

*Mesomorphism and Chemical Constitution. Part III.\* The Effect of Halogen Substitution on the Mesomorphism of the 4-Alkoxybenzoic Acids.*

By G. W. GRAY and BRYNMOR JONES.

[Reprint Order No. 5187.]

The preparation and mesomorphic character of certain 4-*n*-alkoxy-3-halogenobenzoic acids are described. Halogen-substitution results in an increase in the breadth of the molecule which is reflected in the relative thermal stabilities of the mesophases. With fluorine and chlorine the increase is not sufficient to eliminate the mesomorphism, but the thermal stabilities of the phases of the broader chloro-acids are lower than those for the corresponding fluoro-acids. The presence of one bromine atom, or two chlorine atoms, as in 4-*n*-alkoxy-3 : 5-dichlorobenzoic acids, is sufficient to destroy the mesomorphism of the unsubstituted acids.

It is generally recognised that, apart from such molecules as the esters of cholesterol, long rod-shaped molecules are the most likely to exhibit mesomorphism. This is true only if the intermolecular cohesion is sufficient to maintain the linear molecular arrangement in the mesophase at elevated temperatures. When the breadth of a mesomorphic compound is increased by substitution the intermolecular cohesion may be lowered, as a result of the increased separation of the molecules from one another. The melting points and the mesomorphic transition temperatures (smectic-nematic, and smectic- or nematic-isotropic) should then be lower in the substituted than in the unsubstituted compounds.

Such behaviour has been found for 4-*n*-alkoxy-3-fluoro-, -3-chloro-, and -3-bromobenzoic acids, whose physical constants are tabulated below. Figures in parentheses

\* Part II, *J.*, 1954, 1467.

relate to monotropic transitions, or to the lengths of monotropic phases. The usual thirteen ethers (methyl—decyl, dodecyl, hexadecyl, and octadecyl) used in these studies were not prepared, since the lower members show no mesomorphism.

4-Alkoxy-3-fluorobenzoic acids.

Alkyl group	Temp. of transition to			Phase length of	
	smectic	nematic	isotropic	smectic	nematic
Methyl .....	—	—	211.5°	—	—
Butyl .....	—	—	143.5	—	—
Pentyl .....	—	—	137.5	—	—
Hexyl .....	—	—	129.5	—	—
Heptyl .....	—	—	124	—	—
Octyl .....	—	117°	120.5	—	3.5°
Nonyl .....	(<110°) *	112	116.5	(>2°)	4.5
Decyl .....	108	112	116.5	4	4.5
Dodecyl .....	108.5	113	114.5	4.5	1.5
Hexadecyl .....	94	—	111	17	—
Octadecyl .....	(109)	—	114	(5)	—

\* Possible extrapolated value 109°.

3-Fluoro-4-nonyloxybenzoic acid exhibits a monotropic smectic phase, which is seen only if the nematic melt is cooled rapidly. It was impossible to determine this transition, since the slow cooling which is necessary to obtain accurate monotropic transitions resulted in crystallisation at 110°. A value only one degree lower than this is however indicated for the transition from the gradient of the curve (Fig. 1) through the smectic–nematic and smectic–isotropic transitions of the higher ethers. In this series the m. p. rises steeply to the octadecyl ether, whereafter the smectic phase again becomes monotropic. In this case, the isotropic liquid may be cooled without inducing crystallisation, and the reversal to the mesophase was obtained at 109°. A smooth curve (Fig. 1) may be drawn through

FIG. 1. 4-Alkoxy-3-fluorobenzoic acids.

