

The Preparation of 4- and 5-n-Alkoxy-1-naphthoic and 6- and 7-n-Alkoxy-2-naphthoic Acids.

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Each of the series of 4-*n*-alkoxy-1- and 6-*n*-alkoxy-2-naphthoic acids has been prepared by two methods which are compared. A new method of synthesising 5-hydroxy-1-naphthoic acid is compared with recorded methods. The same route has been used to prepare 7-hydroxy-2-naphthoic acid. Several *n*-alkyl ethers of these hydroxy-acids are described.

THE preparation of certain alkoxy-naphthoic acids was undertaken to obtain information about the effect of molecular shape on the mesomorphic behaviour of alkoxyarene-carboxylic acids. The simpler *p*-*n*-alkoxybenzoic acids have already been shown to exhibit mesomorphism (*J.*, 1929, 2660; 1935, 1874; 1939, 420; 1953, 4179), and preliminary reports of the mesomorphic behaviour of the 6-*n*-alkoxy-2-naphthoic acids and their 5-halogeno-derivatives have been made (Gray and Brynmor Jones, *Nature*, 1951, 167, 83; 1952, 170, 451). The preparation of four types of alkoxy-naphthoic acid is now described.

4-*n*-Alkoxy-1-naphthoic acids could not be prepared by alkylation of 4-hydroxy-1-naphthoic acid, first reported by Heller (*Ber.*, 1912, 45, 675). This acid is decarboxylated very easily, and Cavill and Tetaz (*J.*, 1952, 3634) report that it is difficult to obtain free from quinones. The *n*-alkoxy-acids were therefore prepared individually from the appropriate 1-*n*-alkoxynaphthalene, either by conversion into 1-*n*-alkoxy-4-bromonaphthalene and carboxylation of the Grignard compound, or by hydrolysis of 4-*n*-alkoxy-1-naphthonitrile prepared by Friedel and Crafts's reaction. The average over-all yield from the 1-*n*-alkoxynaphthalene was better by the second method (75%) than by the first (60%).

5-Hydroxy-1-naphthoic acid was first prepared (Royle and Schedler, *J.*, 1923, 1641) from the commercially available 5-aminonaphthalene-1-sulphonic acid. Their procedure, involving the intermediates, 5-cyano- and 5-carboxy-naphthalene-1-sulphonic acid, is however tedious. Cason (*J. Amer. Chem. Soc.*, 1941, 63, 830) converted 5-aminonaphthalene-1-sulphonic acid into 5-amino-1-naphthonitrile, and claims that this may be hydrolysed to the hydroxy-acid by 10% sulphuric acid, in a sealed tube at $220^{\circ} \pm 5^{\circ}$ during 4 hr. However, this hydrolysis could not be repeated. Temperatures above 225° gave mainly 1-naphthol; at 200 – 225° the product was a mixture which could not be purified, and between 180° and 200° only very slight hydrolysis to 5-amino-1-naphthoic acid occurred. As an alternative route, 5-amino-1-naphthonitrile was converted into 5-hydroxy-1-naphthonitrile, and this, by hydrolysis, into 5-hydroxy-1-naphthoic acid. This method is reliable, can be operated on any scale, and, although it involves one more stage than Cason's, gives a better yield. Alkylation of the hydroxy-acid gave the alkyl ethers.

6-Methoxy-2-naphthoic acid was prepared by two methods which differ little in overall yield or convenience: carboxylation of the Grignard compound from 2-bromo-6-methoxynaphthalene, and oxidation of 2-acetyl-6-methoxynaphthalene with sodium hypobromite. The methyl ether was readily demethylated to give 6-hydroxy-2-naphthoic acid.

7-Hydroxy-2-naphthoic acid was prepared by the procedure adopted for 5-hydroxy-1-naphthoic acid. 7-Aminonaphthalene-2-sulphonic acid was converted into 7-amino-2-naphthonitrile by distillation with potassium cyanide. Diazotisation yielded 7-hydroxy-2-naphthonitrile, and this, on hydrolysis, gave 7-hydroxy-2-naphthoic acid, from which the ethers were prepared.

