Long-chain Phenols. Part 14.† Synthesis of 6-n-Alkylsalicylic Acids and 3-n-Alkylphenols ‡

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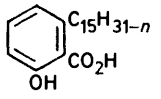
3-Hydroxy-3-alkylphthalides obtained from phthalic anhydride and dialkylcadmium reagents have been reduced to 3-alkylphthalides and thence to 2-alkylbenzoic acids. The basic copper salts upon thermal rearrangement have yielded 6-alkylsalicylic acids and the n-undecyl, n-pentadecyl, and n-heptadecyl compounds have been shown to be identical with the hydrogenated ' anacardic acids ' derived from several different natural products. 3-Alkylphenols were also obtained as by-products from the rearrangement, as well as from the reaction of normal copper salts. 3-Methoxyphthalic anhydride, unlike 3-nitrophthalic anhydride, gave a mixture of the two possible acyl products upon reaction with a dialkylcadmium. Hydroxylation by way of arylthallium bis(trifluoroacetates) was not successful.

CERTAIN of the 6-n-alkylsalicylic acids occur in various *Anacardiacae* species and are formed by the hydrogenation of the unsaturated side chains which co-occur in these various sources. Thus anacardic acid [1-3] (1; $n = 0$, 2, 4, or 6), the principal component phenol of natural cashew nut (*Anacardium occidentale*) shell liquid (CNSL), is the most widely distributed natural phenolic material which gives upon decarboxylation the industrially useful technical CNSL consisting mostly of cardanol.[4] *Anacardium giganteum* [5] contains the n-undecyl member, anagigantic acid (2; R = $C_{11}H_{23}$).



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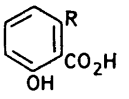

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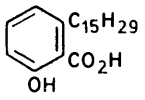

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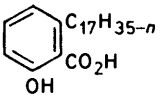


(4)

Ginkgolic acid [6,7] the (8'Z)-monoene (3) occurs in *Ginkgo biloba*. *Pentaspadon motleyi* and *P. officinalis* contain pelandjauic acid [8-10] (4; $n = 0$, 2, 4, or 6). Unusual derivatives (methyl esters and methyl ethers) have been isolated (2; R = $CH_2C{\equiv}C{-}C{\equiv}C{-}Me$) together with four other substances with related acetylenic side-chains from *Chrystanthemum frutescens*.[11] Anacardic acids are probably the biogenetic precursors [12,13] of the unsaturated catechols (urushiol) of *Rhus toxicodendron* [14] and *R. vernicifera*.[15]

Although the structures for these various 6-substituted compounds rest securely upon the 3-methoxyphthalic acid [16,11] obtained upon oxidative degradation, the failure [16] to synthesise (1; $n = 0$) from 3-n-pentadecylphenol by carboxylation, which occurred instead at the 4-position, led one reviewer [17] to speculate curiously and erroneously that there was uncertainty about their structures. Nevertheless, except for the first member, namely 6-methylsalicyclic acid [18] (*Penicillium griseofulvium*) and ginkgolic acid, none has been synthesised. The present work was completed some years ago and described in a preliminary communication.[19]

† Part 13, J. H. P. Tyman, *J. Chromatog.*, 1978, **166**, 159.
‡ Presented in part at the 7th IUPAC Symposium on ' The Chemistry of Natural Products,' Delhi, 1972.

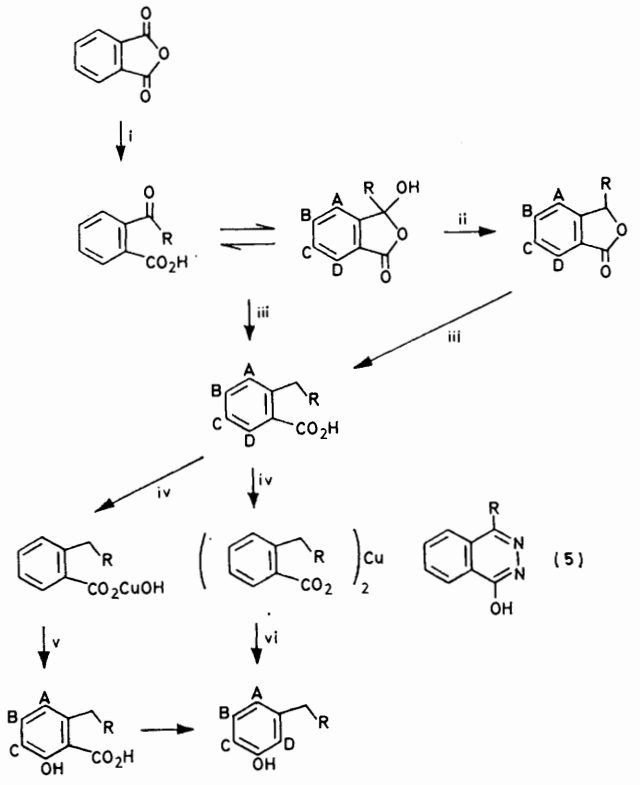
RESULTS AND DISCUSSION

The classical methods used for the synthesis of 6-methylsalicyclic acid based on 2-acetotoluidide,[20] 2,4-dinitrotoluene,[21] or *m*-cresol [22] proceeded by many stages or in low yield, and were not approaches adaptable to the higher members. Direct hydroxylation of appropriately substituted compounds seemed to be a promising possibility and although this type of method has found industrial application [23,24] (Dow process) for the synthesis of phenyl benzoate (and thence phenol) from the intramolecular acylation of copper benzoate, the reaction has been little examined for the preparation of salicylic acids.[25] The overall procedure adopted is shown in Scheme 1. The scheme was applied to the synthesis of the saturated 6-alkylsalicylic acids (2; R = Et, Bu^n, n-$C_{11}H_{23}$, n-$C_{13}H_{27}$, n-$C_{15}H_{31}$, and n-$C_{17}H_{35}$) which were identical with the relevant natural products. The 3-n-alkylphenols, essentially already synthetically [8] accessible by other means, can be obtained also.

Synthetic Route based on Phthalic Anhydride.—Phthalic anhydride was treated with the dialkylcadmium reagent, a reaction briefly examined earlier,[26] to yield the 3-alkyl-3-hydroxyphthalide (ring form), a substance tautomeric with the 2-acylbenzoic acid (the chain form) only to any appreciable extent in alkaline solution. Recent spectroscopic work has clearly shown [27] these substances to be phthalides and not 2-acylbenzoic acids. Reduction with sodium borohydride (chain form present) or by the Clemmensen method gave the 3-alkylphthalide. Wolff–Kishner reduction was ineffective since the hydrazone underwent cyclisation in the case of the undecyl member to give the phthalazine (5; R = $C_{10}H_{21}$) a reaction also found [forming (5; R = Me)] with 2-acetobenzoic acid.[38] Hydrogenolysis,[28] although favourably reported for the preparation of 2-ethylbenzoic acid from sodium 2-acetobenzoate, failed in our hands to give useful yields of 3-alkylphthalides at acceptable reaction temperatures and pressures, either

under acidic or alkaline conditions. The present scheme provides a useful incidental route to the 3-alkylphthalides which presumably could also be obtained by reduction of the 3-alkylidenephthalides, routes to which have been described [29,30] since they occur as natural products and have been used as intermediates for other syntheses.[30]

The 3-alkylphthalides proved remarkably resistant to reduction to 2-alkylbenzoic acids by all the reagents examined except prolonged treatment with hydriodic acid containing red phosphorus, nowadays an almost completely neglected reagent, although once perhaps



SCHEME 1 Reagents: i, RMgx, $CdCl_2$; ii, $NaBH_4$; iii, HI, red P or Pd–C/H^+, H_2; iv, OH^-, $CuSO_4$; v, $PhNO_2$, heat; vi, $PhNO_2$, heat, OH^-

one of the most important. Subsequently we found that reductions of 2-benzoylbenzoic [31] and 2-acetobenzoic [32] acid (3-methyl-3-hydroxyphthalide) had been similarly effected. Prolonged acidic hydrogenolysis with a highly active catalyst was the only other method which gave even small yields of the required products.

The next step in the synthesis of the 6-alkylsalicylic acid required the preparation of the basic copper salt.[25] Owing to the difficulty in reproducing the original conditions the preparations of basic and normal salts were studied in some detail. Although for certain compounds such as *o*-toluic acid the conditions could be made specific, difficulties were encountered with the long chain 2-n-alkylbenzoic acids. The method of separating basic salts by extracting the normal salt and the free acid impurities with acetone was ineffective because all were soluble in most organic solvents. The two different salts were prepared by controlling the proportions of reagents used. Thus predominantly the basic salts resulted from the 2-alkylbenzoic acid and a 2 molar proportion of sodium hydroxide with more than 1 molar proportion of copper sulphate, and substantially the normal salt when the 2-alkylbenzoic acid (1.5—2 mol) was treated with aqueous sodium hydroxide (1 mol) and then with copper sulphate in excess, the unneutralised acid being first removed by ethereal extraction. It seems probable that basic and normal salts contaminate each other to a minor extent. Kaeding rationalised the conflicting earlier results by suggesting that the basic salt gave the salicylic acid and the normal salt the phenyl ester (and thence the phenol by hydrolysis).[23]

