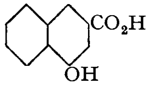
5. *Synthesis of 4-Hydroxy-2-naphthoic Acids.*

By R. D. Haworth, Brynmor Jones, and Yvonne M. Way.

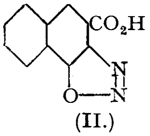
A general method of preparing 4-hydroxy-2-naphthoic acids from benzylsuccinic acids is described. It has been applied to the preparation of 4-hydroxy-, *4-hydroxy-6-methyl-*, *4-hydroxy-6-methoxy-*, *7-chloro-4-hydroxy-*, and 4-hydroxy-1-phenyl-2-naphthoic acids.

The extensive use of γ-acid and other derivatives of 1-naphtholsulphonic acid as dye intermediate products suggested that derivatives of 4-hydroxy-2-naphthoic acid may have a similar application and the object of the present research was the investigation of methods for the preparation of the acid (I) and its derivatives from benzene compounds.

When this work was commenced two independent methods of preparing 4-hydroxy-2-naphthoic acid from naphthalene derivatives were already on record, but their trustworthiness was in some doubt because of the serious discrepancies in the properties reported for the acid and its derivatives. Butler and Royle (J., 1923, **123**, 1653) first reported the conversion of 1-naphthylamine-3-sulphonic acid into (I). The yields were poor (cf. Cason, *J. Amer. Chem. Soc.*, 1941, **63**, 828), and the acid separated from dilute alcohol in small needles, m. p. 182—183°, and gave an acetyl derivative, m. p. 167—168°. Luce, Hofheim, Taunus, and Runne (D.R.-P. 523,358, 1928; *Centr.*, 1931, **2**, 1635) obtained the acid (I) from 4-chloro(or bromo)-3-amino-2-naphthoic acid *via* the diazo-oxide (II) in yellow needles, m. p. 224—225°, giving an acetyl derivative, m. p. 213—214°. While the work in these laboratories was nearing its completion, Cason (*loc. cit.*), presumably without knowledge of the German work, repeated the experiments of Butler and Royle and obtained a small amount of a hydroxy-acid, m. p. 222·5—224·5°. Considerable improvement in yield was effected by distilling sodium 1-naphthylamine-3-sulphonate with potassium cyanide instead of with potassium ferrocyanide, but the outstanding improvement resulted from the observation that 4-amino-2-naphthonitrile was directly converted into 4-hydroxy-2-naphthoic acid in 90% yield by heating with 10% sulphuric acid at 200°. The product melted at 225—226°, gave an acetyl derivative, m. p. 211·5—212·5°, and the structure was confirmed by conversion into 4-hydroxy-2-methylnaphthalene.



(I.)



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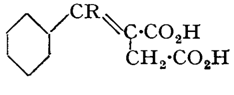
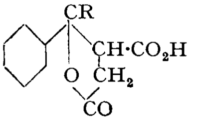
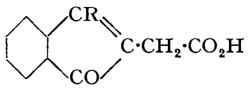


(III.)

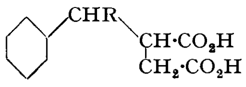
The cyclisation of phenylitaconic acids (III) offers in theory the most attractive route for the synthesis of (I) from benzene derivatives, but numerous difficulties are encountered in practice. In the first place, the preparation of these acids from appropriate aromatic aldehydes or ketones and ethyl succinate or succinic anhydride gives, as a rule, very unsatisfactory yields. Numerous by-products such as dibenzylidenesuccinic acids and paraconic acids (IV) are encountered, and references to the earlier work of Stobbe (*Annalen*, 1899, **308**, 90; *Ber.*, 1908, **41**, 4354) illustrate the difficulties which were not surmounted by our preliminary experiments. Dehydration of the itaconic acids (III), which presumably precedes their cyclisation with reagents such as concentrated sulphuric acid or aluminium chloride, may occur simultaneously in different ways. The itaconic acids (III) may isomerise to the paraconic acids (IV), which frequently either resist dehydration or require reaction conditions which result in decarboxylation of the product. Dehydration alternatively may lead to the itaconic anhydrides which usually, perhaps invariably, cyclise to indones (V) and not to 4-naphthol-2-carboxylic acids. For example, Stobbe and Vieweg (*Ber.*, 1902, **35**, 1727) showed that diphenylitaconic acid (III; R = Ph) was converted by cold concentrated sulphuric acid into the indone (V; R = Ph). During the course of the present experiments it was observed that phenylmethylitaconic acid (III; R = Me) gave with acetyl chloride an oil which was converted by aluminium chloride in nitrobenzene solution into *4-hydroxy-1-methyl-2-naphthoic acid*, m. p. 205—207°, and a yellow substance, m. p. 125—145°, which has not been purified but is probably the indone (V; R = Me). We are inclined to believe that in this experiment the oil obtained is a mixture containing the anhydride and the paraconic acid (IV; R = Me), which yield the indone (V; R = Me) and the hydroxynaphthoic acid respectively in the presence of aluminium chloride.