In all cases except the last, thirteen normal ethers were prepared (methyl—decyl, dodecyl, hexadecyl, and octadecyl). The *n*-alkyl halides, which were not commercially available, were prepared from the normal alcohol, by the action of 48% hydrobromic acid and concentrated sulphuric acid (*Org. Synth.*, 1941, Coll. Vol. I, p. 29).

EXPERIMENTAL

M. p.s are corrected for exposed stem.

1-n-Alkoxy-naphthalenes.—1-Naphthol was alkylated in boiling alcohol (8 hr.) by sodium ethoxide and the n-alkyl bromide or iodide. After distillation under reduced pressure, the ethers were obtained colourless in 65–75% yield (see Table).

1-n-Alkoxy-naphthalenes.

Alkyl	M. p.	B. p.	Alkyl	M. p.	B. p.
Methyl	—	134°/13 mm.	Octyl	—	189°/5 mm.
Ethyl	5°	152°/17 mm.	Nonyl	—	185°/4 mm.
Propyl	—	143°/3 mm.	Decyl	—	212°/4 mm.
Butyl	19·5	160°/4 mm.	Dodecyl	—	227°/3 mm.
Pentyl	29·5	173°/6 mm.	Hexadecyl	31°	258°/1 mm.
Hexyl	—3	166°/4 mm.	Octadecyl	50·5°	236°/10 ⁻² mm.
Heptyl	—	171°/5 mm.			

1-n-Alkoxy-4-bromonaphthalenes.—The 1-n-alkoxy-naphthalenes were brominated by Militzer's method (*J. Amer. Chem. Soc.*, 1938, **60**, 256)—iodine monobromide in chloroform at 10–20°. After removal of the chloroform, the bromo-ethers were distilled under reduced pressure, being obtained colourless in 65–75% yields (see Table).

1-Alkoxy-4-bromonaphthalenes.

Alkyl	M. p.	B. p.	Found (%)		Formula	Required (%)	
			C	H		C	H
Methyl	—	159°/4 mm.	55·6	3·7	C ₁₁ H ₉ OBr	55·7	3·8
Ethyl	48·5°	158°/3 mm.	57·6	4·6	C ₁₂ H ₁₁ OBr	57·4	4·4
Propyl	31	188°/8 mm.	58·6	5·0	C ₁₃ H ₁₃ OBr	58·9	5·0
Butyl	25	199°/5 mm.	60·3	5·5	C ₁₄ H ₁₅ OBr	60·2	5·4
Pentyl	47·5	181°/3 mm.	61·5	5·7	C ₁₅ H ₁₇ OBr	61·5	5·8
Hexyl	45	206°/5 mm.	63·1	6·3	C ₁₆ H ₁₉ OBr	62·6	6·2

4-n-Alkoxy-1-naphthonitriles.—Cyanogen bromide (*Org. Synth.*, 1931, **11**, 30) was not dried by shaking it, when molten, with calcium chloride. When it was distilled slowly from the reaction mixture, the distillate contained little moisture. A known weight of the distillate, dissolved in carbon disulphide, was dried (Na₂SO₄) and used as a standard solution. With 1-n-alkoxy-naphthalenes in carbon disulphide containing aluminium trichloride it gave the nitriles (Karrer, Zebmann, and Zeller, *Helv. Chim. Acta*, 1920, **3**, 267). The carbon disulphide extract was washed with aqueous sodium hydroxide to remove 4-hydroxy-1-naphthonitrile (1–2%), and dried (Na₂SO₄). Removal of the solvent gave solid residues which, on crystallisation from absolute ethyl alcohol, gave the alkoxy-nitriles (see Table) as colourless needles or prisms, in 80% yield.

4-Alkoxy-1-naphthonitriles.

