapidly. A second series of velocity coefficients, measured at 16° and in 99·5% acetic acid, is also recorded.

The mean velocity coefficients are given in Table I, in which the concentrations are in g.-mols./litre and the time in minutes.

TABLE I.

Velocity coefficients for the chlorination of substances of the type



in 99% acetic acid, at 20°.

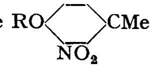
$[Cl_2] = 0·0075$; [ether] = 0·0225; [HCl] = 0·0375.

Alkyl group.	Group R.	*k*.	Alkyl group.	Group R.	*k*.
C_2H_5	*p*-$C_6H_4Me·CH_2$	6·47	*n*-C_3H_7	*p*-$C_6H_4(NO_2)·CH_2$	0·74
..	*p*-$C_6H_4Cl·CH_2$	2·73	,,	*m*-$C_6H_4(NO_2)·CH_2$	0·865
,,	*p*-$C_6H_4(NO_2)·CH_2$	0·99	,,	*o*-$C_6H_4(NO_2)·CH_2$	0·69
,,	*m*-$C_6H_4(NO_2)·CH_2$	1·13			

$[Cl_2] = 0·0075$; [HCl] = 0·0375.

Concn. of ether		0·0225	0·0075
Mol. propn.		3	1
Alkyl group.	Group R.	*k*.	
CMe_3	CH_2Ph	1·89	1·99
,,	*p*-$C_6H_4Me·CH_2$	—	2·71
,,	*p*-$C_6H_4Cl·CH_2$	1·09	—
,,	*p*-$C_6H_4Br·CH_2$	1·06	1·12
,,	*p*-$C_6H_4(NO_2)·CH_2$	—	0·40
,,	*m*-$C_6H_4(NO_2)·CH_2$	0·462	—
CMe_2Et	CH_2Ph	1·57	1·62
,,	*p*-$C_6H_4Me·CH_2$	2·16	2·19
,,	*p*-$C_6H_4Cl·CH_2$	0·915	0·93
,,	*p*-$C_6H_4(NO_2)·CH_2$	0·335	—
,,	*m*-$C_6H_4(NO_2)·CH_2$	0·383	0·395

Type

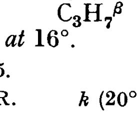


$[Cl_2] = 0·04$; [ether] = 0·12; [HCl] = 0·05.

R = CH_2Ph, *k* = 0·0062; R = *p*-$C_6H_4Br·CH_2$, *k* = 0·0135

TABLE II.

Velocity coefficients for the chlorination of substances of the type



in (a) 99% *acetic acid at* 20°, *and* (b) 99·5% *acetic acid at* 16°.

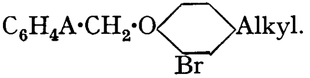
$[Cl_2] = 0·00125$; [ether] = 0·0025; [HCl] = 0·00625.

Group X.	Group R.	*k* (20°).	*k* (16°).	Group X.	Group R.	*k* (20°).	*k* (16°).
Cl	CH_2Ph	174	107·5	Br	CH_2Ph	177	109
,,	*p*-$C_6H_4Me·CH_2$	237	146	—	—	—	—
,,	*p*-$C_6H_4Cl·CH_2$	109	67	Br	*p*-$C_6H_4Cl·CH_2$	110	67
,,	*p*-$C_6H_4Br·CH_2$	106	67	—	—	—	—
,,	*o*-$C_6H_4(NO_2)·CH_2$	37	22·5	Br	*o*-$C_6H_1(NO_2)·CH_2$	38	22

The existence of the same relative directive powers of OR groups in the nuclear chlorination of ethers of the general type *p*-OR·C_6H_4X has been clearly demonstrated for a wide variety of ethers, where X is a halogen atom or a *m*-directing substituent and R an alkyl or substituted benzyl group. Recent extensions (this vol., p. 267) to include di- and poly-substituted ethers have shown, moreover, that when the two substituents are chlorine atoms the same relative directive powers are obtained as in the monosubstituted ethers, but that when one of the substituents is an activating methyl group as, *e.g.*, in the 3-bromo-*p*-tolyl ethers, or when two methyl groups are present as in the 2 : 4-dichloro-3 : 5-dimethylphenyl ethers, the values obtained for a wide range of R groups differ by approximately 15%. When, however, comparison is restricted to substituted benzyl ethers where the variable substituent is in the *m*- or *p*-position, and therefore well removed from the point of reaction, the same relative powers of groups are found in all series. The new data in Table III show a similar agreement for the benzyl and substituted benzyl ethers of several other halogenated alkylphenols.