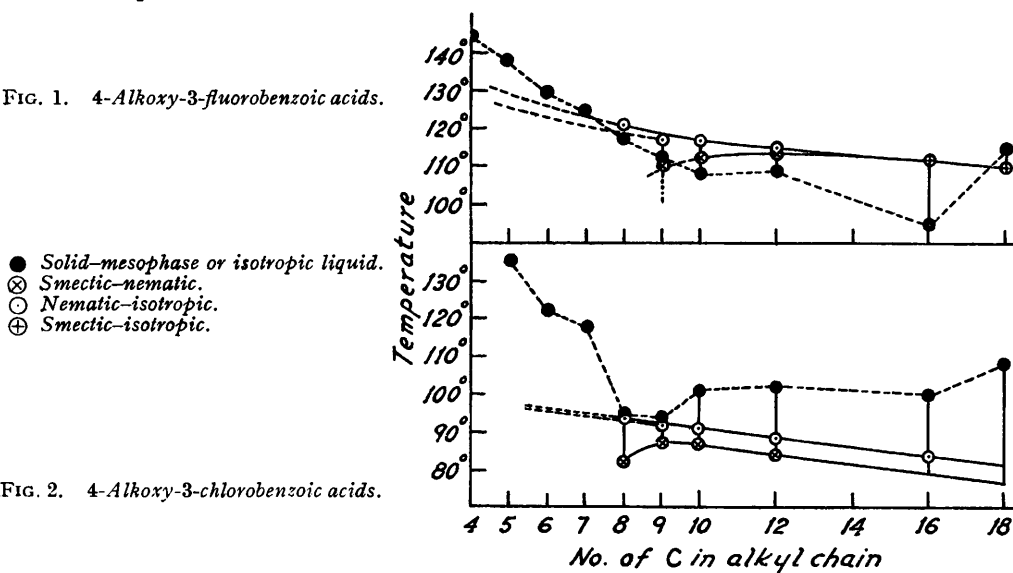


FIG. 2. 4-Alkoxy-3-chlorobenzoic acids.

the smectic– and nematic–isotropic transition points for the acids which have an even number of carbon atoms in the alkyl chain. As is to be expected, the upper transition point of the nonyl ether lies below this curve, because of the usual alternations found in homologues containing odd and even numbers of carbon atoms in the alkyl chain. The curve for the even members has been extrapolated in the direction of the shorter alkyl groups, and an equivalent curve drawn from the upper transition point of the nonyl ether (broken curves in Fig. 1). The heptyl, hexyl, and pentyl ethers are not mesomorphic, but these curves indicate that their upper transition points would be 121°, 126°, and 126.5° respectively. These temperatures are very close to the observed m. p.s for these ethers.

Their melts show very little tendency to supercool, however, and crystallise within 1–3° of their m. p.s, so that the phases, which would be monotropic, are not observed. A curve may be drawn through the smectic–nematic points of the decyl and dodecyl ethers and the smectic–isotropic points of the last two ethers in the series. The latter are purely smectic, and appear from the isotropic liquid in bâtonnets.

4-Alkoxy-3-chlorobenzoic acids.

Alkyl group	Temp. of transition to			Phase length of	
	smectic	nematic	isotropic	smectic	nematic
Methyl .....	—	—	217.5°	—	—
Pentyl .....	—	—	134.5	—	—
Hexyl .....	—	—	121	—	—
Heptyl .....	—	—	117	—	—
Octyl .....	(81.5°)	(93°)	94	(11.5°)	(1°)
Nonyl .....	(86.5)	(91)	93.5	(4.5)	(2.5)
Decyl .....	(86)	(90.5)	100.5	(4.5)	(10)
Dodecyl .....	(83.5)	(88)	101.5	(4.5)	(13.5)
Hexadecyl .....	(78.5) *	(83)	99.5	(4.5)	(16.5)
Octadecyl .....	(76.5) *	(81) *	107.5	(4.5)	(26.5)

\* Extrapolated values.

In the chloro-acids all the mesophases are monotropic, appearing only from the supercooled melts. At the octyl ether, which, like the higher ethers, exhibits both a smectic and a nematic phase, there is a considerable fall in m. p. The transitions for isotropic–nematic (cooling) or nematic–isotropic (heating from the supercooled state) for the octyl to hexadecyl ethers lie on a straight line. The analogous point for the nonyl ether is slightly lower, because of odd–even alternation. As in the fluoro-series, this line has been extrapolated, and another line drawn parallel to it from the nematic–isotropic transition point of the nonyl ether (broken lines in Fig. 2). These lines give the hypothetical transition points for the non-mesomorphic heptyl and hexyl ethers. The values lie well below the observed m. p.s, and the isotropic liquids cannot be supercooled sufficiently rapidly for a phase to appear. Continuation of the straight line to octadecyl yields an extrapolated value, at 81°, for the isotropic–nematic transition. A curve may be drawn through the smectic–nematic transition points of the octyl to dodecyl ethers, and its continuation gives values of 78.5° and 76.5° for the smectic–nematic transitions of the hexadecyl and the octadecyl ether respectively.

