427. *The Halogenation of Phenolic Ethers and Anilides. Part VI. Benzyl and Substituted-benzyl Ethers.*

By Brynmor Jones.

In the course of a previous study (Bradfield and B. Jones, J., 1928, 1006; J., 1931, 2903) of the rates of chlorination of substituted phenolic ethers, a few benzyl and nitrobenzyl ethers were examined and the relative directive effects of the benzyloxy-groups compared. The results of a more comprehensive study of the influence of polar substituents in the benzyl radical upon the velocities of reaction are now reported.

Results of comparative velocity determinations are given in the following tables, the general method being identical with that employed in the earlier work. The velocity

Table I.

Velocity coefficients for the chlorination of substances of the types o- *and* p-$C_6H_4X{\cdot}OR$ *in* 99% *acetic acid, at* 20°.

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

Group X.	Group R.	*k*.	Group X.	Group R.	*k*.
p-CO_2H	CH_3	0·444	*p*-Cl	*o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·175
,,	CH_2Ph	0·314	*p*-Br	CH_3	1·256
,,	*p*-$C_6H_4F{\cdot}CH_2$	0·262	,,	CH_2Ph	0·850
,,	*p*-$C_6H_4Cl{\cdot}CH_2$	0·200	,,	*p*-$C_6H_4Cl{\cdot}CH_2$	0·521
,,	*p*-$C_6H_4Br{\cdot}CH_2$	0·203*	,,	*p*-$C_6H_4Me{\cdot}CH_2$	1·170
,,	*p*-$C_6H_4Me{\cdot}CH_2$	0·441	,,	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·177
,,	*m*-$C_6H_4F{\cdot}CH_2$	0·157	,,	*m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·201
,,	*m*-$C_6H_4Cl{\cdot}CH_2$	0·153	*o*-CO_2H	CH_3	3·483
,,	*m*-$C_6H_4Br{\cdot}CH_2$	0·159	,,	CH_2Ph	2·700
,,	*m*-$C_6H_4Me{\cdot}CH_2$	0·475	,,	*p*-$C_6H_4F{\cdot}CH_2$	2·192
,,	*o*-$C_6H_4F{\cdot}CH_2$	0·160	,,	*p*-$C_6H_4Cl{\cdot}CH_2$	1·827
,,	*o*-$C_6H_4Cl{\cdot}CH_2$	0·152	,,	*p*-$C_6H_4Br{\cdot}CH_2$	1·855
,,	*o*-$C_6H_4Me{\cdot}CH_2$	0·465	,,	*p*-$C_6H_4Me{\cdot}CH_2$	3·710
p-Cl	CH_3	1·226	*o*-Cl	CH_3	4·441
,,	CH_2Ph	0·837	,,	*p*-$C_6H_4F{\cdot}CH_2$	2·481
,,	*p*-$C_6H_4F{\cdot}CH_2$	0·674	,,	*p*-$C_6H_4Cl{\cdot}CH_2$	1·861
,,	*p*-$C_6H_4Cl{\cdot}CH_2$	0·489	,,	*p*-$C_6H_4Br{\cdot}CH_2$	1·850
,,	*p*-$C_6H_4Br{\cdot}CH_2$	0·483	,,	*p*-$C_6H_4Me{\cdot}CH_2$	4·201
,,	*p*-$C_6H_4Me{\cdot}CH_2$	1·153	,,	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·642
,,	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·174	,,	*o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·628
,,	*m*-$C_6H_4F{\cdot}CH_2$	0·394	*o*-Br	CH_3	5·457
,,	*m*-$C_6H_4Cl{\cdot}CH_2$	0·372	,,	*p*-$C_6H_4Cl{\cdot}CH_2$	2·155
,,	*m*-$C_6H_4Br{\cdot}CH_2$	0·377	,,	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·750
,,	*m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·195	,,	*m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·884
,,	*o*-$C_6H_4Cl{\cdot}CH_2$	0·346	,,	*o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·753

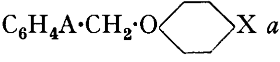
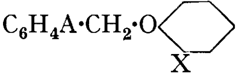
* [Ether] = 0·0075.

[Cl_2] = 0·0075; [ether] = 0·0150; [HCl] = 0·0375.