Alkyl	M. p.	Found (%)			Formula	Required (%)		
		C	H	N		C	H	N
Ethyl	88°	79·2	5·6	7·0	C ₁₃ H ₁₁ ON	79·2	5·6	7·1
Pentyl	60	80·1	7·1	5·9	C ₁₆ H ₁₇ ON	80·3	7·1	5·9
Hexyl	62	80·5	7·4	5·4	C ₁₇ H ₁₉ ON	80·6	7·5	5·5
Heptyl	54	80·7	7·6	5·2	C ₁₈ H ₂₁ ON	80·9	7·8	5·2
Octyl	61	81·2	8·0	5·0	C ₁₉ H ₂₃ ON	81·1	8·2	5·0
Nonyl	53	81·4	8·6	4·6	C ₂₀ H ₂₅ ON	81·4	8·5	4·8
Decyl	64	81·5	8·7	4·3	C ₂₁ H ₂₇ ON	81·5	8·7	4·5
Dodecyl	67	82·0	9·2	4·0	C ₂₃ H ₃₁ ON	81·9	9·2	4·2
Hexadecyl	69	82·3	9·9	3·5	C ₂₇ H ₃₉ ON	82·4	9·9	3·6
Octadecyl	71	82·7	10·3	3·3	C ₂₉ H ₄₃ ON	82·7	10·2	3·3

Unsuccessful attempts were made to dealkylate these nitriles by refluxing them with 48% hydrobromic acid, with aluminium trichloride in carbon disulphide, and with acetic acid saturated with hydrogen bromide.

4-Hydroxy-1-naphthonitrile was very difficult to purify, and the best sample, obtained by crystallisation from 90% ethyl alcohol with heavy loss, had m. p. 172–174°. Its nitrogen content was low, and the acid formed on hydrolysis was impure (m. p. 174–175°; Heller, *loc. cit.*, gives m. p. 183–184°).

4-n-Alkoxy-1-naphthoic Acids.—(a) From the bromo-compounds. Magnesium turnings

(2.45 g., 0.1 g.-atom) and a solution of the 1-n-alkoxy-4-bromonaphthalene (2 g.) in ether (25 ml.) were refluxed for about 5 min. Appearance of turbidity indicated the start of the reaction. If this did not occur, small crystals of iodine were added, until, on the disappearance of the colour, a turbidity was visible. The remainder of the bromo-compound (total of 0.1 mole), in ether (75 ml.), was added dropwise in 30 min. to the stirred mixture, and refluxing continued for 10 hr. The resulting solution was added to ether which had been saturated with solid carbon dioxide. When the excess of carbon dioxide had evaporated, the addition compound was decomposed by stirring it with 17% hydrochloric acid (50 ml.). After the ether had been removed, the brown acid was collected and washed free from magnesium chloride. The crude acid was dissolved in boiling n-sodium hydroxide and filtered from insoluble material, and the pale orange filtrate was acidified. The acids were thus obtained in 80—85% yield as colourless solids which were almost pure after one crystallisation from glacial acetic acid.

(b) *From the nitriles.* The 4-n-alkoxy-1-naphthonitrile (0.1 mole) was refluxed with a solution (250 ml.) prepared by saturating methyl alcohol at 50° with potassium hydroxide. Evolution of ammonia ceased after 15—25 hours' boiling. The diluted mixture was acidified, and the precipitate of the naphthoic acid redissolved in boiling n-sodium hydroxide. The hot solution was filtered and acidified, to give quantitative yields of the colourless acids. These were almost pure after one crystallisation from glacial acetic acid (yields 95—97%).

In both cases, the 4-n-alkoxy-1-naphthoic acids were crystallised from glacial acetic acid until the m. p.s were constant (see Table).

4-Alkoxy-1-naphthoic acids.