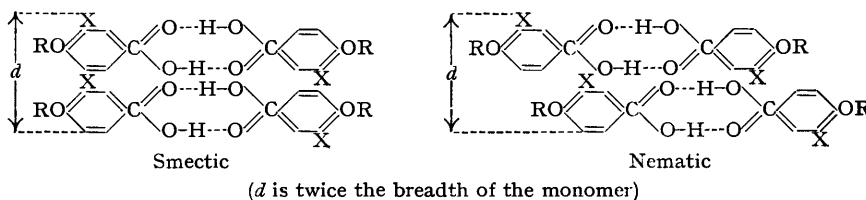
In the chloro-series, nematic properties persist in the hexadecyl and the octadecyl ether, whereas in other homologous series molecules of this length are purely smectic. In the latter cases, there is no preliminary sliding of the molecules to an imbricated nematic state (Friedel, *Ann. Physique*, 1922, **17**, 273; Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1016), and at the mesomorphic–isotropic transition the lateral, planar, and terminal cohesions must loosen simultaneously to give the disordered isotropic state. The large chlorine atom must so weaken the lateral cohesion that the molecules are able to slide in the direction of their long axes, before the cohesion between terminal groups is sufficiently reduced to permit random orientation. The sliding would produce a nematic phase, which would become isotropic at a higher temperature.

The mesomorphic transition points in the fluoro- and the chloro-series exhibit the regularities which are usual in homologous series of mesomorphic compounds (Gray and Brynmor Jones, *J.*, 1953, 4179; 1954, 683, 1467). The 4-alkoxy-3-bromobenzoic acids are not mesomorphic, and melts of the octyl ether (m. p. 111°) and hexadecyl ether (m. p. 99°) could be cooled to 90° and 81° respectively, before crystallising. If therefore these compounds were mesomorphic, their mesophases would appear below these temperatures and would be less stable than the mesophases of the analogous chloro-compounds.

In an earlier preliminary account of the behaviour of the 4-alkoxy-3-fluoro- and -3-chloro-benzoic acids (Gray and Brynmor Jones, *Nature*, 1952, **170**, 451) the phase lengths were derived from transition temperatures determined in a capillary tube: the present determinations were made in an electrically heated microscope block (Gray, *Nature*, 1953,

172, 1137), in which control was more accurate. The results for the 3-fluoro-series were virtually the same, but the 3-chloro-acids soften to some extent before melting, and, in a capillary tube, the impression is created of short enantiotropic phases. When the m. p. is determined on a thin section of solid observed under a microscope, the effect is only one of slight lattice deterioration, which is most marked in the longer-chain homologues. The phases of the chloro-acids are therefore monotropic.

The acids are believed to exist in the mesophases as dimers in their state of lowest potential energy, with the 3-substituents *trans* to one another. The packing of the molecules in the mesophases will however be determined by the breadth of the monomer, and not by the overall breadth of the dimer. This is obvious when two molecules are arranged side by side, in such a way as to give potential smectic and nematic orientations (Friedel; Bernal and Crowfoot, *loc. cit.*).



The breadths of the monomers were obtained by calculation, 1.2 Å being taken as the van der Waals radius of hydrogen. As the breadths increase progressively in the order *p-n*-alkoxy-, 4-*n*-alkoxy-3-fluoro-, 4-*n*-alkoxy-3-chloro-benzoic acids there is a decrease in the mesomorphic-isotropic transition temperatures, and consequently in mesomorphic stability. Only the nematic-isotropic transitions for the octyl-hexadecyl ethers can be obtained in all three series without extrapolation, and these alone are considered in the following Table.