In our work the relatively mild conditions of boiling nitrobenzene (216°) were used for the reactions of the salts. This temperature is somewhat below that of the m.p. of, *e.g.*, either basic copper *o*-toluate (242°, decomp.) or the normal salt (250°, decomp.). Nevertheless, in the reaction of basic copper *o*-toluate in boiling nitrobenzene a maximum % yield of 6-methylsalicylic acid (see Experimental section) was observed suggesting that the salt is transformed into another substance, from which the original acid can be recovered upon work-up. Although the actual isolated yields were low, they approached 50% when the recovered acid was allowed for. In the decomposition reaction of the basic salts the phenol accompanied the salicylic acid, and with the normal salt the phenol, but not the salicylic acid, was formed together with the phenyl ester. These findings may be explained by the intermolecular and intramolecular reactions (1)—(7)

$$(ArCO_2)_2Cu + H_2O \rightleftharpoons ArCO_2CuOH + ArCO_2H \quad (1)$$

$$(ArCO_2)_2Cu \longrightarrow ArCO_2Ar + Cu^0 + CO_2 \quad (2)$$

$$ArCO_2CuOH \longrightarrow Ar(CO_2H)(OH) + Cu \quad (3)$$

$$Ar(CO_2H)(OH) \xrightarrow[Cu^0]{} ArOH + CO_2 \quad (4)$$

$$ArCO_2CuOH \rightleftharpoons ArCO_2H + CuO \quad (5)$$

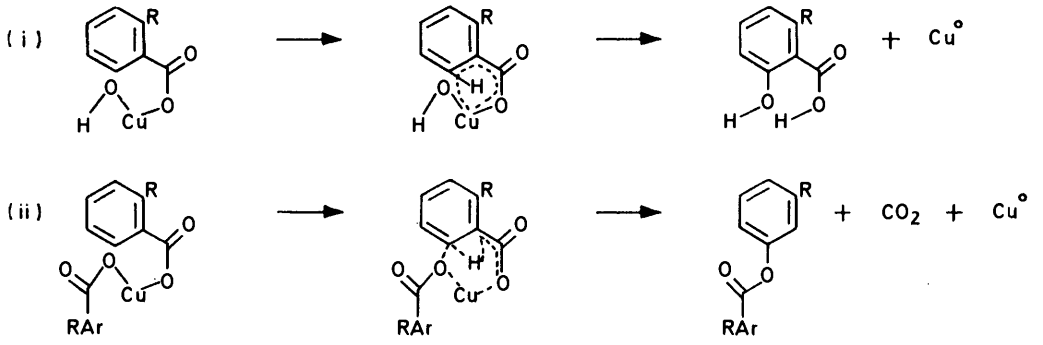
$$ArCO_2CuOH + H_2O \longrightarrow ArCO_2H + Cu(OH)_2 \quad (6)$$

$$ArCO_2H + ArOH \rightleftharpoons ArCO_2Ar + H_2O \quad (7)$$

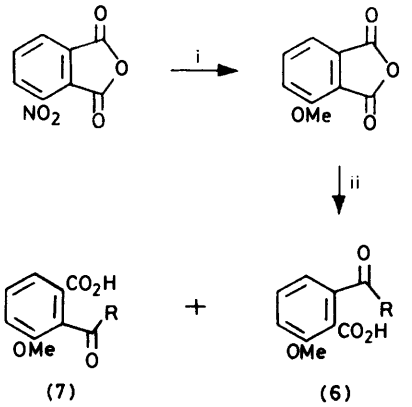
Equilibrium (1) lies to the right since, probably due to its insolubility, the basic salt did not appreciably react with the acid. Initially traces of water are likely to be unavoidably present. Although the refluxing nitrobenzene would result in a gradual azeotropic removal of water the duration would be comparable to that of the actual decomposition experiment. Copper is an effective decarboxylation catalyst and anacardic acids are known to react under these conditions. In other (thermogravimetric) work copper oxide was found in addition to copper.[33] It has been generally always considered that the OH or acyl group enters *ortho* to the carboxy. However in the decomposition of the

normal copper salts of *o*-toluic and *p*-toluic acids other minor products have been observed. Copper *o*-toluate gave, after hydrolysis of the ester, *m*- and *o*-cresol in yields of 90 and 10%, respectively while copper *p*-toluate gave yields of 85 and 15%, respectively. Nevertheless intramolecular decomposition mechanisms (i) and (ii) for the basic and normal salts involving a six-membered transition state seem the most probable major pathway.

Other mechanisms[23,24,34] seem less likely since they



proceed by way of intermediates which have never been detected. A heterolytic mechanism apparently favoured above three others discussed [24] seems improbable since it is shown with a five-valent carbon in the crucial stage. Despite mechanistic uncertainties the decomposition of basic copper salts to salicylic acids has preparative simplicity.*



SCHEME 2 Reagents: i, Sn, $SnCl_2$–H^+; HNO_2–H^+; CH_2N_2; ii, RMgx, $CdCl_2$

Synthetic Route based on 3-Methoxyphthalic Anhydride.—In view of the low yield from the rearrangement of the basic salt of the 2-alkylbenzoic acid, although being quite reasonable based on the high recovery of unconverted material, it was of interest to investigate the interaction of 3-methoxyphthalic anydride with the dialkylcadmium reagents. The reaction sequence is shown in Scheme 2.

Diethyl-, di-(n-propyl)-, and di-(n-butyl)-cadmium interacted with 3-methoxyphthalic anhydride to give mixtures of the 2-methoxy-6-acyl compound (6) and the 2-acyl-3-methoxy compound (7). After recrystallisation, the ^1H n.m.r. spectra appeared to indicate some concentration of one isomer but with some loss of yield in the process. The identity of the material was not established. Our experience appears to concur with that of previous experience[35] in the reaction of di(isopropyl)-cadmium and di(isobutenyl)cadmium with 3-methoxyphthalic anhydride.

The surprising fact that 3-nitrophthalic anhydride with dimethylcadmium forms apparently solely 2-acetyl-3-nitrobenzoic acid [36] was confirmed in the present work but the transformation of the nitro- into the methoxy-group to establish the identity of the earlier product could not be effected, and opportunity for reaction of 3-nitrophthalic anhydride with higher dialkyl cadmium reagents did not occur.

Thallation Reactions with Thallium(III) *Trifluoroacetate.*—Unlike the believed intramolecular hydroxylation achieved with basic copper salts, the intermolecular substitution of aromatic species achieved by way of thallation [37] and subsequent reactions seemed capable of being readily applied in the case of hydroxylation. Although standard hydroxylation of activated nuclei could be achieved, the claimed preparation of salicylic acid [37,†] from benzoic acid, details of which have never appeared, could not be confirmed. The interaction of the carboxy-group in the more sterically hindered 2-n-alkylbenzoic acids could not be achieved.

EXPERIMENTAL

Infrared spectra were recorded on a Pye–Unicam SP 200 instrument (liquids as films and solids as KBr discs). ^1H N.m.r. spectra (with Me_4Si as standard) were determined on Varian T60 and HA100 (PCMU, Harwell) spectrometers. Mass spectra were carried out on an RMS4 Perkin-Elmer–Hitachi and an MS902 (ULIRS, School of Pharmacy, University of London) instrument and by the PCMU. Microanalyses were performed by Dr. F. B. Strauss, Oxford.

Thin-layer chromatography was carried out on Kieselgel G (60) (Merck) on analytical plates (8 × 10 cm × 0.25 mm) and preparative plates (20 × 20 cm × 1 mm) in solvents A (chloroform–ethyl acetate, 94 : 6), B (chloroform–ethyl acetate, 95 : 5), C (chloroform–ethyl acetate, 96 : 4), D

* The claim [24] that non-oxidisable substituents gave improved yields could not be confirmed in our work and 2-chlorobenzoic acid was no improvement upon 2-alkylbenzoic acid.

† It is perhaps significant that salicylic acid and triphenylphosphine oxide have the same m.p.

(chloroform–ethyl acetate–formic acid, 95 : 5 : 2), E [chloroform–light petroleum (b.p. 40—60°), 1 : 1], F (chloroform–ethyl acetate, 17 : 3), or G (chloroform–ethyl acetate–formic acid, 96 : 4 : 3).

Column chromatography was carried out on Spence Grade H alumina.

Materials.—Magnesium turnings were washed with ether and dried (100 °C) for 2 h. Cadmium chloride was finely powdered and dried (200 °C) for 4 h. Alkyl bromides were prepared and examined for absence of OH absorption in the i.r. spectrum, and if necessary they were passed in light petroleum through alumina. Phthalic anhydride was melted, cooled, and powdered before used. Hydriodic acid was decolourised by boiling with red phosphorus or prepared by passing H_2S through an iodine–water mixture. Light petroleum refers to the fraction of b.p. 40—60° (unless otherwise stated).

Reactions.—All Grignard reactions of long-chain bromides were conducted under nitrogen on account of the oxidation observed previously,[2] the apparatus being evacuated and then filled with N_2 as described. Dialkylcadmium reagents were prepared by adding $CdCl_2$ to ice-cold Grignard reagents, refluxing the mixture for 1—2 h, and then cooling prior to addition of solid phthalic anhydride. Diethyl ether was a more useful solvent than benzene.

Purifications.—Several useful procedures were introduced and are worth noting for general use. All ' 2-acylbenzoic ' acids were finally extracted with chloroform in which phthalic acid was insoluble and could be removed along with the drying agent. ' Phthalide ' impurities in 2-n-alkylbenzoic acids were separated by extraction of the latter with cold dilute ammonia (sodium carbonate was ineffective). 6-n-Alkylsalicylic acids were conveniently separated from 2-n-alkylbenzoic acids by preferential esterification of the latter with ethanol–sulphuric acid followed by washing with alkali to remove the former. Diazomethane could also be used but this methylated both types of carboxy-group (but not the phenolic OH).

Normal and Basic Copper Salts.—Since it was not found possible to reproduce certain described experimental procedures, some typical experiments were carried out on the preparations of basic copper *o*-toluate and normal copper *o*-toluate and their transformations upon heating into 6-methylsalicylic acid and *m*-cresol.