Group X.	Group R.	*k*.	Group X.	Group R.	*k*.
p-CO_2H	CH_3	0·458	*p*-CO_2H	*p*-$C_6H_4F{\cdot}CH_2$	2·30
,,	*p*-$C_6H_4Cl{\cdot}CH_2$	0·208	,,	*p*-$C_6H_4Cl{\cdot}CH_2$	1·94
o-CO_2H	CH_3	3·60	,,	*p*-$C_6H_4Me{\cdot}CH_2$	3·89
,,	CH_2Ph	2·72			

TABLE II.

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

 *and*  . *Values of* $100k_X^{OR}/k_X^{OMe}$.

		$C_6H_4A{\cdot}CH_2$														
	CH_3.	A = H.	p-CH_3.	p-F.	p-Cl.	p-Br.	p-NO_2.	m-CH_3.	m-F.	m-Cl.	m-Br.	m-NO_2.	o-CH_3.	o-F.	o-Cl.	o-NO_2.
X = p-CO_2H	100	70	99	59	45	44	—	107	35	35	36	—	105	36	33	—
p-Cl	100	67	94	55	40	39	14·2	—	32	30	31	15·9	—	—	28	14·2
p-Br	100	68	93	—	42	—	14·1	—	—	—	—	16·0	—	—	—	—
o-CO_2H	100	77	107	64	53	53	—	—	—	—	—	—	—	—	—	—
o-Cl	100	—	95	56	42	42	14·4	—	—	—	—	—	—	—	—	14·1
o-Br	100	—	—	—	40	—	13·8	—	—	—	—	16·2	—	—	—	13·8

TABLE III.

Relative directive effects of the groups CO_2H, Cl, Br *in compounds of the types* o- *and* p-$C_6H_4X{\cdot}OR$. *Values of* $100k_X^{OR}/k_{p\cdot CO_2H}^{OR}$.

X =	p-CO_2H.	o-CO_2H.*	p-Cl.	o-Cl.	p-Br.	o-Br.
R = CH_3	100	784	276	1000	283	1229
CH_2Ph	100	860	266	—	270	—
p-$C_6H_4Me{\cdot}CH_2$	100	841	262	953	266	—
p-$C_6H_4F{\cdot}CH_2$	100	837	257	948	—	—
p-$C_6H_4Cl{\cdot}CH_2$	100	914	245	931	261	1078
m-$C_6H_4F{\cdot}CH_2$	100	—	250	—	—	—
m-$C_6H_4Cl{\cdot}CH_2$	100	—	243	—	—	—
m-$C_6H_4Br{\cdot}CH_2$	100	—	238	—	—	—

Examination of iodobenzyl ethers was not possible owing to the formation of iododichlorides.

* See discussion (below).

coefficients are again slightly altered by a change in the relative concentrations of ether and chlorine, but with one exception standard conditions have been employed throughout, so the results are strictly comparable. Owing to the low solubility of p-(p'-bromobenzyloxy)-benzoic acid in 99% acetic acid at 20°, the molecular proportion of ether to chlorine was 1 : 1, and not 3 : 1 as in all other cases.

For purposes of comparison, the relative directive effects of the OR groups, as measured by ratios of velocities, are again referred to the methyl ether as 100 and given in Table II; Table III contains the relative effects of CO_2H, Cl, and Br as p- and o-substituents.

Discussion of Results.—As in the cases discussed in the preceding papers, the relative effects of the groups OR and X are independent, both contributing additively to the energy of activation of chlorination.

The examination of o-substituted-phenyl ethers involves a departure from the type of ether mainly studied hitherto in that two positions (4 and 6) in the phenyl nucleus are substituted. Consequently, it is of particular importance that the relationships obtaining in the p-series are found also with ethers of o-chloro- and o-bromo-phenol (cf. Part V). Minor anomalies are observed, however, in the ethers of salicylic acid, all the substituent groups R so far examined giving higher directive powers than those usually found. The values obtained from velocity coefficients at two different concentrations are compared in Table IV with the mean values for the other series.

TABLE IV.

Relative directive powers of the groups $C_6H_4A{\cdot}CH_2{\cdot}O$. *Values of* $100k_X^{OR}/k_X^{OMe}$.

Ethers of o-$RO{\cdot}C_6H_4{\cdot}CO_2H$.