X = 3-substituent	H	F	Cl
Average transition (mesomorphic-isotropic for C <sub>8</sub> to C <sub>16</sub> )	140.3°	115.8°	89.1°
Decrease in average transition .....	24.5°	26.7°	
Increase in molecule breadth (Å) .....	0.43	0.75	

In comparing the change from unsubstituted to fluoro-acid and from unsubstituted to chloro-acid, two opposing effects must be considered in each case. These are the increase in breadth, which should decrease the mesomorphic stability, and the introduction of the carbon-halogen dipole, which should increase the mesomorphic stability. The C-F and C-Cl dipoles being taken as 1.57 and 1.73 μ \* respectively, the decrease in average transition temperature/Å from unsubstituted to fluoro-acid should be greater than that from unsubstituted acid to chloro-acid. This is shown qualitatively by calculating the ratios of the decrease in average transition to the breadth increases. These ratios are the fall in average transition temperature/Å, and are 56.98 from unsubstituted to fluoro-acid, and 43.39 from unsubstituted to chloro-acid, in agreement with the order predicted above.

The smectic-nematic transition temperatures also decrease with increasing molecular breadth, and the average values for the decyl and the dodecyl ethers have been considered similarly to the mesomorphic-isotropic transitions.

X = 3-substituent	H	F	Cl
Average smectic-nematic transition (C <sub>10</sub> and C <sub>12</sub> ) ...	125.5°	112.5°	84.75°
Decrease in average transition .....	13°	27.75°	
Increase in molecule breadth (Å) .....	0.43	0.75	

The ratios are now 30.23 from unsubstituted to fluoro-acid, and 34.53 from unsubstituted to chloro-acid. The order is reversed from that for the mesomorphic-isotropic transitions, and is in disagreement with the order of the effective dipole moments.

In neither case has it been possible to find a mathematical relation which will give values for the relative effects of the dipoles and the breadth increases in accordance with the

\* Dipole moments from H. B. Watson's "Modern Theories of Organic Chemistry," 2nd Edn., Oxford Univ. Press, London, 1941, 60.

observed transitions. These results can only indicate qualitatively that relatively small increments in molecular breadth do decrease the thermal stability of the mesophases. Before it is possible to suggest even an approximate mathematical treatment for the effect of substitution on mesomorphic systems, further data will have to be obtained by an examination of other substituted homologous series.

It must be assumed that the 4-alkoxy-3-bromobenzoic acids are too broad to be mesomorphic, as a result of their weaker intermolecular cohesion. The 4-alkoxy-3:5-dichlorobenzoic acids (breadth increment from unsubstituted acid = 1.5 Å) are not mesomorphic, and the low m. p.s of the pentyl and the hexadecyl ethers, 103° and 60.5° respectively, imply a still lower intermolecular cohesion in the crystal. Indeed, any molecular arrangement which would give smectic behaviour would be much more open than that for the 3-chloro-acids, and the cohesion would be still further reduced by opposition of the carbon-halogen dipoles between different molecules. On the other hand, a nematic packing of the dichloro-acids can be as close as for the monochloro-derivatives, and it is difficult to account for their lack of mesomorphism solely on the basis of their greater breadth. There is however a further factor to be considered, namely, the steric effect of the chlorine atoms in the 3:5-positions. This is sufficient to force the O-CH<sub>2</sub> bond out of the plane of the ring system, so that the breadth of the alkyl chain is at an angle to this plane. In this way the monomer's thickness may be increased to about 4.8 Å, compared to the thickness of 3.7 Å for the unsubstituted, 3-fluoro-, and 3-chloro-acids. The result will be a reduction in the cohesion between the planes of the aromatic rings, sufficient to give a low crystal lattice energy, and presumably to make mesophases impossible by rendering them stable only at temperatures which are too low to be obtained without crystallisation. The breadth of the dichloro-acid molecules is probably of little significance compared to the effect of this thickening of the molecule.

#### EXPERIMENTAL

(M. p.s are corrected for exposed stem.)