(*i*) *o*-Toluic acid (68 g, 0.5 mol) in aqueous sodium hydroxide [from water (550 cm^3) and sodium hydroxide (40 g)] was stirred with copper sulphate (250 g, 1.096 mol) in water (750 cm^3) and the resultant precipitate washed with water (5 × 100 cm^3) and acetone (5 × 25 cm^3) and dried (air) to obtain the greenish blue basic salt, 102 g (94.4%), m.p. 241—242° (decomp.) [lit.,[25] 248° (decomp.)] (Found: C, 44.25; H, 3.9. Calc. for $C_8H_8CuO_3$: C, 44.45; H, 3.7%.), $\nu_{max.}$ (KBr) 3 600 and 890 cm^{-1} (s, OH and CuOH stretch).

(*ii*) *o*-Toluic acid (68 g) in water (300 cm^3) containing sodium hydroxide (20 g, 0.5 mol) was stirred with copper sulphate (200 g, 0.87 mol) in water (500 cm^3) and the emerald precipitate collected, washed with water (5 × 100 cm^3), and dried (air) to give the normal copper salt, 93 g (96%), m.p. 250—255° (decomp.) [lit.,[25] 254—255° (decomp.)] (Found: C, 57.6; H, 4.4. Calc. for $C_{16}H_{14}CuO_4$: C, 57.5; H, 4.2), $\nu_{max.}$ (KBr) 814, 793, 740, and 675 cm^{-1} (w, –Cu– and –Cu–O– vibrations).

The normal copper salt was dissolved in dry acetone and refluxed during the gradual addition of water until no more precipitate appeared. The cooled mixture gave upon filtration the basic salt identical with that obtained in (*i*).

Preparation of 6-Alkylsalicylic Acids via Basic Copper Salts.—*6-Methylsalicylic acid.* Basic copper *o*-toluate (2.155 g, 0.001 mol) was refluxed in nitrobenzene (24 cm^3) for 16 min. The cooled mixture was acidified, extracted with ether, washed with sodium hydroxide solution, acidified, and further extracted with ether. Two preparative t.l.c. purifications (solvent B) of the recovered organic material gave 6-methylsalicylic acid (24 mg, 1.6%), m.p. 170—173° (lit.,[38] 173°), giving a positive (purple) ferric chloride test.

Dry heating of the basic salt at 230—240 °C (5 min) gave an acidic fraction consisting of *m*-cresol. From the neutral part, after separation of nitrobenzene by steam-distillation and hydrolysis of the residual *m*-cresyl *o*-toluate, further *m*-cresol was obtained (total yield 50 mg). From the normal salt (3.34 g, 0.01 mol), by refluxing (40 min) in nitrobenzene (20 cm^3) and processing the acidic and neutral portions as previously, a total yield of 75 mg of *m*-cresol was obtained.

Since dry heating was unsatisfactory, refluxing in nitrobenzene by means of an external oil-bath was adopted for transformations of the basic salt. Starting from the basic salt (2.155 g) and at 210 °C, the Table summarises the

Yields of 6-methylsalicylic acid and *m*-cresol

Time/min	6-methylsalicylic acid (mg)	*m*-cresol (mg)
2		
4		
6	13	
8	13	
10	15	
12	19	Trace
14	20	Trace
16	24	10
18	21	20
20	17	25

relation between time of heating and yield of 6-methylsalicylic acid/*m*-cresol. These experiments were then used as a guide for higher homologues.

3-n-Decyl-3-hydroxyphthalide (*2-n-Undecanoylbenzoic Acid*).—To the Grignard reagent prepared (3 h) from magnesium (1.2 g, 0.05 mol), and n-decyl bromide (11.0 g, 0.05 mol) in ether (75 cm^3) cadmium chloride (4.5 g, 0.024 5 mol) was added after the mixture had been cooled to 0 °C. The mixture was refluxed (1 h) and cooled, phthalic anhydride (7.4 g, 0.05 mol) was added, more ether (50 cm^3) introduced, and stirring and refluxing continued for 2 h. After cooling and decomposition with dilute hydrochloric acid (150 cm^3; 3M) the ethereally extracted mixture was treated with dilute sodium hydroxide (2 × 50 cm^3; 2.5M). The ethereally washed basic extract was acidified, extracted with chloroform (3 × 50 cm^3), dried, filtered (to remove drying agent and phthalic acid), and the recovered organic material crystallised from light petroleum to give *3-n-decyl-3-hydroxyphthalide* (8.0 g, 57%), m.p. 61—62°, as fluffy white shining leaflets (Found: C, 74.3; H, 9.0. $C_{18}H_{26}O_3$ requires C, 74.5; H, 8.95%), R_F 0.31 (solvent B), τ($CDCl_3$) 2.05—2.68 (4 H, m, ArH), 5.2 (1 H, s, OH, D_2O exchangeable), 7.77 (2 H, t, CH_2CO), 8.64 [16 H, m, $(CH_2)_8$], and 9.05 (3 H, t, CH_3), $\nu_{max.}$ (KBr) 3 430 (s, OH), 2 870, 2 800 (s, CH_2), 1 710 (s, C=O), and 750 cm^{-1} (m, Ar C–H). (A small by-product noted in one experiment appeared from chromatographic and spectroscopic evidence to be 3,3-

didecylphthalide, possibly formed by reaction of free n-decylmagnesium bromide with the keto-acid.)

3-*n-Decylphthalide*.—(*i*) To 2-n-undecanoylbenzoic acid (2.0 g, 0.007 mol) in industrial methylated spirit (25 cm^3), sodium borohydride was added with stirring until effervescence ceased. Acidification, ethereal recovery, drying, and recrystallisation from light petroleum (CO_2, acetone) yielded 3-*n-decylphthalide* (1.4 g, 66%), m.p. 36—37°.

(*ii*) Clemmensen reduction (72 h at ambient temperature) of 2-n-undecanoylbenzoic acid (0.59 g) with concentrated hydrochloric acid (2 cm^3) and water (3 cm^3) containing zinc wool (2.0 g) amalgamated with mercuric chloride (0.15 g) in water (2.5 cm^3) and concentrated sulphuric acid (0.1 cm^3) gave, after work-up and crystallisation, 3-n-decylphthalide (0.3 g, 56%), m.p. 35—37°.

(*iii*) Hydrogenolysis (18 h) at 50 °C of the free acid (0.5 g) in ethanol (15 cm^3) containing concentrated sulphuric acid (1 drop) and 10% Pd–C (0.25 g) with hydrogen (50 lbf in^{-2}) followed by work-up and recrystallisation of the recovered product from light petroleum (CO_2, acetone) gave 3-n-decylphthalide (0.2 g, 40%), m.p. 36—37°.

(*iv*) Hydrogenolysis (18 h) at 80 °C with hydrogen and Pd–C (0.25 g) of the sodium salt from the acid (0.5 g) in aqueous ethanol (15 ml), and the product isolated as before, gave prisms (0.12 g, 23%), m.p. 35—37° (Found: C, 78.75; H, 9.45. $C_{18}H_{26}O_2$ requires C, 78.85, H, 9.5%), R_F (solvent C) 0.5, τ($CDCl_3$), 2.0—2.3 (H_D, d of d, J_o 7, J_m 1.5, J_p 0 Hz, ArH), 2.3—2.5 (H_A, H_B, m, ArH), 2.5—2.7 (H_C, m, ArH), 4.4—4.7 (1 H, t, CH), 8.0—8.15 (2 H, q, CH_3), 8.15—8.95 (16 H, m, C_8H_{16}), and 9.0—9.3 (3 H, t, Me), $\nu_{max.}$ (KBr) 1 745 (s, 5-membered phthalide ring) and 760 cm^{-1} (m, Ar C–H).

2-*n-Undecylbenzoic Acid*.—(*i*) 2-n-Undecanoylbenzoic acid (1.2 g), colourless hydriodic acid (20 ml), and red phosphorus (1.0 g) were refluxed (40 h) in the dark. The cooled and diluted (H_2O) mixture was extracted with ether. After washing (aqueous sodium thiosulphate), the organic material was purified by extraction with ammonia and the recovered acidic material recrystallised from light petroleum (CO_2, acetone) to give white prisms of 2-*n-undecylbenzoic acid* (0.5 g, 43%), m.p. 40—41°.

(*ii*) 2-n-Undecanoylbenzoic acid (5.0 g) in ethanol (75 cm^3) containing concentrated sulphuric acid (5 drops) and 10% Pd–C (1.0 g) was hydrogenolysed (16 h) with hydrogen (45 lbf in^{-2}) at ambient temperature. The product was worked up in the usual way, extracted with dilute ammonia, and the recovered acidic material recrystallised from light petroleum (CO_2 acetone) to give 2-undecylbenzoic acid (0.5 g, 10%), m.p. 40—41°.

(*iii*) 3-n-Decylphthalide (2.74 g) was refluxed (30 h) in the dark with colourless hydriodic acid containing red phosphorus (1.0 g) and worked up as already described to give 2-n-undecylbenzoic acid (yield 1.53 g, 56%), m.p. 40—41° (Found: C, 78.55; H, 10.0. $C_{18}H_{28}O_2$ requires C, 78.25; H, 10.15%), R_F 0.4 (solvent A), τ($CDCl_3$) —1.43 (1 H, s, CO_2H, D_2O exch.), 2.00, 2.60, and 2.75 (H_D, H_A, H_C, H_B, m, J_o 9, J_m 2 Hz, ArH), 6.98 (2 H, t, CH_2), 8.75 (8 H, m, C_9H_{18}), and 9.73 (3 H, t, Me), $\nu_{max.}$ (KBr) 1 680 (s, C=O of acid) and 750 cm^{-1} (m, Ar C–H).