		$C_6H_4A{\cdot}CH_2$.				
Mol. proptn. ether : Cl_2.	R = CH_3.	A = H.	p-F.	p-Cl.	p-Br.	p-CH_3.
3 : 1	100	78	63	53	53	107
2 : 1	100	76	64	54	—	108
Other phenyl ethers (mean)	100	68	57	42	42	95

The divergence between the ethers of salicylic acid and other phenyl ethers is exhibited in another way in Table V, where the effects of moving the CO_2H, Cl, and Br groups from the *p*- to the *o*-position are compared for the different OR groups.

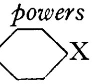
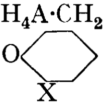
TABLE V.

R =	CH_3.	$C_6H_4A{\cdot}CH_2$. A = H.	*p*-F.	*p*-Cl.	*p*-Br.	*p*-CH_3.	*p*-NO_2.	*m*-NO_2.
Values of $100k^{OR}_{o\cdot CO_2H}/k^{OR}_{p\cdot CO_2H}$	784	860	837	914	—	841	—	—
,, $100k^{OR}_{o\cdot Cl}/k^{OR}_{p\cdot Cl}$	362	—	368	380	383	364	369	—
,, $100k^{OR}_{o\cdot Br}/k^{OR}_{p\cdot Br}$	435	—	—	414	—	—	424	440

It is clear that in the acid series the variations in the ratios for the different groups are 2—3 times as great as in the chloro- and the bromo-series.

It is noteworthy, however, that, compared with one another, the relative effects of the various benzyl groups are similar to the mean values, and, referred to the benzyl ether as 100, the values for the ethers of salicylic acid fall more nearly into line (see Table VI). Nevertheless, the anomaly of the methyl ether remains.

TABLE VI.

Relative directive powers of the groups $C_6H_4A{\cdot}CH_2{\cdot}O{\cdot}$ *in compounds of the types* $C_6H_4A{\cdot}CH_2{\cdot}O$X *and* $C_6H_4A{\cdot}CH_2{\cdot}O$. *Values of* $100k^{OR}_X/k^{OCH_2Ph}_X$.
X

	para.						*meta.*					*ortho.*			
A =	H.	CH_3.	F.	Cl.	Br.	NO_2.	CH_3.	F.	Cl.	Br.	NO_2.	CH_3.	F.	Cl.	NO_2.
p-CO_2H	100	140	83	64	63	—	151	50	49	50	—	148	51	48	—
p-Cl	100	138	81	58	58	20·8	—	47	45	45	23·3	—	—	41	20·9
p-Br	100	138	—	61	—	20·8	—	—	—	—	23·6	—	—	—	—
o-CO_2H	100	140	83	69	69	—	—	—	—	—	—	—	—	—	—
o-Cl	—	140	83	62	62	21·4	—	—	—	—	—	—	—	—	20·9
o-Br	—	—	—	60	—	21·0	—	—	—	—	24·7	—	—	—	21·1

The possibility that this anomaly results from such causes as molecular association or co-ordination must not be overlooked, especially since reaction velocity in solution is often notoriously susceptible to environmental influences. Sidgwick and his collaborators have shown that the co-ordination prevalent in *o*-substituted phenols of the type $C_6H_4X{\cdot}OH$ (where X = NO_2, CHO, CO_2Me) vanishes in the methyl ethers. Nevertheless, a second-order effect may be possible in the free acids (Sidgwick and Callow, J., 1924, **125**, 527; Sidgwick and Bayliss, J., 1930, 2027).

Although the quantitative aspect of these results has hitherto been considered only in relation to the kinetic activation theory of reaction velocity, yet their bearing on current electronic theories of reaction, particularly as these concern the halogens, is not without interest.

The velocity coefficients for the chlorination of the series of *p*-substituted-benzyl ethers fall into the expected order, the reactivities of the halogenobenzyl ethers being intermediate between those of the nitro- and the methyl-benzyl ethers. The general polar series $CH_3 >$ H > Halogens > NO_2 is thus again observed. As anticipated, this order obtains also in the *o*- and the *m*-series, but, whilst the order of the different groups is that expected from a consideration of their well-known inductive and electromeric effects, the order of the halogens among themselves is not that of their inductive effects. The relative directive powers of the *p*- and *m*-halogenobenzyloxy-groups and the corresponding *p*/*m* ratios are given below:

	F.	Cl.	Br.
p	57	42	42
m	34	33	34
p/*m* ratio	1·68	1·27	1·24

The uniformity of the directive effects of the *m*-halogenobenzyloxy-groups and the consistently greater reactivity of the *p*-fluoro- than of the *p*-chloro- and *p*-bromo-benzyl ethers in the different series of ethers is clear from the velocity ratios in Tables II and VI.