The mesomorphic and polymorphic transitions were determined in an electrically heated block (Gray, *loc. cit.*). The enantiotropic mesomorphic changes were measured in the usual way: all the values except those from the solid to the mesophase were checked both by heating and by cooling the specimen. The changes observed in polarised light were from the solid to the fine mosaic of smectic focal-conics, from the solid or smectic phase to the highly threaded, mobile nematic phase, and from the solid or mesophase to the extinct isotropic liquid. The monotropic mesomorphic transitions were determined by observing carefully the isotropic liquid as it cooled slowly until the nematic phase and, at a lower temperature, the smectic phase appeared. It was sometimes possible to raise the temperature while the specimens were in these monotropic states without inducing crystallisation, and thus to obtain the transitions in reverse. Good agreement was found with the values obtained on cooling. Frequently the low rate of cooling (about 1° per min.), which was necessary for accurate measurement of the transitions, was too slow, and crystallisation occurred. In these cases, values of the transition temperatures could be obtained only by extrapolation of the curves constructed from experimentally observed values for the other members of the series.

*Polymorphic Transition Temperatures.*—See Tables. Here solid I is the stable solid at room temperature.

4-n-Alkoxy-3-fluorobenzoic acids.		4-n-Alkoxy-3-chlorobenzoic acids.	
Alkyl	Solid I–solid II transition temp.	Alkyl	Solid I–solid II transition temp.
Butyl .....	137.5°	Heptyl .....	111.0°
Pentyl .....	99.5	Octyl .....	90.0
Hexyl .....	74.0	Nonyl .....	85.0
Heptyl .....	101.5		
Octyl .....	94.0		
Nonyl .....	109.0		
Decyl .....	106.0		
Octadecyl .....	75.5		

Both the decyl and the dodecyl ethers exhibit a monotropic solid.

The dodecyl ether exhibits two monotropic forms.

*Preparation of Materials.*—*o*-Fluoroanisole was obtained from *o*-anisidine in 40% yield by decomposition of the dry diazonium borofluoride (Balz and Schiemann, *Ber.*, 1927, 60, 1186). It was purified by fractionation and had b. p. 160—162°.

*4-Bromo-2-fluoroanisole.*—The *o*-fluoroanisole (18.9 g., 0.15 mole) was treated in chloroform (50 ml.) gradually with bromine (24 g., 0.15 mole) at room temperature. When the initial reaction had subsided, the mixture was refluxed gently until bromination was complete (2.5 hr.). The cooled solution was washed with water and with dilute sodium hydroxide and dried. After the solvent had been recovered, and pale yellow oil distilled under reduced pressure, *4-bromo-2-fluoroanisole* was obtained as a colourless liquid, b. p. 148—150°/14 mm., in 95% yield (Found : C, 41.0; H, 3.0; Br, 38.9.  $C_7H_6OBrF$  requires C, 41.0; H, 2.9; Br, 39.0%).

*3-Fluoro-4-methoxybenzoic Acid.*—The Grignard compound from *4-bromo-2-fluoroanisole* was prepared in anhydrous ether-benzene and converted into the acid by the method described by Fries and Schimmelschmidt (*Ber.*, 1925, 58, 2835) for 6-methoxy-2-naphthoic acid. After carboxylation and acidification, and removal of most of the ether, the crude acid was collected and freed from neutral matter by dissolution in hot dilute sodium hydroxide. The product obtained on acidification (28.5 g., 67%) had m. p. 211.5°, unchanged by crystallisation from glacial acetic acid and ethyl alcohol. The acid crystallised as colourless prisms (Found : C, 56.4; H, 4.1.  $C_8H_7O_3F$  requires C, 56.5; H, 4.1%). The benzene layer in the filtrate from the crude acid gave only a small amount of impure acid on extraction with aqueous alkali.

*3-Fluoro-4-hydroxybenzoic Acid.*—*3-Fluoro-4-methoxybenzoic acid* (45 g.) was demethylated by refluxing 48% hydrobromic acid (100 ml.) and glacial acetic acid (100 ml.) for 6—7 hr. More than half of the hydroxy-acid (m. p. 148—157°) was obtained crystalline on cooling; the remainder, of the same m. p., was isolated by removal of the solvent under reduced pressure. Crystallisation from water, and filtration of the hot solution to remove some insoluble material, yielded colourless needles, m. p. 145—147° (36 g., 87%). Further crystallisation from 30% acetic acid raised the m. p. to 146—147° (Found : C, 53.0; H, 3.8. Calc. for  $C_7H_5O_3F$ : C, 53.9; H, 3.2%). Attempts at further purification failed to improve the m. p. and the analysis. The ethers of this hydroxy-acid were very readily purified, and the use of the impure material was not a handicap.