TABLE III.

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

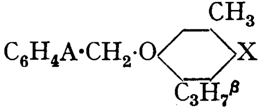


Values of $100k_{\text{Alkyl}}^{O\cdot CH_2\cdot C_6H_4A}/k_{\text{Alkyl}}^{O\cdot CH_2Ph}$.

Alkyl group.	A = H.	*p*-Me.	*p*-Cl.	*p*-Br.	*p*-NO_2.	*m*-NO_2.
CH_3	100	138	58	56	21	24
C_2H_5	100	139	59	—	21	24
n-C_3H_7	—	—	—	—	21	24
CMe_3	100	136	58	56	20	24
CMe_2Et	100	136	58	—	21	24

In the highly reactive 6-chloro- and 6-bromo-thymyl ethers the velocity coefficients are less accurate but here, too, the velocity ratios approximate very closely to those obtaining in other series :

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

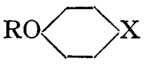


in 99% acetic acid, at 20°.

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

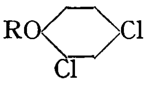
Group X.	A = H.	*p*-CH_3.	*p*-Cl.	*p*-Br.	*o*-NO_2.
Cl	100	136	62	61	21
Br	100	—	—	61	20·5

On reviewing the data in this and earlier papers, it is clear that for ethers of varying types and complexity, such as

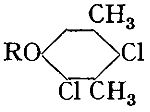


(X = F, Cl, Br, or CO_2H.)

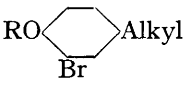
(I.)



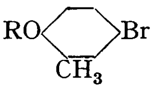
(II.)



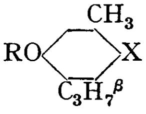
(III.)



(IV.)



(V.)



(X = Cl or Br.)

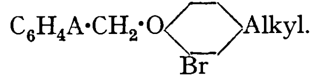
(VI.)

the relative directive powers of the various benzyloxy-groups are the same irrespective of the number and of the polar character of the substituents in the nucleus which undergoes substitution.

Further illustrations of the well-known effect of alkyl groups in enhancing the reactivity of the nucleus to which they are attached towards electrophilic reagents were given in Part X (*loc. cit.*). The new data in Tables I and II afford other examples. The presence of the methyl and the *iso*propyl group in the 6-chloro- and 6-bromo-thymyl ethers increases the rate of chlorination 212 times as compared with those of *p*-chloro- and *p*-bromo-phenyl ethers, although in the thymyl ethers there remains only one *o*-position available for substitution. When, however, the relative influences of the various alkyl groups on the rate of reaction of the 3-bromo-*p*-alkylphenyl benzyl ethers are compared, it is seen that an irregular sequence Me<Et>Pr$^{\alpha}$>Bu$^{\gamma}$>Amyl$^{\gamma}$ is obtained (Table IV). Similar results have recently been found in other reactions, and their significance has been discussed at some length by several investigators (cf. Baker and Nathan, J., 1935, 1844; Watson, *Ann. Reports*, 1938, **35**, 249).

TABLE IV.

Relative influences of alkyl groups in compounds of the type



Values of $100k^{\mathrm{O\cdot CH_2\cdot C_6H_4A}}_{\mathrm{Alkyl}}/k^{\mathrm{O\cdot CH_2\cdot C_6H_4A}}_{\mathrm{CH_3}}$.

Alkyl =	CH_3.	C_2H_5.	n-C_3H_7.	CMe_3.	CMe_2Et.
A = H	100	—	—	48	40
p-Me	100	118	—	—	39
p-Cl	100	122	—	49	41
p-Br	100	—	—	48	—
p-NO_2	100	122	92	—	42
m-NO_2	100	121	93	49	41
Mean	100	121	92·5	48·5	40·5

Since the completion of this work, Hughes, Ingold, and Taher (J., 1940, 949) have analysed critically the question of the relative polar influences of alkyl groups and have demonstrated in the unimolecular nucleophilic substitutions of *p*-alkylbenzhydryl chlorides a regular electron release capacity in the order Me>Et>Pr$^{\beta}$>Bu$^{\gamma}$.

EXPERIMENTAL.

Details of the measurements of the velocity coefficients of chlorination and of the precautions taken to ensure accurate values have been given in previous papers. The usual procedure of crystallising each compound at least three times from ethyl alcohol or glacial acetic acid was followed, and the constancy of the velocity coefficients after further crystallisations is illustrated by the following mean values obtained in individual experiments. 3-Bromo-*p*-*tert*.-butylphenyl *p*-chlorobenzyl ether had k 1·09 after three crystallisations from ethyl alcohol, and k 1·095 after a further crystallisation from the same solvent. Similarly 3-bromo-*p*-*tert*.-amylphenyl benzyl ether gave mean values of 1·58 and 1·56.