In substitution reactions of the type now under discussion, the electron-attracting inductive effect of the halogens retards substitution, while the electron-repelling electromeric effect favours it (cf. Robinson, J., 1933, 1114). In the present series the main influence is undoubtedly the inductive effect, since the velocity coefficients for all the halogenobenzyl ethers are appreciably lower than those of the parent benzyl ethers, but if the inductive effects are in the order $F > Cl > Br > I$, as commonly accepted, or approximately equal, as shown by the values for the *m*-substituted ethers, then, to account for the directive powers of the three *p*-halogenobenzyloxy-groups now being considered, an electron-repelling effect, transmitted no doubt as an inductive effect decreasing from fluorine to bromine, is clearly essential. An inductive effect in the order $F > Cl > Br > I$, and an electromeric effect as originally suggested in the order $I > Br > Cl > F$, should result in the *p*-fluorobenzyl ether having a lower reactivity than the bromobenzyl ether, whereas actual measurement shows the reverse to be the case. The figures for the *p*/*m* ratio (p. 1837) may be taken as a measure of the relative strengths of the mesomeric (or electromeric) effects of the halogens, and fall from fluorine to chlorine (cf. Baddeley, Bennett, Glasstone, and B. Jones, this vol., p. 1827).

The lower reactivity of the *m*- and *o*-halogenobenzyl ethers is accounted for by the fact that in the *m*-position the reaction-favouring influence of the mesomeric effect is almost or quite inoperative, whilst in the *o*-position the greater influence of the inductive effect, resulting from the closer proximity of the halogen to the oxygen atom, outweighs any relayed mesomeric effect.

The greater nuclear reactivity of *p*- than of *m*-halogenobenzyl ethers is apparent also from Oxford and Robinson's values for the directive powers of the benzyloxy-groups in substituted benzyl ethers of guaiacol (J., 1927, 2240; Robinson, *loc. cit.*). Referred to the methoxy-group as 100, the values for *p*- and *m*-chlorobenzyloxy-groups are 82 and 69 respectively, giving a *p*/*m*-ratio of 1·19, in good agreement with the value 1·27 found in the present series.

In view of the fact that most of the evidence for the inversion of the order of the mesomeric and electromeric effects of the halogens has up to the present been obtained from studies of side-chain reactivity, and of the dissociation constants of halogen-substituted acids, phenols, and anilines, the present data relating to a substitution reaction are of particular significance. Although little or no scope is given in this reaction for the exercise of the full electromeric potentialities of the halogens, the results, nevertheless, point definitely to a mesomeric ("permanent electromeric") effect falling from fluorine to bromine.

In accordance with expectation, introduction of the nitro-group into any position decreases the reactivity very considerably, the relative directive effects of the three nitrobenzyloxy-groups being $o : m : p = 14{\cdot}0 : 16{\cdot}0 : 14{\cdot}1$. The order $m > p$ agrees with that of acid strengths of *m*- and *p*-nitrobenzoic and phenylacetic acids, where the *p*-acid is in each case the stronger (Dippy, Watson, and Williams, this vol., p. 349). Moreover, the existing data for side-chain reactions also show the influence of the nitroxyl group to be usually weaker in the *m*- than in the *p*-position. The data for *o*-nitroxyl, however, are much less definite, the order for *o*- and *p*- varying from one reaction to another (cf. Williams, J., 1930, 40).

The main results of these investigations may therefore be summarised as follows: (1) For a wide range of new alkyl, ω-substituted-alkyl, and substituted-benzyl ethers of the type *o*- and *p*-$RO{\cdot}C_6H_4X$, the two substituent groups OR and X contribute characteristically and additively to the energy of activation of chlorination; with ethers of salicylic acid, and with *o*-chlorophenyl *iso*propyl ether, minor anomalies are observed. (2) The constant reactivity characteristic of long-chain compounds is observed from propyl to heptyl, the octyl and cetyl ethers exhibiting slightly lower reactivities; as anticipated, the introduction of a phenyl group or a bromine atom into the ethyl and the propyl group produces a marked decrease in reactivity. (3) For polar groups in the benzyl radical, the order of reactivity for *p*-substituents is $CH_3 > H > F > Cl > Br > NO_2$; in the *m*-position the halogens show almost identical effects. (4) To account for the relative reactivities of the halogenobenzyl ethers, a mesomeric effect in the order F>Cl>Br would appear to be necessary.