Alkyl	M. p.	Found (%)		Formula	Required (%)	
		C	H		C	H
Methyl	248°	71.2	5.2	C ₁₂ H ₁₀ O ₃	71.3	4.9
Ethyl	220	72.1	5.6	C ₁₃ H ₁₂ O ₃	72.2	5.6
Propyl	203	73.1	6.1	C ₁₄ H ₁₄ O ₃	73.1	6.1
Butyl	213.5	73.7	6.3	C ₁₅ H ₁₆ O ₃	73.8	6.5
Pentyl	207	74.4	7.0	C ₁₆ H ₁₈ O ₃	74.4	7.0
Hexyl	212	74.9	7.5	C ₁₇ H ₂₀ O ₃	75.0	7.4
Heptyl	189	75.3	7.6	C ₁₈ H ₂₂ O ₃	75.5	7.7
Octyl	183.5	75.9	8.1	C ₁₉ H ₂₄ O ₃	76.0	8.0
Nonyl	161	76.3	8.2	C ₂₀ H ₂₆ O ₃	76.4	8.3
Decyl	174.5	77.0	8.6	C ₂₁ H ₂₈ O ₃	76.8	8.5
Dodecyl	147.5	77.5	9.0	C ₂₃ H ₃₂ O ₃	77.5	9.0
Hexadecyl	136	78.4	9.6	C ₂₇ H ₄₀ O ₃	78.6	9.7
Octadecyl	137.5	79.4	9.9	C ₂₉ H ₄₄ O ₃	79.1	10.0

5-Amino-1-naphthonitrile.—Sodium 5-aminonaphthalene-1-sulphonate (70 g.) and potassium cyanide (140 g.) were ground together and dry-distilled in an all-glass retort, from a salt-bath at 500—600°. The red-brown distillate solidified and was dissolved in boiling 0.3N-hydrochloric acid (1.3 l.). The solution, cooled to 30°, was filtered to remove some tar; the filtrate was neutralised with concentrated aqueous ammonia, and the orange-brown precipitate of 5-amino-1-naphthonitrile collected. The dried product (15.7 g.) was distilled under reduced pressure and gave a pale yellow solid (11.3 g., 23.5%), b. p. 187—193°/2—3 mm. Although this material softened and melted over the range 120—140°, it gave very satisfactory results in the next stage of the synthesis. After two crystallisations from 80% ethyl alcohol yellow needles, m. p. 140°, were obtained (Found: C, 78.4; H, 4.8; N, 16.7. Calc. for C₁₁H₈N₂: C, 78.6; H, 4.8; N, 16.7%). A large number of preparations gave yields of 22—26%, after distillation under reduced pressure.

5-Hydroxy-1-naphthonitrile.—A solution of 5-amino-1-naphthonitrile suitable for rapid diazotisation was prepared by dissolving the amine (5.04 g., 0.03 mole) in glacial acetic acid (60 ml.) at 80° and, while this was vigorously agitated, adding quickly 60 ml. of a 40% w/w solution of sulphuric acid at 80°. Stirring was continued while the mixture was cooled rapidly to 0°. A solution of sodium nitrite (4.2 g., 0.06 mole) in water (30 ml.) was then added at 0° and the mixture stirred at 0—5° until a clear solution was obtained. Urea was added in small portions until the solution was free from nitrite. The ice-cold diazonium solution was immediately added dropwise to a vigorously stirred and boiling solution of sulphuric acid (180 ml.; 40% w/w) in 30 min. Refluxing was continued for 1 hr., and the mixture cooled. Water (300 ml.) was added and the crystals and solution were extracted with ether. The ethereal layer was extracted twice with n-sodium hydroxide, and acidification gave a pink precipitate of 5-hydroxy-1-naphthonitrile (4.3 g., 83%). One crystallisation from aqueous acetic acid (35 ml. of glacial acetic acid and 65 ml. of water) gave orange needles (3.36 g., 66—

67%), m. p. 204—206°. This material was converted into the acid, but two further crystallisations from aqueous acetic acid gave pale yellow needles, m. p. 209·5° (Found : C, 77·8; H, 4·1; N, 8·2. C₁₁H₇ON requires C, 78·1; H, 4·1; N, 8·3%).

5-Hydroxy-1-naphthoic Acid.—5-Hydroxy-1-naphthonitrile (8·4 g.) was refluxed with a solution of potassium hydroxide (50 g. in 100 ml. of water) for 4—5 hr. On acidification of the diluted hydrolysate, the light brown 5-hydroxy-1-naphthoic acid (8·46 g., 90%), m. p. 238° (decomp.), was obtained. This product was used for the preparation of the ethers, since two crystallisations from water failed to raise the m. p.