The satisfactory nature of the velocity coefficients obtained in all cases when the ether : chlorine ratio was 3 : 1, and the steady rise when this ratio was reduced to 1 : 1 in the *p*-ethylphenyl and *p*-*n*-propylphenyl ethers, are illustrated by the data in Table V.

With the highly reactive 6-halogenothymyl ethers chlorination occurred so rapidly in some cases that the main part of the reaction was completed in a few minutes. The standard procedure employed in these velocity measurements was modified therefore as follows : Three 10 c.c. portions of the reaction mixture were withdrawn as quickly as possible after the commencement of the reaction and run into an excess of an aqueous solution of potassium iodide in three flasks, and the liberated iodine estimated by titration after the last withdrawal. This meant that some of the flasks had to stand several minutes before the titration was made and as a result some oxidation occurred. To minimise the effect of this as far as possible the air in the potassium iodide solutions was previously displaced by a steady current of nitrogen from a cylinder. A stream of nitrogen was also passed through the solution during the titration. Complete details for two ethers at two temperatures are given in Table VI.

With the exception of those marked by an asterisk, the analyses were micro-determinations by Dr. Ing. A. Schoeller.

Materials.—The *p*-ethylphenol required for the preparation of the 3-bromo-*p*-ethylphenol was obtained from a commercially pure specimen of *p*-hydroxyacetophenone by Clemmensen's

TABLE V.

3-Bromo-p-tert.-*butylphenyl benzyl ether.*

[ether] = 0·0225; [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
12·00	5·15	1·890
18·80	4·02	1·895
22·38	3·56	1·887
27·45	2·97	1·905
		Mean 1·894

[ether] = [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
44·20	4·99	1·987
55·50	4·53	1·987
66·50	4·16	1·985
		Mean 1·986

3-Bromo-p-tert.-*amylphenyl benzyl ether.*

[ether] = 0·0225; [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
13·10	5·39	1·554
19·50	4·44	1·556
27·37	3·50	1·576
32·25	3·10	1·547
		Mean 1·558

[ether] = [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
31·08	5·99	1·639
46·75	5·30	1·603
60·12	4·77	1·631
		Mean 1·624

3-Bromo-p-*ethylphenyl* p-*chlorobenzyl ether.*

[ether] = 0·0225; [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
9·78	4·78	2·71
14·00	3·83	2·73
17·10	3·28	2·73
		Mean 2·72

[ether] = [Cl_2] = 0·0075; [HCl] = 0·0375.

Time, mins.	Titre, c.c.	*k*.
0	8·28	—
28·05	5·13	2·92
39·00	4·38	3·05
51·72	3·69	3·21

TABLE VI.

In each case the concentrations of the reactants were as follows:

[ether] = 0·0025; [Cl_2] = 0·00125; [HCl] = 0·00625.

6-Chlorothymyl benzyl ether.

Medium 99·5% acetic acid; t = 16°.

Time, mins.	Titre, c.c.	*k*.
0	3·04	—
2·417	1·70	110
4·666	1·10	108
6·966	0·73	109
		Mean 109

Medium 99% acetic acid; t = 20°.

Time, mins.	Titre, c.c.	*k*.
0	3·04	—
1·716	1·60	173
2·616	1·22	171
3·533	0·90	177
		Mean 174

6-Chlorothymyl p-*bromobenzyl ether.*

Medium 99·5% acetic acid; t = 16°.

Time, mins.	Titre, c.c.	*k*.
0	3·04	—
3·233	1·83	71
5·25	1·50	63
7·65	1·10	66
		Mean 67

Medium 99% acetic acid; t = 20°.

Time, mins.	Titre, c.c.	*k*.
0	3·04	—
2·033	1·84	111
4·00	1·30	103
6·283	0·82	109
		Mean 108

method. To a well-stirred solution of the ethylphenol in carbon tetrachloride at 0° was added dropwise the calculated amount of bromine dissolved in ten times its volume of carbon tetrachloride. When addition was complete the mixture was allowed to stand for one hour and the hydrogen bromide then removed by repeated treatment with water. The tetrachloride extract was dried, the solvent removed, and the 3-bromo-*p*-ethylphenol fractionated under reduced pressure; almost all of it distilled at 118°/22 mm. From this specimen the following five compounds were prepared.