EXPERIMENTAL.

The preceding paper and the earlier parts of this series give details of the measurements of the velocity coefficients of chlorination.

The ethers were prepared by standard methods from the parent hydroxy-compound and the substituted benzyl chloride or bromide. The fluoro-, chloro-, and methyl-benzyl chlorides were prepared by direct chlorination of the corresponding toluenes at their b. p.'s, and the product in each case was carefully fractionated. Since with the bromotoluenes nuclear bromine is readily displaced by chlorine under these conditions, and a mixture of bromobenzyl chloride and chlorobenzyl bromide formed, the bromotoluenes were brominated at their b. p.'s, and the bromides used for the preparation of the ethers. In this way, freedom from the corresponding chlorobenzyl ether was ensured, and the bromides had the added advantage of being more reactive than the chlorides (cf. Bennett and B. Jones, this vol., p. 1815).

p-*Chlorophenyl Ethers.*—The p-*fluorobenzyl ether*, prepared from *p*-chlorophenol, sodium ethoxide, and *p*-fluorobenzyl chloride in the usual manner, and the p-*chlorobenzyl ether* crystallise from alcohol as colourless prisms, m. p. 60° (Found : * C, 65·8; H, 4·5. $C_{13}H_{10}OClF$ requires C, 66·0; H, 4·3%) and 81° (Found : C, 61·6; H, 3·9. $C_{13}H_{10}OCl_2$ requires C, 61·65; H, 4·0%), respectively. The p-*bromobenzyl ether*, prepared from *p*-chlorophenol, sodium ethoxide, and *p*-bromobenzyl bromide, crystallises similarly, m. p. 93° (Found: C, 52·4; H, 3·3. $C_{13}H_{10}OClBr$ requires C, 52·4; H, 3·4%); the m-*isomeride*, prepared analogously, crystallises similarly, m. p. 43° (Found : C, 52·5; H, 3·4%).

The p-*methylbenzyl ether* crystallises well from alcohol and glacial acetic acid, being obtained from the former as colourless prisms, m. p. 97° (Found : C, 72·1; H, 5·5. $C_{14}H_{13}OCl$ requires C, 72·3; H, 5·6%). The m-*fluorobenzyl ether* distils as a colourless liquid, b. p. 223—225°/12 mm., and solidifies in a freezing mixture. The specimen used for the velocity measurements (Found : C, 65·9; H, 4·24%) was frozen twice from small volumes of (a) ligroin (b. p. 40—60°), (b) alcohol.

The m- and o-*chlorobenzyl ethers* are colourless liquids, b. p. 222—224°/12 mm. (Found : C, 61·3; H, 3·9%), and 191°/12 mm. (Found : C, 61·7; H, 3·95%), respectively.

The o-*nitrobenzyl ether*, prepared from *o*-nitrobenzyl chloride and *p*-chlorophenol in sodium ethoxide, melts at 73° after crystallisation from acetic acid and alcohol (Found : C, 58·9; H, 3·7. $C_{13}H_{10}O_3NCl$ requires C, 59·2; H, 3·8%).

o-*Chlorophenyl Ethers.*—The p-*fluorobenzyl ether*, first obtained as an oil, b. p. 170°/12 mm., solidified on long standing to a white crystalline solid, m. p. 35° (Found : C, 66·4; H, 4·3%). The p-*chloro-* and the p-*methyl-benzyl ether* both crystallise from alcohol as colourless prisms, m. p. 69° (Found : C, 61·67; H, 3·98%) and 76° (Found : C, 72·3; H, 5·5%), respectively; the latter was first purified by distillation.

The o-*nitrobenzyl ether* crystallises as pale yellow prisms, m. p. 84·5° (Found: C, 59·1; H, 3·8%), from acetic acid.

p-*Bromophenyl Ethers.*—The p-*chlorobenzyl ether* crystallised from alcohol as colourless prisms with straight extinction, m. p. 98° (Found : C, 52·6; H, 3·2%); and the p-*methylbenzyl ether*, crystallised once from alcohol and twice from glacial acetic acid, had m. p. 105° (Found : C, 60·4; H, 4·6. $C_{14}H_{13}OBr$ requires C, 60·6; H, 4·7%).

o-*Bromophenyl Ethers.*—p-*Chlorobenzyl ether*, colourless prisms from alcohol, m. p. 69° (Found : C, 52·4; H, 3·5%); o- and m-*nitrobenzyl ethers*, m. p. 107° (Found : C, 50·7; H, 3·4. $C_{13}H_{10}O_3NBr$ requires C, 50·7; H, 3·3%) and 100° (Found : C, 50·7; H, 3·2%), respectively.