*4-n-Alkoxy-3-fluorobenzoic Acids.*—*3-Fluoro-4-hydroxybenzoic acid* (1.56 g., 0.01 mole), potassium hydroxide (1.1 g., 0.02 mole), water (5 ml.), ethyl alcohol (40 ml.), and the *n*-alkyl halide (0.015 mole) were refluxed (alkyl iodide 8 hr.; alkyl bromide 16 hr.). Aqueous potassium hydroxide (10 ml., 10%) was added, and refluxing continued for 2 hr. to hydrolyse any ester. The pure *alkoxy-acids* were obtained as colourless needles or prisms after one crystallisation from absolute alcohol, two from benzene, and one from glacial acetic acid. After the first crystallisation the acids were almost pure: the yields at this stage were 80—85%.

#### 4-n-Alkoxy-3-fluorobenzoic acids.

Alkyl	Found (%)		Formula	Required (%)		Alkyl	Found (%)		Formula	Required (%)	
	C	H		C	H		C	H		C	H
Butyl ...	62.4	6.3	$C_{11}H_{13}O_3F$	62.3	6.1	Nonyl ...	68.2	8.3	$C_{16}H_{23}O_3F$	68.1	8.2
Pentyl	63.7	6.7	$C_{12}H_{15}O_3F$	63.7	6.6	Decyl.....	69.1	8.5	$C_{17}H_{25}O_3F$	68.9	8.5
Hexyl...	65.2	7.1	$C_{13}H_{17}O_3F$	65.0	7.1	Dodecyl...	70.6	8.8	$C_{19}H_{29}O_3F$	70.4	9.0
Heptyl	66.2	7.4	$C_{14}H_{19}O_3F$	66.2	7.5	Hexadecyl	72.5	9.8	$C_{23}H_{37}O_3F$	72.6	9.7
Octyl ...	67.3	7.8	$C_{15}H_{21}O_3F$	67.2	7.8	Octadecyl	73.4	9.9	$C_{25}H_{41}O_3F$	73.5	10.1

*3-Chloro-4-hydroxybenzoic Acid.*—*p*-Hydroxybenzoic acid (13.8 g., 0.1 mole) was treated in acetic acid (100 ml.) with a solution of dichloramine-r (12 g., 0.05 mole) in acetic acid (100 ml.) and concentrated hydrochloric acid (0.5 ml.). After 2 hr. the acetic acid (100 ml.) was removed under reduced pressure. The cooled liquors deposited colourless crystals, m. p. 169—172° (14 g.). One crystallisation from water gave *3-chloro-4-hydroxybenzoic acid*, m. p. 172° (12.3 g., 70%).

*4-n-Alkoxy-3-chlorobenzoic Acids.*—*3-Chloro-4-hydroxybenzoic acid* was alkylated in the same way as *3-fluoro-4-hydroxybenzoic acid*. After one crystallisation from glacial acetic acid the *ethers* were obtained as colourless needles or prisms in yields of 85—95%. These were purified by crystallisation from benzene (twice) and from absolute alcohol (twice).

*3-Bromo-4-hydroxybenzoic Acid.*—*p*-Hydroxybenzoic acid was brominated in acetic acid with the theoretical amount of bromine. The acid precipitated on dilution with water was washed and dissolved in aqueous sodium hydrogen carbonate. The solution was filtered, and the acid liberated. Crystallisation from water gave colourless needles of the bromo-acid, m. p. 177.5° (80%).