The p-*methylbenzyl ether* had m. p. 36°, and crystallised from alcohol in clusters of colourless prisms (Found: C, 62·8; H, 5·4. $C_{16}H_{17}OBr$ requires C, 62·9; H, 5·6%). The p-*chlorobenzyl ether*, m. p. 29°, was crystallised three times from ethyl alcohol (Found: C, 55·3; H, 4·3.

$C_{15}H_{14}OClBr$ requires C, 55·3; H, 4·3%). The p-*nitrobenzyl ether* had m. p. 81° after four crystallisations from ethyl alcohol, from which it separated in yellow prisms (Found: C, 53·8; H, 4·2. $C_{15}H_{14}O_3NBr$ requires C, 53·6; H, 4·2%). The m- and the o-*nitrobenzyl ether* melted at 86° (Found: C, 53·8; H, 4·2%) and 97° (Found: C, 53·6; H, 4·2%), respectively. Both crystallised from ethyl alcohol in colourless prisms, but the *o*-compound readily became brown on exposure to light.

3-Bromo-*p*-*n*-propylphenol was obtained from a purchased specimen of *p*-hydroxypropiophenone by a method similar to that employed for the preparation of the 3-bromo-*p*-ethylphenol. The specimen obtained distilled at 134°/25 mm., but its lachrymatory character suggested that the propyl group had been attacked to some extent during the bromination. As a result, difficulty was experienced in obtaining pure specimens of ethers which were liquids at ordinary temperatures, and velocity coefficients for the three crystalline nitrobenzyl ethers alone were determined. These were prepared by the usual methods from the pure nitrobenzyl chlorides.

The p-*nitrobenzyl ether*, m. p. 76°, was crystallised in turn from ethyl alcohol, twice from glacial acetic acid, and finally from ethyl alcohol, from which it crystallised in long, pale yellow prisms (Found: C, 55·0; H, 4·6. $C_{16}H_{16}O_3NBr$ requires C, 54·8; H, 4·6%). From the same solvent the m-*nitrobenzyl ether* crystallised in long glistening prisms, m. p. 67° (Found: C, 55·0; H, 4·6%). The o-*nitrobenzyl ether*, m. p. 64°, which crystallised similarly, was more sensitive to the action of light and gradually became brown (Found: C, 54·8; H, 4·6%).

p-*tert.*-Butylphenol was readily prepared in good yield by boiling gently under reflux 1 mol. of phenol and 1·1 mols. of *tert.*-butyl bromide until hydrogen bromide ceased to be evolved in quantity (cf. Bennett and Reynolds, J., 1935, 131). The mixture was cooled and poured into twice its volume of cold water, whereupon the *tert.*-butylphenol solidified. The hydrogen bromide was removed by washing and decantation, and the phenol dried and crystallised from ligroin; m. p. 98°. Bromination to give 3-bromo-*p*-*tert.*-butylphenol was carried out as for the 3-bromo-*p*-ethylphenol. The specimen used for the preparations of the ethers had m. p. 52°.

The *benzyl ether*, first obtained as a colourless liquid, b. p. 225°/19 mm., was dissolved in the minimum quantity of ligroin (b. p. 40—60°), and the solution cooled in ice until the ether separated as a crystalline solid. This operation was repeated twice, small volumes of ethyl alcohol being used in place of ligroin, and the final product was crystallised from alcohol. It separated in clusters of colourless prisms, m. p. 29° (Found: C, 63·5; H, 5·9. $C_{17}H_{19}OBr$ requires C, 63·9; H, 6·0%). The p-*methylbenzyl ether*, m. p. 49°, crystallised from alcohol in colourless, matted prisms (Found: C, 64·75; H, 6·3. $C_{18}H_{21}OBr$ requires C, 64·9; H, 6·4%). From alcohol the p-*chlorobenzyl ether* (Found: C, 57·8; H, 5·1. $C_{17}H_{18}OClBr$ requires C, 57·7; H, 5·1%), m. p. 73°, and the p-*bromobenzyl ether* (Found: C, 51·5; H, 4·7. $C_{17}H_{18}OBr_2$ requires C, 51·3; H, 4·6%), m. p. 78°, crystallised in glistening colourless prisms. The p-*nitrobenzyl ether*, after three crystallisations from glacial acetic acid, from which it crystallised in long, yellow prisms, had m. p. 94° (Found: C, 56·0; H, 5·1. $C_{17}H_{18}O_3NBr$ requires C, 56·05; H, 5·0%). The m-*nitrobenzyl ether* crystallised from alcohol in clusters of colourless prisms, m. p. 75° (Found: C, 56·0; H, 5·0%).