6-*n-Undecylsalicylic acid*.—2-n-Undecylbenzoic acid (2.76, 0.01 mol) in water (25 cm^3) containing sodium hydroxide (1.0 g) was stirred with a solution from copper sulphate (3.75 g, 0.015 mol) and water (30 cm^3). The precipitate was collected, washed with water (10 × 25 cm^3) and acetone (5 × 25 cm^3), and air-dried to give the greenish blue basic copper salt of 2-n-undecylbenzoic acid (3.4 g, 96%), R_F 0.015 (solvent B). The basic salt (3.55 g, 0.01 mol) in nitrobenzene (25 cm^3) was refluxed (¼ h), the mixture cooled, decomposed with 3M-hydrochloric acid (40 cm), and the combined ethereal extracts washed with dilute aqueous sodium hydroxide (2 × 25 cm^3). The combined and ethereally washed extracts were acidified, and the organic material recovered * to give a crude product which after two preparative t.l.c. purifications gave a band of low R_F, further purified by recrystallisation from n-hexane to give needles of 6-n-undecylsalicylic acid (20 mg), m.p. 81—82° (lit.,[5] 81—82°). We were unable to obtain a sample of the natural material (Found: C, 73.35; H, 9.25. $C_{18}H_{28}O_3$ requires C, 73.95; H, 9.6%), R_F 0.12 (solvent B), τ($CDCl_3$) —1.5 to —1.0 (2 H, hb br s,† OH · · · CO_2H exch. D_2O), 2.6—2.8 (H_B, d of d, J_o 8 Hz, ArH), 3.15—3.4 (H_A, H_C, 2 sets, d of d, J_o 8, J_m 1.8 Hz, ArH), 6.9—7.2 (2 H, t, CH_2Ar), 8.3—9.0 (18 H, m, C_8H_{18}), and 9.0—9.2 (3 H, t, Me), $\nu_{max.}$ (KBr) 3 550 (s, hb-OH), 1 710 (s, C=O of acid), and 745 cm^{-1} (s, Ar C–H).

1-*Hydroxy-4-n-decylphthalazine*.—To a warm solution of 2-n-undecylbenzoic acid (0.5 g) in ' digol ' (2 cm^3) containing potassium hydroxide (2.0 g), hydrazine hydrate (0.2 cm^3; 98—99%) was added and the mixture heated on a steam-bath (4 h). The cooled mixture was diluted with water (50 cm^3), acidified, and the recovered material recrystallised from light petroleum (b.p. 60—80°) to give shining needles of 1-*hydroxy-4-n-decylphthalazine* (0.41 g, 83%), m.p. 86—87° (Found: C, 75.6, H, 9.0; N, 10.2. $C_{18}H_{26}ON_2$ requires C, 75.5; H, 9.09; N, 9.79%), R_F 0.53 (solvent C), τ($CDCl_3$) —1.2 to 0.85 (1 H, s, OH, NH, exch. D_2O), 1.4—1.7 (1 H, t, ArH), 2.1—2.4 (3 H, m, ArH), 6.84—7.27 (2 H, t, CH_2Ar), 8.08—8.96 (16 H, m, C_8H_{16}), and 8.96—9.40 (3 H, t, Me), $\nu_{max.}$ (KBr) 3 495, 3 200 (m, CONH), and 1 650 cm^{-1} (s, C=N conj.). This substance appears to be present as a hydroxy-compound containing some of the amide tautomer.

3-*n-Undecylphenol*.—(i) *By the copper salt method*. To a cold solution of 2-n-undecylbenzoic (2.76 g, 0.01 mol) in water (30 cm^3) containing potassium hydroxide (0.56 g, 0.01 mol), copper sulphate (2.5 g, 0.01 mol) in water (30 cm^3) was added and the precipitated normal copper salt of 2-n-undecylbenzoic acid was collected, washed with water (10 × 20 cm^3), and dried to obtain 3.1 g (84.5%) of the emerald salt. The salt (3.067 g) was refluxed (40 min) in nitrobenzene (25 cm^3) and the cooled acidified reaction mixture (10% HCl; 50 cm^3) extracted with ether (2 × 24 cm^3). The ethereal solution was washed with 10% w/v aqueous sodium hydroxide (2 × 24 cm^3) and the ethereally recovered acidic material chromatographed on alumina (350 g) with chloroform (550 cm^3) as solvent to give 18 fractions, from which fractions 10—15 afforded 3-n-undecylphenol as an oil (31 mg), R_F 0.5 (solvent C) (single spot), τ(CCl_4) 3.07 (H_B, m, 8 lines, J_o 8, J_p 1.5 Hz, ArH), 3.5 (H_A, H_C, H_D, m, numerous lines, J_o 8, J_m 3, J_p 1.5 Hz, ArH), 7.47, (2 H, t, CH_2Ar), 8.8 [18 H, m, $(CH_2)_9$], and 9.17 (3 H, t, Me). Unaccountably, elemental analysis of this

* An alternative purification of the recovered organic material consisted of esterification by refluxing (2 h) in ethanol (25 cm^3) containing concentrated sulphuric acid (2 drops), concentration, dilution with water (75 cm^3), and extraction with ether (2 × 20 cm^3) and dilute sodium hydroxide (2 × 10 cm^3). The ethereally washed alkaline solution was regenerated to recover the acidic material which was recrystallised from n-hexane to give 6-n-undecylsalicylic acid (19 mg), m.p. 80—81°.

† hb = Hydrogen-bonded.

substance was unsatisfactory. 3-n-Undecylphenyl 2-n-undecylbenzoate was present in the organic neutral material.

(ii) *By the Grignard reaction.* To the cooled Grignard reagent prepared from magnesium (0.6 g, 0.25 mol), n-decyl bromide (5.1 g, 0.22 mol), and ether (60 cm^3) by refluxing (2 h), was added over 5 min 3-methoxybenzaldehyde (3.0 g, 0.022 mol) in ether (5 cm^3). The organic material from the mixture, worked up in the usual way and also washed with 10% w/v sodium bisulphite–water (25 cm^3), was chromatographed on alumina (300 g) with chloroform–ethyl acetate (98 : 2, 1 l) as eluant. Of the fifty fractions collected, fractions 5—21 were combined to give 1-(3-*methoxyphenyl*)*undecan*-1-*ol* as an oil (3.2 g, 53%), R_F 0.83 (solvent C) (Found: C, 78.2; H, 10.85. $C_{18}H_{30}O_2$ requires C, 77.7; H, 10.8%). After the alcohol (2.78 g) had been refluxed (40 h, dark) with colourless hydriodic acid (40 cm^3) and red phosphorus (1.0 g), the mixture was diluted with water, extracted with ether, washed (aqueous $Na_2S_2O_3$), and dried and the recovered organic material was chromatographed on alumina (300 g) with chloroform (1 l) as eluant. Fractions 10—15 of the twenty collected gave 3-undecylphenol as an oil (1.73 g, 66.5%).

The 1-(3-methoxyphenyl)undecan-1-ol (1.0 g), hydrogenolysed (30 h) with hydrogen (30 lbf in^{-2}) in ethanol (10 cm^3) containing concentrated sulphuric acid (1 drop) and 10% Pd–C (0.1 g) gave, after work-up in the usual way, almost pure 3-*undecylanisole* (0.81 g, 86%) as a oil (Found: C, 82.9; H, 11.65. $C_{18}H_{30}O$ requires C, 82.45; H, 11.45%), R_F 0.85 (solvent C).

(iii) *By dialkylcadmium reaction.* The ethereal Grignard reagent solution from n-decyl bromide (11.0 g, 0.05 mol), magnesium (2.4 g), and ether (75 cm^3) was treated with cadmium chloride (9.0 g, 0.05 mol) and the cooled mixture refluxed (2 h) with 3-methoxybenzoyl chloride (8.0 g, 0.047 mol) in ether (20 cm^3). The organic material, recovered in the usual way, was chromatographed on alumina (500 g) with chloroform (1 l) as solvent to yield twenty-five fractions from which fractions 13—20 gave upon recovery 3-*n-undecanoylanisole* as an oil (5.27 g, 41%), R_F 0.85 (solvent C) (Found: C, 77.95; H, 10.05. $C_{18}H_{28}O_2$ requires C, 78.25; H, 10.15%).

3-n-Undecanoylanisole (2.0 g) in ethanol (50 cm^3) containing concentrated sulphuric acid (5 drops) and Pd–C (0.5 g) was hydrogenolysed (30 h) with hydrogen (45 lbf in^{-2}). The organic material, recovered in the usual way, gave after purification on alumina 3-n-undecylanisole as an oil (1.52 g, 80%) (Found: C, 82.3; H, 11.45%).

3-n-Undecanoylanisole (1.0 g) was refluxed (40 h, dark) with colourless hydriodic acid (30 cm^3) and red phosphorus (1.0 g), and the recovered organic material, after the usual work-up ($Na_2S_2O_3$ wash), purified by preparative t.l.c. (solvent C) to give 3-n-undecylphenol as an oil (0.5 g, 46%).

The various products gave the following ^1H n.m.r. and i.r. spectra. 3-n-Undecylanisole had τ($CDCl_3$), 2.8 (1 H, m, ArH), 3.1—3.43 (3 H, m, ArH), 6.18 (3 H, s, MeO), 7.37 (2 H, t, CH_2Ar), 8.67 (16 H, m, C_8H_{16}), and 9.1 (3 H, t, Me), $\nu_{max.}$ (film) 2 900, 2 830 (s, CH_2), and 770 cm^{-1} (m, Ar C–H). 3-n-Undecanoylanisole had τ($CDCl_3$) 2.50 (2 H, m, ArH), 2.69 (2 H, m, ArH), 6.07 (3 H, s, MeO), 6.9—7.22 (2 H, t, CH_2DO), 8.2—8.95 (16 H, m, C_8H_{16}), and 9.06 (3 H, t, Me), $\nu_{max.}$ (film) 1 695 cm^{-1} (s, ArCO). 1-(3-Methoxyphenyl)undecan-1-ol had τ($CDCl_3$) 2.6—2.9 (1 H, m, ArH), 3.0—3.35 (3 H, m, ArH), 5.2—5.5 (1 H, t, HC), 6.17 (3 H, s, MeO), 7.72 (1 H, s, OH, D_2O exch.), 8.2—8.4 (2 H, q, CH_2), 8.4—8.9 (16 H, m, C_8H_{16}), and 8.9—9.05 (3 H, t, Me), $\nu_{max.}$ (film) 3 400 (s, OH) and 795 (m, Ar C–H).