The acetyl derivative crystallised from benzene in small, colourless plates, m. p. 204—205° (cf. Cason, *J. Amer. Chem. Soc.*, 1941, **63**, 830).

5-Methoxy-1-naphthoic Acid.—5-Hydroxy-1-naphthoic acid, in alkaline solution, was methylated with methyl sulphate at 40—60°. Any ester in the product was removed by 1 hour's refluxing with 10% methyl-alcoholic sodium hydroxide. The pale yellow methoxy-acid melted at 220—227°: after two crystallisations from 95% ethyl alcohol, and one sublimation at 190°/2 mm., it was obtained as colourless needles, m. p. 232·5° (Found : C, 71·3; H, 5·2. Calc. for C₁₂H₁₀O₃: C, 71·3; H, 4·9%).

5-n-Alkoxy-1-naphthoic Acids.—5-Hydroxy-1-naphthoic acid (1·88 g., 1 mol.), potassium hydroxide (0·7 g., 2 mols.), water (5 ml.), ethyl alcohol (40 ml.), and the *n*-alkyl halide (1·5 mols.) 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 *alkoxy-acids* were obtained as pure, colourless products after two crystallisations from glacial acetic acid, one from 95% ethyl alcohol, and, except in the case of the last three members of the following Table, one sublimation at 175—185°/2 mm. After the first crystallisation the acids were almost pure; the yields at this stage were 80—90%.

5-Alkoxy-1-naphthoic acids.

Alkyl	M. p.	Found (%)		Formula	Required (%)	
		C	H		C	H
Ethyl	201°	71·9	5·8	C ₁₃ H ₁₂ O ₃	72·2	5·6
Propyl	189	72·9	5·9	C ₁₄ H ₁₄ O ₃	73·1	6·1
Butyl	172	73·7	6·4	C ₁₅ H ₁₆ O ₃	73·8	6·5
Pentyl	143	74·2	7·1	C ₁₆ H ₁₈ O ₃	74·4	7·0
Hexyl	154	74·7	7·4	C ₁₇ H ₂₀ O ₃	75·0	7·4
Heptyl	135·5	75·5	7·6	C ₁₈ H ₂₂ O ₃	75·5	7·7
Octyl	142·5	75·9	7·9	C ₁₉ H ₂₄ O ₃	76·0	8·0
Nonyl	143	76·4	8·3	C ₂₀ H ₂₆ O ₃	76·4	8·3
Decyl	137	76·7	8·4	C ₂₁ H ₂₈ O ₃	76·8	8·5
Dodecyl	125	77·4	9·0	C ₂₃ H ₃₂ O ₃	77·5	9·0
Hexadecyl	117·5	78·6	9·8	C ₂₇ H ₄₀ O ₃	78·6	9·7
Octadecyl	122	79·2	9·9	C ₂₉ H ₄₄ O ₃	79·1	10·0

6-Bromo-2-naphthol.—Mossy tin was prepared in the following way. Stannous chloride (112 g., 0·5 mole) was dissolved in water (150 ml.), and zinc dust (30 g., 0·46 g.-atom) added with shaking. Heat was evolved and the mossy tin was precipitated immediately. When cold, the tin was filtered off, washed well with cold water, and dried under vacuum. The yield was approx. 55 g.

2-Naphthol (144 g., 1 mole) was suspended in glacial acetic acid (400 ml.) and brominated at room temperature. Without isolation, the 1 : 6-dibromo-2-naphthol was reduced to 6-bromo-2-naphthol by addition of successive quantities of mossy tin to the boiling solution (cf. *Org. Synth.*, 1940, **20**, 18). The product (214—223 g., 96—100%), m. p. 123—127°, was sufficiently pure for the next stage, although it contained some tin salts.

2-Bromo-6-methoxynaphthalene.—6-Bromo-2-naphthol with methyl sulphate in alkali (French and Sears, *J. Amer. Chem. Soc.*, 1948, **70**, 1279) gave the colourless ether, m. p. 103—105°, b. p. 189—199°/20 mm. (60—70%). One crystallisation from absolute ethyl alcohol gave colourless needles, m. p. 106—107°.