## 4-n-Alkoxy-3-chlorobenzoic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	Cl		C	H	Cl
Methyl *	51.5	3.8	19.1	C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> Cl	51.5	3.8	19.0
Pentyl *	59.6	6.3	14.6	C <sub>12</sub> H <sub>15</sub> O <sub>3</sub> Cl	59.4	6.2	14.7
Hexyl	60.7	6.6	13.9	C <sub>13</sub> H <sub>17</sub> O <sub>3</sub> Cl	60.8	6.6	13.8
Heptyl	62.2	7.2	13.1	C <sub>14</sub> H <sub>19</sub> O <sub>3</sub> Cl	62.1	7.0	13.1
Octyl	63.3	7.5	12.5	C <sub>15</sub> H <sub>21</sub> O <sub>3</sub> Cl	63.3	7.4	12.5
Nonyl	64.4	7.7	12.0	C <sub>16</sub> H <sub>23</sub> O <sub>3</sub> Cl	64.3	7.7	11.9
Decyl	65.3	7.8	11.5	C <sub>17</sub> H <sub>25</sub> O <sub>3</sub> Cl	65.3	8.0	11.4
Dodecyl	66.9	8.5	10.4	C <sub>19</sub> H <sub>29</sub> O <sub>3</sub> Cl	66.95	8.5	10.4
Hexadecyl	69.6	9.5	8.9	C <sub>23</sub> H <sub>37</sub> O <sub>3</sub> Cl	69.6	9.3	8.95
Octadecyl	70.7	9.7	8.4	C <sub>25</sub> H <sub>41</sub> O <sub>3</sub> Cl	70.7	9.7	8.4

\* Not new.

4-n-Alkoxy-3-bromobenzoic Acids.—Only the octyl and hexadecyl ethers were prepared, and these were almost pure after one crystallisation from glacial acetic acid (the yields at this stage were 85%). Both were crystallised thrice from glacial acetic acid and once from benzene to give colourless plates of the *octyl ether*, m. p. 111° (Found: C, 55.0; H, 6.5; Br, 24.4. C<sub>15</sub>H<sub>21</sub>O<sub>3</sub>Br requires C, 54.8; H, 6.4; Br, 24.3%), and the *hexadecyl ether*, m. p. 99° (Found: C, 62.6; H, 8.4; Br, 18.2. C<sub>23</sub>H<sub>37</sub>O<sub>3</sub>Br requires C, 62.6; H, 8.4; Br, 18.1%).

3 : 5-Dichloro-4-hydroxybenzoic Acid.—Chlorine was passed through a solution of *p*-hydroxybenzoic acid in glacial acetic acid for 4 hr. at 60–80°. The resulting thick suspension was cooled and the solid collected. It was stirred with aqueous sodium dithionite, refiltered, washed with water, and dried. The product (76%) was nearly pure, and had m. p. 265–267°. Crystallisation from a large volume of glacial acetic acid gave colourless needles of the dichloro-acid, m. p. 267°. Ugryumov (*J. Gen. Chem. U.S.S.R.*, 1949, 19, 1167) gives m. p. 265°.

4-n-Alkoxy-3 : 5-dichlorobenzoic Acids.—The *pentyl* and *hexadecyl ethers* were prepared. The crude ethers contained some unchanged hydroxy-acid, and for 0.01 mole of the ethers this was removed by shaking with 30 and 70 ml. of cold benzene in the cases of the *pentyl* and *hexadecyl ethers* respectively. The solutions were filtered and evaporated to yield the colourless ethers, which were then purified by further crystallisation. The *pentyl ether*, crystallised from glacial acetic acid and light petroleum ether (b. p. 60–80°), had m. p. 103° (Found: C, 51.8; H, 5.1; Cl, 25.6. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>Cl<sub>2</sub> requires C, 52.0; H, 5.1; Cl, 25.6%). The *hexadecyl ether*, crystallised twice from light petroleum (b. p. 40–60°), melted at 60.5° (Found: C, 64.1; H, 8.3; Cl, 16.5. C<sub>23</sub>H<sub>36</sub>O<sub>3</sub>Cl<sub>2</sub> requires C, 64.0; H, 8.3; Cl, 16.5%).

Grants to the Department from the Distillers Company Limited and from Imperial Chemical Industries Limited are gratefully acknowledged.

UNIVERSITY COLLEGE, HULL.

[Received, March 6th, 1954.]