3-*n-Dodecyl*-3-*hydroxyphthalide* (2-*n-Tridecanoylbenzoic Acid*).—A solution of di-(n-dodecyl)cadmium from n-dodecyl bromide (24.9 g, 0.1 mol), magnesium (2.4 g, 0.1 mol), and ether (105 cm^3), treated with cadmium chloride (9.2 g, 0.05 mol) in the usual way, was refluxed (1h) with phthalic anhydride (14.8 g, 0.1 mol). The cooled mixture was acidified, extracted with ether, washed with dilute sodium hydroxide solution, and acidified, and the recovered organic material was crystallised from light petroleum to give 3-*n-dodecyl*-3-*hydroxyphthalide* (4.31 g, 45%), m.p. 73—74° (Found: C, 75.85; H, 9.5. $C_{20}H_{30}O_3$ requires C, 75.45; H, 9.45%), R_F 0.32 (solvent B), τ($CDCl_3$) 2.12—2.4 (H_D, d of d, J_o 7.5, J_m 2, J_p 0 Hz, ArH), 2.4—2.72 (3 H, m, ArH), 3.42—3.6 (1 H, s, OH, D_2O exch.), 7.8 (2 H, t, CH_2-CO), 8.71 (20 H, m, $C_{10}H_{20}$), and 9.14 (3 H, t, Me), $\nu_{max.}$ 3 400 (s, OH), 1 710 (s, C=O), and 675 cm^{-1} (m, Ar C–H).

3-*n-Dodecylphthalide*.—To 2-n-tridecanoylbenzoic acid (0.1 g) in ethanol (10 cm^3), sodium borohydride was added until effervescence ceased. The acidified mixture was worked up in the usual way and the organic material recrystallised from light petroleum to give 3-*n-dodecylphthalide* (70 mg, 74%), m.p, 51—52°, R_F 0.5 (solvent C) (Found: C, 79.3; H, 10.35. $C_{20}H_{30}O_2$ requires C, 79.45, H, 9.95%).

2-*n-Tridecylbenzoic Acid*.—(*i*) 2-n-Tridecanoylbenzoic acid (5.0 g), colourless hydriodic acid (50 cm^3), and red phosphorus (1.0 g) were refluxed (48 h, dark) and the diluted mixture worked up as described followed by recrystallisation of the acidic organic material from light petroleum (CO_2, acetone) to give 2-*n-tridecylbenzoic acid* (2.51 g, 52.5%), m.p. 63—65°.

(*ii*) 3-n-Dodecylphthalide (3.02 g, 0.01 mol) was reduced with colourless hydriodic acid (50 cm^3) and red phosphorus (1.0 g) by prolonged refluxing and the product worked up and recrystallised as described earlier to give a product, m.p. 64—65°, undepressed on admixture with the product from (*i*), R_F 0.41 (solvent A) (Found: C, 79.4; H, 10.2. $C_{20}H_{32}O_2$ requires C, 78.95; H, 10.5%), τ(CCl_4) −2.51 (1 H, s, CO_2H, D_2O exch.), 1.82 (H_D, m, J_o 9, J_m 2, Hz, ArH), 2.72 (H_A, H_B, H_C, m, ArH), 6.8—7.2 (2 H, t, CH_2Ar), 8.79 (22 H, m, $C_{11}H_{22}$), and 9.15 (3 H, t, Me), $\nu_{max.}$ (KBr), 1 690 (s, C=O) and 750 cm^{-1} (m, Ar C–H).

6-*n-Tridecylsalicylic Acid*.—2-n-Tridecylbenzoic acid (6.08 g, 0.02 mol) in a solution of water (25 cm^3) and potassium hydroxide (2.4 g, 0.042 mol) was extracted after 24 h with ether and the aqueous solution treated with copper sulphate (10.5 g, 0.046 mol) in water (60 cm^3). The precipitated cupric hydroxide and basic copper 2-n-tridecylbenzoate were collected and separated by the higher solubility of the latter in ether to give the oily but purer basic salt (7.0 g, 93%), R_F 0.015 (solvent B). The basic salt (7.0 g) in nitrobenzene (30 cm^3) was refluxed (15 min) and the mixture cooled, acidified, and extracted with ether (2 × 50 cm^3), and the acidic materials separated by the esterification procedure described to give the required product, which was purified (t.l.c., solvent D) and recrystallised from n-pentane to give 6-*n-tridecylsalicylic acid* (90 mg), m.p. 73—74°, R_F 0.14 (solvent B) (Found: C, 74.9; H, 10.0. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.0%), τ(CCl_4) −0.05 (2 H, br s, $CO_2H \cdots OH$, D_2O exch.), 2.75 (H_B, d of d, J_o 8 Hz, ArH), 3.3 (H_A, H_C, 2 sets, d of d, J_o 8, J_m 1.8 Hz, ArH), 7.12 (2 H, t, CH_2Ar), 8.76 (22 H, m, $C_{11}H_{22}$), and 9.14 (3 H, t, Me).

3-*n-Tridecylphenol*.—2-n-Tridecylbenzoic acid (6.08 g, 0.02 mol) was dissolved in water (100 cm³) containing potassium hydroxide (0.56 g), warmed, and after 24 h the mixture was extracted with ether (3 × 25 cm³). The aqueous portion was treated with copper sulphate (3.25 g, 0.01 mol) in water (20 cm³) and the oily normal copper salt of 2-n-tridecylbenzoic acid was washed with ether (2 × 24 cm³) to give 6.2 g (93%). The normal salt (6.0 g, 0.009 mol) was refluxed (40 min) in nitrobenzene (20 cm³) and worked up as previously to give, after preparative t.l.c., 3-*n-tridecylphenol* (0.12 g), m.p. 44—45°. The neutral portion from the separation, upon hydrolysis, gave more 3-n-tridecylphenol (0.2 g), R_F 0.5 (solvent C) (Found: C, 82.85; H, 11.5. $C_{19}H_{32}O$ requires C, 82.6; H, 11.6%), τ(CCl_4) −1.60 (1 H, s, OH, D_2O exch.), 2.00 (H_B, m, ArH), 2.80 (H_A, H_C, H_B, m, ArH), 7.02 (2 H, t, CH_2Ar), 8.33—9.0 (22 H, m, $C_{11}H_{22}$), and 9.16 (3 H, t, Me).

3-*n-Tetradecyl*-3-*hydroxyphthalide* (2-*n-Pentadecanoylbenzoic Acid*).—A solution of di-(n-tetradecyl)cadmium prepared from n-tetradecyl bromide (13.8 g, 0.05 mol), magnesium (1.2 g, 0.05 mol), and ether (70 cm³), followed by cadmium chloride (4.5 g, 0.025 mole), was treated after 4 h with phthalic anhydride (7.4 g, 0.05 mol) by refluxing (1 h). The cooled mixture was acidified, extracted with ether, washed with dilute sodium hydroxide, re-extracted with ether, and the organic material recovered in the usual way from the alkaline solution. Recrystallisation from light petroleum (b.p. 60—80°) gave white shiny leaflets of 3-*n-tetradecyl*-3-*hydroxyphthalide* (8.65 g, 50%), m.p. 80—81°, R_F 0.32 (solvent B) (Found: C, 76.45; H, 9.95. $C_{22}H_{34}O_3$ requires C, 76.3; H, 9.8%), τ($CDCl_3$), 2.24 (H_D, d of d, J_o 7.5, J_m 2, J_p 0 Hz, ArH), 2.45 (3 H, m, ArH), 5.76—5.9 (1 H, s, ~~OH, D_2O ex~~ch.), 7.8 (2 H, t, CH_2CO), 8.72 (24 H, m, $C_{12}H_{24}$), and 9.15 (3 H, t, Me), $\nu_{max.}$ (KBr) 3 450 (s, OH), 1 710 (s, C=O), and 695 cm^{-1} (m, Ar C–H).

3-*n-Tetradecylphthalide*.—To 2-n-pentadecanoylbenzoic acid (12.0 g) in ethanol (65 cm³) sodium borohydride was added until effervescence ceased. The concentrated acidified mixture was worked up in the usual way to give, after recrystallisation of the organic material from pentane, fine waxy needles of 3-*n-tetradecylphthalide* (10.1 g, 88%), m.p. 57—58°, R_F 0.52 (solvent C) (Found: C, 79.3; H, 10.3. $C_{22}H_{34}O_2$ requires C 79.55; H, 10.3%), τ(CCl_4), 2.1 (H_D, d of d, J_o 7.5, J_m 1.5, J_p 0 Hz, ArH), 2.3 (H_A, H_B, H_C, m, ArH), 4.5—4.8 (1 H, t, CH), 8.1 (2 H, q, CH_2-CO), 8.7 (24 H, m, $C_{12}H_{24}$), and 9.05 (3 H, t, Me), $\nu_{max.}$ (KBr), 1 750 (s, C=O phthalide ring) and 758 cm^{-1} (m, Ar C–H).