6-Methoxy-2-naphthoic Acid.—The Grignard compound from 2-bromo-6-methoxynaphthalene was prepared in ether-benzene and converted into the acid as described by Fries and Schimmelschmidt (*Ber.*, 1925, **58**, 2835). The crude acid was dissolved in hot *n*-sodium hydroxide, and the solution was filtered and acidified. The precipitate, crystallised from xylene, formed colourless needles, m. p. 206° (50—55%).

2-Acetyl-6-methoxynaphthalene.—This was prepared by the action of acetyl chloride on 2-bromo-6-methoxynaphthalene in the presence of anhydrous aluminium trichloride in nitro-

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benzene (Robinson and Rydon, *J.*, 1939, 1399). Distillation of the product under reduced pressure (b. p. 165—170°/3—4 mm.) and crystallisation from methanol gave colourless blades (50%), m. p. 104—105°.

6-Methoxy-2-naphthoic Acid.—A solution of sodium hypobromite, prepared from sodium hydroxide (140 g.), water (600 ml.), and bromine (50 ml.) at 0—5°, was added dropwise to a stirred solution of the 2-acetyl-6-methoxynaphthalene (50 g.) in dioxan (350 ml.) during 30 min., the temperature being kept at 35—40°, but later raised to 50—55° to ensure complete oxidation. Excess of bromine was destroyed with sodium dithionite, and the mixture was diluted with water (2 l.). After the dioxan and bromoform had been removed by steam-distillation, the hot alkaline solution was filtered. Acidification with concentrated hydrochloric acid yielded the pale yellow acid (48.7 g.); one crystallisation from xylene gave colourless needles of 6-methoxy-2-naphthoic acid, m. p. 205—206° (35—37 g., 70—75%).

6-Hydroxy-2-naphthoic Acid.—6-Methoxy-2-naphthoic acid (8.4 g.) was heated for 2.5 hr. with acetic acid (35 ml.), 48% hydrobromic acid (35 ml.), and glacial acetic acid (20 ml.) saturated with hydrogen bromide, the methoxy-acid dissolving. The dark solution was cooled, and the light brown crystals were collected and washed with water. One crystallisation from water (1.2 l.) gave pale tan needles (69—75%), m. p. 250° (Found: C, 70.2; H, 4.2. Calc. for $C_{11}H_8O_3$: C, 70.2; H, 4.3%).

The *acetyl* (Found: C, 67.7; H, 4.2. $C_{13}H_{10}O_4$ requires C, 67.8; H, 4.35%) and *benzoyl* (Found: C, 74.1; H, 4.0. $C_{18}H_{12}O_4$ requires C, 74.0; H, 4.1%) derivatives crystallised from ethyl acetate in very small needles, m. p. 228° (decomp.) and 257° respectively. For the *benzenesulphonyl* derivative (Found: C, 62.2; H, 3.8. $C_{17}H_{12}O_5S$ requires C, 62.2; H, 3.7%) the m. p. was 228.5° after crystallisation from acetic acid.

6-n-Alkoxy-2-naphthoic Acids.—6-Hydroxy-2-naphthoic acid was alkylated in the same way as 5-hydroxy-1-naphthoic acid. After one crystallisation from glacial acetic acid the ethers were obtained as colourless needles in 85—90% yield and crystallised twice from glacial acetic acid and twice from xylene (see Table).

6-Alkoxy-2-naphthoic acids.