3-Bromo-*p*-*tert.*-amylphenol, b. p. 146—148°/19 mm., was prepared by the bromination of a purchased specimen of *p*-*tert.*-amylphenol, m. p. 94°. From this the following six ethers were prepared.

The *benzyl ether*, b. p. 234°/19 mm., solidified on cooling. It was frozen twice from small volumes of alcohol and then crystallised twice from the same solvent, separating in colourless, slender prisms, m. p. 44° (Found: C, 65·2; H, 6·3. $C_{18}H_{21}OBr$ requires C, 64·9; H, 6·35%). From alcohol, the p-*methylbenzyl ether* crystallised in clusters of colourless prisms, m. p. 49° (Found: C, 65·7; H, 6·6. $C_{19}H_{23}OBr$ requires C, 65·7; H, 6·7%), and the p-*chlorobenzyl ether* in slender prisms, m. p. 86° (Found: C, 58·8; H, 5·7. $C_{18}H_{20}OClBr$ requires C, 58·8; H, 5·5%). The p-*nitrobenzyl ether* crystallised from glacial acetic acid in yellow prisms, m. p. 82° (Found: C, 56·8; H, 5·0. $C_{18}H_{20}O_3NBr$ requires C, 57·1; H, 5·3%); the m-*isomer* in colourless, elongated prisms, m. p. 68° (Found: C, 57·2; H, 5·2%), and the o-*isomer* in clusters of slender prisms, m. p. 64° (Found: C, 57·1; H, 5·2%).

3-Nitro-*p*-*tert.*-butylphenol was prepared by the careful nitration of *p*-*tert.*-butylphenol in glacial acetic acid. After three crystallisations from glacial acetic acid, from which it separated in very pale yellow, slender prisms, the *benzyl ether* melted at 53° (Found: * C, 71·7; H, 6·7. $C_{17}H_{19}O_3N$ requires C, 71·5; H, 6·7%). The p-*bromobenzyl ether* was crystallised in turn from ethyl alcohol, glacial acetic acid, and methyl alcohol. It separated from the last in long, colourless prisms, m. p. 66° (Found: * Br, 21·5. $C_{17}H_{18}O_3NBr$ requires Br, 21·9%).

Chlorothymyl ethers. Five ethers of this series were prepared from a purchased specimen of chlorothymol of m. p. 59°. The first four were crystallised from ethyl alcohol. The *benzyl ether* formed colourless prisms, m. p. 55° (Found: C, 74·1; H, 7·0. $C_{17}H_{19}OCl$ requires C, 74·3; H, 7·0%); the p-*methylbenzyl ether* clusters of colourless prisms, m. p. 51° (Found: C, 74·3; H, 7·3. $C_{18}H_{21}OCl$ requires C, 74·8; H, 7·3%); the p-*chlorobenzyl ether*, m. p. 59° (Found: C, 65·9; H, 5·9. $C_{17}H_{18}OCl_2$ requires C, 66·0; H, 5·9%), and the p-*bromobenzyl ether*, m. p. 69° (Found: C, 57·7; H, 5·1. $C_{17}H_{18}OClBr$ requires C, 57·7; H, 5·1%), formed clusters of colourless, slender prisms. The o-*nitrobenzyl ether*, m. p. 117° (Found: C, 63·75; H, 5·6. $C_{17}H_{18}O_3NCl$ requires C, 63·8; H, 5·7%), crystallised from glacial acetic acid in long, colourless prisms. The 6-bromothymol was prepared by careful bromination of a commercially pure specimen of thymol; the product was distilled under reduced pressure and then seeded with 6-chlorothymol. The solid obtained was collected quickly in a well-cooled funnel, washed with a little ligroin (b. p. 40—60°), and finally crystallised from the same solvent; m. p. 55°. Its *benzyl ether*, m. p. 51° (Found: C, 63·9; H, 6·0. $C_{17}H_{19}OBr$ requires C, 63·9; H, 6·0%), crystallised from alcohol in colourless prisms, and the p-*chlorobenzyl ether*, m. p. 60° (Found: C, 57·7; H, 5·1. $C_{17}H_{18}OClBr$ requires C, 57·7; H, 5·1%), in colourless, elongated prisms. The o-*nitrobenzyl ether*, m. p. 116° (Found: C, 56·2; H, 5·0. $C_{17}H_{18}O_3NBr$ requires C, 56·0; H, 5·0%), separated from glacial acetic acid in colourless, slender prisms.

The author is indebted to the Chemical Society for a grant.

THE UNIVERSITY, SHEFFIELD.

[*Received, May* 22*nd*, 1941.]