2-*n-Pentadecylbenzoic Acid*.—3-n-Tetradecylphthalide (6.92 g, 0.02 mol), colourless hydriodic acid (50 cm³), and red phosphorus (1.5 g) were refluxed (48 h, dark) and the product worked up as described previously. Recrystallisation from light petroleum (CO_2, acetone) gave 2-n-pentadecylbenzoic acid (4.1 g, 62%), m.p. 45—46°, R_F 0.42 (solvent A), τ(CCl_4), −2.55 (1 H, br s, CO_2H, D_2O exch.), 1.9 (H_D, m, J_o 9, J_m 2 Hz, ArH), 2.71 (H_A, H_B, H_C m, ArH), 6.92 (2 H, t, CH_2Ar), 8.75 (26 H, m, $C_{13}H_{26}$), and 9.05 (3 H, t, Me), $\nu_{max.}$ (KBr) 3 400 (m, OH), 1 600 (s, C=O), and 778 cm^{-1} (w, Ar C–H).

6-*n-Pentadecylsalicylic Acid*.—2-n-Pentadecylbenzoic acid (3.32 g, 0.01 mol) in aqueous potassium hydroxide [from potassium hydroxide (1.2 g, 0.021 mol)] was heated, left overnight, and then treated with copper sulphate (3.75 g, 0.015 mol) in water (50 cm³) to give a bluish green precipitate of the basic copper salt of 2-n-pentadecylbenzoic acid which was collected, washed with water (10 × 50 cm³), acetone (3 × 50 cm³), and dried in air (yield 3.7 g, 92%), R_F 0.02 (solvent B). The basic salt (4.115 g, 0.01 mol) in nitrobenzene (30 cm³) was refluxed (15 min), cooled, acidified, extracted with ether, and the acidic material esterified and separated. After preparative t.l.c. (solvent A) and recrystallisation from n-hexane, 6-*n-pentadecylsalicylic acid* was obtained, m.p. 84°, identical with natural (15 : 0) anacardic acid isolated from natural cashew nut shell liquid [2] and hydrogenated,[2,39] R_F 0.16 (solvent B) (Found: C, 76.1; H, 10.4. $C_{22}H_{36}O_3$ requires C, 75.85; H, 10.3%), τ(CCl_4) −1.43 (2 H, br s, $CO_2H \cdots OH$, D_2O exch.), 2.7 (H_B, m, d of d, J_o 8 Hz, ArH), 3.31 (H_A, H_B, 2 sets d of d, J_o 8, J_m 1.8 H, ArH), 7.05 (2 H, t, CH_2Ar), 8.74 (26 H, m, $C_{13}H_{26}$), and 9.28 (3 H, t, Me).

3-*n-Pentadecylphenol*.—2-n-Pentadecylbenzoic acid (6.64 g, 0.02 mol), was mixed with water (50 cm³) containing potassium hydroxide (0.56 g, 0.01 mol), heated (30 min), left overnight, and then extracted with ether to remove unchanged 2-n-pentadecylbenzoic acid (3.34 g). The aqueous soap layer was mixed with copper sulphate (3.75 g, 0.015 mol) in water (30 cm³) to give the normal copper salt of 2-n-pentadecylbenzoic acid, which was collected, washed, and dried (3.5 g, 97% yield). The normal copper salt (3.62 g, 0.005 mol) was refluxed (40 min) in nitrobenzene (25 cm³) and the acidic material recovered in the usual way. Preparative t.l.c. (solvent A) afforded prisms of 3-n-pentadecylphenol (20 mg), m.p. 51—52°, undepressed on admixture with (15 : 0) cardanol. The neutral part upon hydrolysis also furnished 3-n-pentadecylphenol (0.1 g) by way of 3-n-pentadecylphenyl 2-n-pentadecylbenzoate.

3-*n-Hexadecyl*-3-*hydroxyphthalide* (2-*n-Heptadecanoylbenzoic Acid*).—Di-(n-hexadecyl)cadmium [prepared from n-hexadecyl bromide (30.5 g, 0.1 mol), magnesium turnings (2.4 g, 0.1 mol), and ether (125 cm³) followed by cadmium chloride (9.2 g, 0.05 mol)], was treated with phthalic anhydride (14.8 g, 0.1 mol) by refluxing (1.5 h). The cooled, acidified mixture was worked up in the usual way to afford 3-*n-hexadecyl*-3-*hydroxyphthalide* as white waxy leaflets (18.7 g, 50%), m.p. 87—88° (from chloroform) (Found: C, 77.0; H, 10.2. $C_{24}H_{38}O_3$ requires C, 77.0; H, 10.15%), R_F 0.33 (solvent B), τ($CDCl_3$), 3.58 (1 H, br s, OH, D_2O exch.), 7.83 (2 H, t, CH_2CO), 8.73 (28 H, m, $C_{14}H_{28}$), and 9.08 (3 H, t, Me), $\nu_{max.}$ (KBr), 3 450 (s, OH), 1 710 (vs, C=O), and 750 cm^{-1} (m, Ar C–H).

2-*n-Hexadecylphthalide*.—2-n-Heptadecanoylbenzoic acid (3.0 g) in ethanol (50 cm³) was treated with sodium borohydride until effervescence ceased. Usual work-up gave 3-*n-hexadecylphthalide*, (1.96 g, 70%), m.p. 58—59° (from light petroleum) (Found: C, 80.4; H, 10.55. $C_{24}H_{38}O_2$ requires C, 80.45; H, 10.6%), τ(CCl_4) 2.05 (H_D, m, ArH), 2.40 (H_A, H_B, H_C, m, ArH), 4.4—4.6 (1 H, t, CH), 7.9 (2 H, q, CH_2CO), 8.7 (28 H, m, $C_{14}H_{28}$), and 9.1 (3 H, t, Me), $\nu_{max.}$ (KBr), 1 745 (s, C=O, phthalide ring) and 760 cm^{-1} (m, Ar C–H).

2-*n-Heptadecylbenzoic Acid*.—2-n-Heptadecanoylbenzoic acid (3.58 g, 0.01 mol), refluxed (48 h, dark) with colourless hydriodic acid (50 cm³) and red phosphorus (1.0 g) and worked up in the usual way, gave 2-*n-heptadecylbenzoic acid* (3.0 g, 83%), m.p. 62—63° (from pentane), R_F 0.42 (solvent A) (Found: C, 80.1; H, 11.2. $C_{24}H_{40}O_2$ requires C, 80.0; H, 11.1%), τ(CCl_4) −2.1 (1 H, s, CO_2H, D_2O exch.), 2.02 (H_D, m, J_o 9, J_m 2 Hz, ArH), 2.75 (H_A, H_B, H_C, m, ArH), 6.82—7.1 (2 H, t, CH_2Ar), 8.81 (30 H, m, $C_{15}H_{30}$), and 9.15 (3 H, t, Me).

6-*n-Heptadecylsalicylic Acid*.—2-n-Heptadecylbenzoic acid (7.2 g, 0.02 mol) in water (75 cm³) containing potassium hydroxide (2.4 g, 0.043 mol) was heated and after 24 h mixed with copper sulphate (5.5 g, 0.022 mol) in water (50 cm³) to give, after work-up, washing, and drying, the basic copper salt of 2-n-heptadecylbenzoic acid (7.6 g, 93%). The basic salt (7.5 g) in nitrobenzene was refluxed (15 min), worked up in the usual way, and separated by the esterification procedure followed by preparative t.l.c. to give 6-*n-heptadecylsalicylic acid* (92 mg), m.p. 88—89° (from pentane), R_F 0.18 (solvent B) (Found: C, 76.4; H, 10.55. $C_{24}H_{40}O_3$ requires C, 76.6; H, 10.65%).

Hydrogenation of Pelandjauic Acid [8].—A few mg of a surviving sample from the collection of Dr. H. J. Backer (1940) was purified and hydrogenated as follows. Pelandjauic acid, a sticky intractable material (5 mg), was triturated with ether (10 cm³), filtered, the ether evaporated off, and the residue in ethanol (15 cm³) containing 10% Pd–C (5 mg) hydrogenated at atmospheric pressure until no further uptake occurred. The mixture was worked up in the usual way to give (17 : 0) pelandjauic acid as white prisms, m.p. 85—88°, showing no depression of m.p. with the preceding synthetic sample, R_F 0.18 (solvent B), τ(CCl_4) 0.71 (2 H, br s, $CO_2H \cdots OH$, D_2O exch.), 2.75 (H_B, d of d, J_o 8 Hz, ArH), 3.3 (H_A, H_C, 2 sets, d of d, J_o 8, J_m 1.8 Hz, ArH), 7.05 (2 H, t, CH_2Ar), 8.7 (30 H, m, $C_{15}H_{30}$), and 9.05 (3 H, t, Me).

6-*Ethylsalicylic Acid*.—Dimethyl cadmium [from methyl iodide (14.2 g, 0.1 mol), magnesium (2.4 g, 0.1 mol), and ether (125 cm³) followed by cadmium chloride (9.15 g, 0.05 mol)] was treated with phthalic anhydride (14.8 g, 0.1 mol), refluxed (1 h), cooled, and then worked up in the usual way ($CHCl_3$ extraction) to give ' 2-acetylbenzoic acid ', 3-methyl-3-hydroxyphthalide (8.9 g, 54%) m.p. 117—118° [from light petroleum (b.p. 60—80°)] (lit.,[26] 114—115°, lit.,[28] 117—118°), R_F 0.30 (solvent B) (Found: C, 66.0; H, 4.9. Calc. for $C_9H_8O_3$: C, 65.85; H, 4.85%), τ[$(CD_3)_2CO$], 2.0—2.6 (4 H, m, ArH), 4.6—4.7 (1 H, s, OH), and 7.8—8.1 (3 H, s, CH_3CO).