The method employed for the preparation of the benzyloxybenzoic acids is the same as that for the alkoxybenzoic acids (preceding paper ; see also this vol., p. 1874).

p-(p'-*Fluorobenzyloxy*)*benzoic acid* crystallised from glacial acetic acid, in which it is only sparingly soluble at room temperature, as colourless prisms, m. p. 213° (Found : C, 68·0; H, 4·5. $C_{14}H_{11}O_3F$ requires C, 68·0; H, 4·5%). The p'-*chloro-acid* was crystallised thrice from glacial acetic acid, in which it is only sparingly soluble at 20°; m. p. 218° (Found : C, 63·7; H, 4·1. $C_{14}H_{11}O_3Cl$ requires C, 63·7; H, 4·2%); and the p'-*bromo-acid*, similarly crystallised (maximum solubility 0·3—0·5 g./100 c.c. at 20°), had m. p. 231° (Found : C, 54·8; H, 3·7. $C_{14}H_{11}O_3Br$ requires C, 54·75; H, 3·6%).

---

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

p-(p'-*Methylbenzyloxy)benzoic acid* crystallises from glacial acetic acid, in which it is sparingly soluble, as aggregates of colourless prisms; m. p. 212° (Found: C, 74·0; H, 5·7. $C_{15}H_{14}O_3$ requires C, 74·0; H, 5·8%). The m'-*methyl-acid*, m. p. 157° (Found: C, 73·9; H, 5·8%), is slightly more soluble in this solvent.

p-(m'-*Fluorobenzyloxy)benzoic acid* and the m'-*chloro-* and m'-*bromo-acids*, m. p. 194° (Found: C, 68·2; H, 4·7%), m. p. 194° (Found: C, 63·7; H, 4·2%), m. p. 202° (Found: C, 54·5; H, 3·6%) respectively, all crystallise as colourless prisms from glacial acetic acid, in which their solubility at room temperature is low.

p-(o'-*Fluorobenzyloxy)benzoic acid* crystallises from glacial acetic acid as clusters of colourless prisms, sparingly soluble at 20°; m. p. 181° (Found: C, 68·1; H, 4·5%); the o'-*chloro-acid* was crystallised once from glacial acetic acid and twice from ethyl acetate; m. p. 189° (Found: C, 64·1; H, 4·3%).

p-(o'-*Methylbenzyloxy)benzoic acid*, m. p. 169° (Found: C, 73·7; H, 5·8%).

o-*Benzyloxybenzoic acid*. Two specimens, prepared (*a*) from salicylic acid, benzyl chloride, and sodium hydroxide, and (*b*) from methyl salicylate, sodium methoxide, and benzyl chloride, had identical m. p.'s and velocity coefficients. Method (*b*), which involves the hydrolysis of the ester, afforded the better yield; m. p. 77° (Found: C, 73·5; H, 5·2. Calc.: C, 73·7; H, 5·3%).

o-(p'-*Fluorobenzyloxy)benzoic acid*, prepared by alkaline hydrolysis of the ester formed by refluxing methyl salicylate, sodium ethoxide, and *p*-fluorobenzyl chloride, is very soluble in glacial acetic acid, and was crystallised twice from chloroform–ligroin (b. p. 40—60°) and once from a small volume of acetic acid; m. p. 87° (Found: C, 68·4; H, 3·4%). The p'-*chloro*-analogue, prepared similarly, crystallised from glacial acetic acid as white needles, m. p. 115° (Found: C, 63·5; H, 4·6%); and the p'-*methyl-acid* was crystallised from ligroin (b. p. 40—60°) and glacial acetic acid, in which it is very freely soluble; m. p. 111° (Found: C, 73·9; H, 5·8%).

The author thanks Professor G. M. Bennett and Dr. A. E. Bradfield for their interest, and the Chemical Society for a grant.

THE UNIVERSITY, SHEFFIELD. [*Received, October* 17*th*, 1935.]