Alkyl	M. p.	Found (%)		Formula	Required (%)	
		C	H		C	H
Methyl	206°	71.2	5.0	$C_{12}H_{10}O_3$	71.3	4.9
Ethyl	213	72.3	5.4	$C_{13}H_{12}O_3$	72.2	5.6
Propyl	208	72.9	6.1	$C_{14}H_{14}O_3$	73.1	6.1
Butyl	198	73.9	6.4	$C_{15}H_{16}O_3$	73.8	6.5
Pentyl	179.5	74.3	6.9	$C_{16}H_{18}O_3$	74.4	7.0
Hexyl	147	74.9	7.4	$C_{17}H_{20}O_3$	75.0	7.4
Heptyl	163	75.1	7.7	$C_{18}H_{22}O_3$	75.5	7.7
Octyl	161.5	75.9	8.0	$C_{19}H_{24}O_3$	76.0	8.0
Nonyl	147.5	76.6	8.4	$C_{20}H_{26}O_3$	76.4	8.3
Decyl	139	76.8	8.6	$C_{21}H_{28}O_3$	76.8	8.5
Dodecyl	119	77.4	9.1	$C_{23}H_{32}O_3$	77.5	9.0
Hexadecyl	107	78.9	9.7	$C_{27}H_{40}O_3$	78.6	9.7
Octadecyl	114	79.2	9.9	$C_{29}H_{44}O_3$	79.1	10.0

6-*iso*Pentyl-2-naphthoic acid, crystallised thrice from acetic acid, had m. p. 194° (Found: C, 74.3; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%).

6-(3:5:5-Trimethylhexyloxy)-2-naphthoic acid, similarly crystallised, had m. p. 170° (Found: C, 76.6; H, 8.2. $C_{20}H_{26}O_3$ requires C, 76.4; H, 8.3%).

7-Amino-2-naphthonitrile.—7-Aminonaphthalene-2-sulphonic acid (35 g.) and potassium cyanide (70 g.) were dry-distilled, and the product was treated in the same way as that from 5-amino-1-naphthonitrile. Precipitation with ammonia gave the amine (3.3 g.), m. p. 140—160°. One crystallisation from benzene or absolute ethyl alcohol gave pale yellow needles, m. p. 194—196° (1.7 g., 7.1%). This material was pure enough for the conversion into the hydroxy-nitrile. Two further crystallisations from benzene raised the m. p. to 197° (Found: C, 78.4; H, 4.8; N, 16.7. Calc. for $C_{11}H_8N_2$: C, 78.6; H, 4.8; N, 16.7%).

7-Hydroxy-2-naphthonitrile.—7-Amino-2-naphthonitrile was diazotised and hydrolysed to give the hydroxy-nitrile in the same manner as 5-hydroxy-1-naphthonitrile. One crystallisation from 35% acetic acid gave orange-yellow plates, m. p. 183—185° (76%). Two further crystallisations from the same solvent yielded pale yellow plates, m. p. 186.5° (Found: C, 78.1; H, 4.1; N, 8.2. $C_{11}H_7ON$ requires C, 78.1; H, 4.1; N, 8.3%).

7-Hydroxy-2-naphthoic Acid.—7-Hydroxy-2-naphthonitrile (2.5 g.) was heated in 2N-potassium hydroxide (50 ml.) until ammonia was no longer evolved (4—5 hr.). The solution

was cooled, diluted with an equal volume of water, and acidified with concentrated hydrochloric acid, giving 7-hydroxy-2-naphthoic acid as a pale pink solid (2.4 g., 90%), m. p. 266—269°. This material was used for the alkylations. Two crystallisations from water gave pale yellow needles, m. p. 269—270° (Found: C, 70.1; H, 4.4. Calc. for $C_{11}H_8O_3$: C, 70.2; H, 4.3%).

The 7-*n*-alkoxy-2-naphthoic acids were prepared in the same way as the 5-alkoxy-1-naphthoic acids.

7-*n*-Octyloxy-2-naphthoic acid, obtained in 90% yield after one crystallisation from glacial acetic acid, formed pale yellow needles, m. p. 139.5—141.5°. Further crystallisations from 90% ethyl alcohol and xylene raised the m. p. to 141.5°, but failed to remove all the colour. Colourless prisms were obtained by sublimation at 170°/2—3 mm., and had m. p. 142.5° (Found: C, 76.0; H, 7.9. $C_{19}H_{24}O_3$ requires C, 76.0; H, 8.0%).

7-*n*-Hexadecyloxy-2-naphthoic acid (90% yield) was similarly obtained colourless only on sublimation at 210—220°/4 mm., forming needles, m. p. 138° (Found: C, 78.6; H, 9.7. $C_{27}H_{40}O_3$ requires C, 78.6; H, 9.7%).

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