' 2-Acetylbenzoic acid ' (6.8 g, 0.041 mol), colourless hydriodic acid (75 cm³), and red phosphorus (1.5 g) were refluxed (52 h, dark) and then worked up in the usual way to give 2-ethylbenzoic acid as white prisms (4.08 g, 66%), m.p. 66—67° (from n-pentane) (lit.,[32] 68°), R_F 0.4 (solvent A) (Found: C, 72.3; H, 6.7. Calc. for $C_9H_{10}O_2$: C, 72.0; H, 6.65%), τ(CCl_4) −4.25 (1 H, s, CO_2H, D_2O exch.), 1.9 (H_D, m, ArH), 2.68 (H_A, H_B, H_C, m, ArH), 6.87 (2 H, q, CH_2Ar), and 8.73 (3 H, t, Me).

2-Ethylbenzoic acid (1.50 g, 0.01 mol) in water (20 cm³) containing potassium hydroxide (0.8 g, 0.02 mol) was treated with copper sulphate (3.0 g, 0.012 mol) in water (25 cm³) to give the basic salt of 2-ethylbenzoic acid finally as a solid, m.p. 228—230°, containing some free 2-ethylbenzoic acid. The basic salt, without further purification, (5.0 g, 0.023 mol) in nitrobenzene (35 cm³) was refluxed (15 min), cooled, and the mixture worked up in the usual way. Separation by the esterification procedure followed by recrystallisation gave 6-*ethylsalicylic acid*, (0.1 g), m.p. 118—119°, R_F 0.11 (solvent B) (single spot) (Found: C, 66.1; H, 6.25. $C_9H_{10}O_3$ requires C, 65.05; H, 6.0%), τ($CDCl_3$) 1.46—2.00 (2 H, s, $CO_2H \cdots OH$, D_2O exch.), 2.4—3.43 (H_A, H_B, H_C, m, ArH), 6.7—7.29 (2 H, q, CH_2Ar), and 8.75 (3 H, t, Me).

3-Ethylphenol, from the decarboxylation of the acid, was obtained as an oil, R_F 0.5 (solvent C), τ($CDCl_3$), 2.83 (H_B, m, 8 lines, ArH), 3.3 (H_A, H_C, H_D, m, ArH), 4.4 (1 H, s, HOAr, D_2O exch.), 7.4 (2 H, q, CH_2Ar), and 8.8 (3 H, t, Me); H_A, H_D were nearly equivalent; H_D (4 lines), J_m 3, J_p (not clear); H_A, H_C appeared as 4 lines, J_o 7, J_m 1.5 Hz.

6-*n-Butylsalicylic Acid*.—Di-(n-propyl)cadmium [from 1-bromopropane (12.3 g, 0.1 mol), magnesium (2.4 g, 0.1 mol), and ether (100 cm³) followed by cadmium chloride (9.2 g, 0.05 mol)], was treated with phthalic anhydride (14.8 g, 0.1 mol), refluxed (1 h), and worked up in the usual way to give from light petroleum (60—80°) white waxy leaflets of 3-*hydroxy*-3-*n-propyl-phthalide* (13.45 g, 75%), m.p. 88—89° [from light petroleum (b.p. 60—80°)], R_F 0.3 (solvent B) (Found: C, 69.2; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.25%); τ ([$^2H_6$]DMSO) 2.2 (4 H, m, ArH), 3.42—3.62 (1 H, s, OH, D_2O exch.), 7.31—7.50 (2 H, t, CH_2-C=O), 8.74 (2 H, m, CH_2), and 9.16 (3 H, t, Me), $\nu_{max.}$ (KBr) 3 300 (m, OH) and 1 728 cm^{-1} (s, C=O).

2-n-Butanoylbenzoic acid (2.0 g, 0.010 4 mol) in ethanol (50 cm³) was reduced with sodium borohydride and worked up in the usual way to give a crude product which was chromatographed on alumina (250 g) with chloroform (750 cm³) as solvent to give twenty fractions. Fractions 7—15 contained 3-*n-propylphthalide* as an oil (1.53 g, 83%), R_F 0.5 (solvent C) (Found: C, 75.3; H, 6.85. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.8%), τ(CCl_4) 2.1—2.74 (4 H, m, ArH), 4.31—4.77 (1 H, t, HC), 8.0—8.3 (2 H, q, CH_2CO), 8.3—8.8 (2 H, m, CH_2), and 9.0 (3 H, t, Me), $\nu_{max.}$ (film) 1 745 cm^{-1} (phthalide ring).

3-n-Propylphthalide (10.0 g, 0.056 mol) with colourless hydriodic acid (75 cm³) and red phosphorus was refluxed (50 h, dark) and the mixture worked up in the usual way to give, after recrystallisation from light petroleum (CO_2, acetone), 2-*n-butylbenzoic acid* (6.33 g, 62.5%), m.p. 38—38.5°, R_F 0.40 (solvent A) (Found: C, 74.25; H, 7.75. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.85%), τ(CCl_4) −1.95 (1 H, br s, CO_2H, D_2O exch.), 2.01 (H_D, m, ArH), 2.75 (H_A, H_B, H_C, m, ArH), 6.95 (2 H, t, CH_2Ar), 8.41 (4 H, m, C_2H_4), and 9.0 (3 H, t, Me), $\nu_{max.}$ (KBr) 1 698 cm^{-1} (s, C=O),

2-n-Butylbenzoic acid (5.3 g, 0.03 mol) in water (75 cm³) containing sodium hydroxide (2.4 g, 0.06 mol) was heated and the cooled mixture treated with copper sulphate (8.5 g, 0.034 mol) in water (50 cm³). The blue-green basic copper salt of 2-n-butylbenzoic acid was isolated, washed with water (10 × 50 cm³) and acetone (4 × 25 cm³), and dried to give a yield of 7.1 g (93%), $\nu_{max.}$ (film) 890 (w, –Cu–OH) and 750 cm^{-1} (w, –Cu–O–). The basic salt (7.0 g, 0.029 mol) in nitrobenzene was refluxed (15 min) and the cooled mixture worked up in the usual way to give, after separation of the product by the esterification procedure, preparative t.l.c. (solvent C), and recrystallisation from light petroleum, 6-*n-butylsalicylic acid* (87 mg), m.p. 93—95°, R_F 0.12 (solvent B) (Found: C, 67.95; H, 7.1. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.2%), τ(CCl_4) −2.4 (2 H, br s, $CO_2H \cdots HO$, D_2O exch.), 2.62—3.29 (3 H, m, ArH), 6.6—7.0 (2 H, t, CH_2Ar), 8.35 (4 H, m, C_2H_4), and 8.95 (3 H, t, Me), $\nu_{max.}$ (KBr), 3 400 (s, OH) and 1 720 cm^{-1} (s, C=O).

Methyl 6-*n-Butyl*-2-*methoxybenzoate*.—(*i*) 6-n-Butylsalicylic acid (1.0 g) in 25% w/v aqueous sodium hydroxide (10 cm³) was vigorously shaken with dimethyl sulphate (5 cm³) in the warm (75 °C) for 15 min, stirred for 1 h at that temperature, and the acidified mixture worked up in the usual way, including washing with 5% ferric chloride solution of the ethereal extract, to give after preparative t.l.c. (solvent B) oily 6-n-butyl-2-methoxybenzoic acid (0.45 g, 42%), R_F 0.25 (solvent C) which in ether (10 cm³)

was methylated with ethereal diazomethane to give, as an oil, *methyl 6-n-butyl-2-methoxybenzoate* (0.53 g, 100%), R_F 0.83 (solvent C) (Found: C, 70.4; H, 8.3. $C_{13}H_{18}O_3$ requires C, 70.25; H, 8.1%).

(*ii*) 6-n-butylsalicylic acid (0.1 g) in dry benzene (20 cm³) containing anhydrous potassium carbonate (2.5 g) and dimethyl sulphate (2.0 cm³) was refluxed (48 h), worked up, and the organic material purified by preparative t.l.c. (solvent C) to give the methyl ester *O*-methyl ether, τ(CCl_4) 2.84 (1 H, m, ArH), 3.20 (2 H, m, ArH), 6.09 (3 H, s, OMe), 6.22 (3 H, s, CO_2Me), 7.12—7.8 (2 H, t, CH_2Ar), 8.59 (4 H, m, C_2H_4), and 9.07 (3 H, t, Me). The O-methyl ether acid showed τ(CCl_4) −2.13 (1 H, s, CO_2H_7, D_2O exch.), 2.73 (1 H, m, ArH), 3.23 (2 H, m, ArH), 6.09 (3 H, s, OMe), 7.48 (2 H, t, CH_2Ar), 8.65 (4 H, m, C_2H_4), and 9.11 (3 H, t, Me).

Attempted Synthesis of 6-n-Butanoylsalicylic Acid.—The basic copper salt (92% yield) of 2-butanoylbenzoic acid [from the acid (3.84 g, 0.02 mol) in water (50 cm³)], with sodium hydroxide (1.60 g, 0.04 mol) followed by copper sulphate (5.5 g), was heated in refluxing nitrobenzene (15 min) and worked up in the usual way. No 6-n-butanoylsalicylic acid could be found and 2-n-butanoylbenzoic acid was almost quantitatively recovered.

6-Chlorosalicylic Acid.—2-Chlorobenzoic acid (31.3 g, 0.2 mol) in 2M-sodium hydroxide solution (200 cm³, 0.4 mol) was mixed with copper sulphate (100 g, 0.43 mol) in water (300 cm³) giving the blue-green basic copper salt which was collected, washed with water (10 × 100 cm³) and acetone (4 × 50 cm³), and dried in air to afford a yield of 40.0 g (85%). The basic salt (20 g) was heated in refluxing nitrobenzene (75 cm³) (15 min), the cooled mixture worked up, and the recovered 2-chlorobenzoic acid collected by filtration. Continuous ethereal extraction of the filtrate afforded 6-chlorosalicylic acid; purification by preparative t.l.c. (solvent A) gave prisms (80 mg), m.p. 168—170°, (lit.,[40] 171—172°), R_F 0.12 (solvent B) (Found: C, 48.55; H, 2.8. Calc. for $C_7H_5ClO_3$: C, 48.7; H, 2.9%), τ($CDCl_3$) −1.65 (2 H, br s, $CO_2H \cdots HO$, D_2O exch.), 2.45—2.85 (3 H, m, ArH), $\nu_{max.}$ (KBr) 3 390br (s, OH), 1 700 (s, C=O), and 758 cm⁻¹ (s, C–Cl). From five such reactions involving 100 g of 2-chlorobenzoic acid, 95 g of 2-chlorobenzoic acid was recovered together with 2.81 g (38%) of 6-chlorosalicylic acid (based on the 2-chlorobenzoic acid used). The yields of anacardic acids were as high as 50% when the recovered 2-n-alkylbenzoic acid was treated several times. The same applies to 3-n-alkylphenols from the normal salts.

Organocadmium Alkyl Reactions with 3-Methoxyphthalic Anhydride.—*3-Methoxyphthalic anhydride.* This preparation is given on account of inadequate details in the literature.[35] 3-Nitrophthalic acid (100 g, 0.47 mol) was reduced with granulated tin (50 g) in water (100 cm³) containing concentrated hydrochloric acid (450 cm³) with the gradual addition (30 min) of stannous chloride (450 g). The stirred mixture was cooled occasionally, left for 24 h, filtered, and the recovered solid recrystallised (ethanol) to give 3-aminophthalic acid (29.9 g, 35%), m.p. 192° (lit.,[41] 193—194° (Found: C, 53.55; H, 3.8; N, 7.7. Calc. for $C_8H_7O_4N$: C, 53.05; H, 3.85; N; 7.75%), R_F 0.10 (solvent A), τ([$^2H_6$]DMSO), 2.21 (1 H, m, ArH), 2.2—2.6 (3 H, m, 2 ArH and CO_2H, D_2O exch. left 2 ArH), 4.69 (1 H, m, CO_2H, D_2O exch.), and 7.64 (2 H, s, H_2N, D_2O exch.). 3-Aminophthalic acid (50 g, 0.27 mol) dissolved in 60% aqueous sulphuric acid (650 cm³) at −10 °C was treated with sodium nitrite (19.1 g, 0.276 mol) in water (50 cm³), left for 3 h, and then heated at 120—130 °C (10 min). The dark red solution was diluted with water (250 cm³) and continuously extracted with ether. The organic layer was treated with barium chloride (50 g), the solvent removed, and the residue extracted with boiling xylene (3 × 50 cm³) to give 3-hydroxyphthalic anhydride (19 g, 42%), m.p. 198—200°, (lit.,[35,42] 199—200°) (Found: C, 58.5; H, 2.75. Calc. for $C_8H_4O_4$: C, 58.55; H, 2.45%), τ([$^2H_6$]-DMSO) −1.65 (1 H, br s, OH, D_2O exch.) and 2.0—2.86 (3 H, m, ArH), $\nu_{max.}$ (KBr) 3 450 (s, OH) and 1 750 cm⁻¹ (s, 4 ring anhydride).

Hydrolysis of the anhydride (1.48 g) in water (5 cm³) gave after evaporation to dryness on the steam-bath, 3-hydroxyphthalic acid (1.82 g, 100%), m.p. 160—162° (lit.,[43] 161—163°), τ([$^2H_6$]DMSO) 0.60 (3 H, br s, 2 CO_2H, OH, D_2O exch.), 2.4—3.00 (3 H, m, ArH), $\nu_{max.}$ (KBr) 3 550 (br, s, OH) and 1 725 cm⁻¹ (s, C=O). 3-Hydroxyphthalic anhydride (19.0 g, 0.11 mol) in ether (100 cm³) was treated with ethereal diazomethane until no further effervescence occurred. Evaporation gave 3-methoxyphthalic anhydride (20.62 g, 100%), m.p. 157—159° (lit.,[42] 160°), $\nu_{max.}$ (KBr) no OH absorption, τ([$^2H_6$]DMSO) 2.00 (3 H, m, ArH) and 5.98 (3 H, s, MeO).

6-Acetyl-2-methoxy- and 2-acetyl-3-methoxy-benzoic acids. To dimethylcadmium [from methyl iodide (2.84 g, 0.02 mol) and magnesium (0.48 g, 0.02 mol) in ether (70 cm³) followed by cadmium chloride (1.9 g, 0.01 mol) during 30 min] was added 3-methoxyphthalic anhydride (1.6 g, 0.009 mol) in ether (150 cm³) and the mixture refluxed (1 h). The organic material was recovered in the usual way and purified by preparative t.l.c. (R_F 0.15, solvent C) to give white *prisms* (100 mg), m.p. 131—138° (from benzene). Further recrystallisation raised the m.p. to 146—149° (Found: C, 62.0; H 5.25. $C_{10}H_{10}O_4$ requires C, 61.85; H, 5.15%), τ([$^2H_6$]DMSO) 2.2—2.6 (3 H, m, ArH), 6.05 (3 H, s, Me), 6.67 (1 H, br s, OH, D_2O exch.) and 8.05 (3 H, t, CH_3CO). The OMe chemical shift suggests the sample is homogeneous but it was not ascertained which isomer was present.

2-Methoxy-6-n-propanoyl- and 3-methoxy-2-n-propanoylbenzoic acids. In a similar way, diethylcadmium [from ethyl bromide (5.5 g, 0.05 mol) and magnesium (1.25 g, 0.05 mol) in ether (80 cm³) followed by cadmium chloride (4.7 g, 0.025 mol)] was treated with 3-methoxyphthalic anhydride (2.5 g, 0.014 mol) in ether (100 cm³), and the mixture refluxed (1 h). The organic material, recovered (after 24 h) by acidification and the usual work-up, gave 2.8 g of acidic material, and after recrystallisation from n-pentane 2.4 g (82%) of white prisms, m.p. 100—108°, τ([$^2H_6$]DMSO) 2.2—2.75 (4 H, m, 3 ArH and acidic OH, D_2O exch.), 6.95 (3 H, s, OMe), 7.6—7.8 (3 H, s, CH_2CO and 1 acidic OH), and 9.1—9.3 (3 H, t, Me). These results suggest the presence of ring and chain tautomers of probably one isomer. Di-(n-propyl)cadmium behaved similarly with 3-methoxyphthalic anhydride and an inseparable mixture was obtained at the first crystallisation.

On account of the above, the preparation of 2-acetyl-3-nitrobenzoic acid was repeated to afford pale orange needles in 53% yield, m.p. 159—160° (lit.,[36] 159—160°), R_F 0.1 (solvent A) (Found: C, 52.6; H, 3.25. Calc. for $C_9H_7O_5N$: C, 51.65; H, 3.35%), τ([$^2H_6$]DMSO) −0.5 to 0.5 (1 H, s, CO_2H, D_2O exch.), 1.4—2.7 (3 H, m, ArH), and 7.60 (3 H, s, CH_3CO), $\nu_{max.}$ (KBr), 3 400br (s, OH) and 1 720 and 1 700 cm⁻¹ (s, C=O of acid and ketone). During attempts to convert the NO_2 to NH_2 and thence to OH and OMe,

different products, at present unresolved, to those of the original authors were obtained at the first stage.

Reactions with Thallium(III) *Trifluoroacetate* (*TTFA*).—Thallium(III) trifluoroacetate was obtained by refluxing (9.6 h) thallium(III) oxide (10 g) and trifluoroacetic acid (50 cm^3) in the dark. The clear solution was evaporated to dryness *in vacuo* to give a solid, m.p. 100—105° (lit.,[37] 100°).

3,4-*Dimethylphenol*. *o*-Xylene (1.06, 0.01 mol) and TTFA (5.43 g, 0.01 mol) in trifluoroacetic acid (15 cm^3) were mixed and stirred and the white precipitate of 3,4-dimethylphenylthallium bis(trifluoroacetate) was collected (5.1 g, 96%), m.p. 185—189° (lit.,[37] 184—190°). The thalliated *o*-xylene (2.67 g, 0.005 mol) and lead tetra-acetate (2.46 g, 0.005 mol) in trifluoroacetic acid (15 cm^3) were stirred (30 min) and triphenylphosphine (1.31 g, 0.005 mol) in trifluoroacetic acid (10 cm^3) added with stirring. The concentrated mixture was acidified (6M-HCl), filtered, and worked up to obtain 3,4-dimethylphenol (0.5 g, 83%). Aeration of thalliated *o*-xylene also gave a small yield of the same product.

Attempted Preparation of Salicylic Acids.—A mixture of TTFA (2.71 g, 0.005 mol), trifluoroacetic acid (25 cm^3), and benzoic acid (0.61 g, 0.005 mol) was refluxed (24 h, dark), concentrated, and left at 0 °C overnight to give thalliated benzoic acid as fine white needles (1.89 g, 70%), m.p. 248° (lit.,[37] 247—248°). Upon oxidation as for 3,4-dimethylphenol, using thalliated benzoic acid (2.75 g, 0.005 mol), lead tetra-acetate (2.46 g, 0.005 mol), and triphenylphospine (1.31 g, 0.005 mol) in trifluoroacetic acid, no salicylic acid (m.p. 156°) was isolated but only triphenylphosphine oxide (1.29 g), m.p. 156—157°, undepressed on admixture with a genuine sample. Under no conditions could salicylic acid be obtained.

2-Chlorobenzoic acid and 2-n-pentadecylbenzoic acid, upon refluxing for 4 days with TTFA in trifluoroacetic acid, failed to form more than traces of either 2-carboxy-3-chlorophenylthallium bis(trifluoroacetate) or 2-carboxy-3-n-pentadecylphenylthallium bis(trifluoroacetate).

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