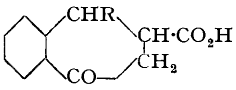
(IV.)



(V.)



(VI.)



(VII.)

The yield of hydroxynaphthoic acid amounts to about 15—20% and the method is of no general preparative interest.

This loss of yield due to indone formation needs to be eliminated, and this can be achieved in two ways. Borsche (*Annalen*, 1936, **526**, 1) showed that the tertiary ester of (III; R = Ph), obtained from benzophenone and ethyl succinate and subsequent partial hydrolysis, was converted by sodium acetate and acetic anhydride into ethyl 4-acetoxy-1-phenyl-2-naphthoate, but this method of avoiding indone formation is neither generally applicable nor does it obviate the objectionable preparation of itaconic acids. Indone formation may be completely eliminated, however, by reducing the itaconic acids to benzylsuccinic acids (VI), the anhydrides of which are readily converted into 1-tetralone-3-carboxylic acids (VII) by the action of aluminium chloride in nitrobenzene (Haworth and Sheldrick, J., 1935, 636). The conversion of the anhydride of diphenylitaconic acid (III; R = Ph) into the indone (V; R = Ph) is probably due to the double bond preventing the approach of that carbonyl group effective in tetralone formation. In the case of the anhydride of the dihydro-derivative (VI) the molecular rigidity is removed and consequently tetralone formation would be facilitated. In view of the difficulty experienced in the preparation of itaconic acids only diphenylmethylsuccinic acid (VI; R = Ph) has been prepared by reducing the corresponding itaconic acid, and other methods for the preparation of acids of type (VI) have been sought.

Ethyl hydroxymethylenesuccinate condenses readily with veratrole, giving high yields of diveratrylsuccinic acid (Haworth and Sheldrick, *loc. cit.*), but the reaction does not occur with benzene, gives only poor yields with anisole, and is not of general application.

The most convenient reaction for the preparation of benzylsuccinic acids depends upon the condensation of an appropriate benzyl chloride with ethyl sodio-α-acetosuccinate to give ethyl α-aceto-α-benzylsuccinates, which were converted into the required benzylsuccinic acids by alkaline hydrolysis. The method has proved suitable for the preparation of benzyl-, *4-methylbenzyl-*, *4-methoxybenzyl-*, and *3-chlorobenzyl-succinic acids*, but experiments with 4-nitrobenzyl chloride and α-methylbenzyl chloride were unsuccessful. The conversions of the benzylsuccinic acids into their anhydrides and subsequently into the 1-tetralone-3-carboxylic acids (VII) presented no difficulties. By the action of bromine in chloroform solution these carboxylic acids were converted into 2-bromo-1-tetralone-3-carboxylic acids, which yielded 4-hydroxy-2-naphthoic acids (I) on warming with diethylaniline. Usually high yields were obtained during the dehalogenation, but decarboxylation with the formation of 1-naphthols occurs to a small extent in some cases. By this method 4-hydroxy-2-naphthoic acid, m. p. 220°, was obtained, and the following substituted hydroxynaphthoic acids have also been prepared: *4-hydroxy-6-methyl-2-naphthoic acid*, m. p. 240—241°, *4-hydroxy-6-methoxy-2-naphthoic acid*, m. p. 238—239°, 4-hydroxy-1-phenyl-2-naphthoic acid, m. p. 205—208° (compare Borsche, *loc. cit.*), and *7-chloro-4-hydroxy-2-naphthoic acid*, m. p. 285—287°. The constitutions assigned to the acids are rigidly established by the method of preparation with the exception of the last-named, and in this case the structure was confirmed by oxidation with alkaline potassium permanganate to 4-chlorophthalic acid.

Of the unsuccessful attempts to develop alternatives routes to the 4-hydroxy-2-naphthoic acids, one only merits mention. *o*-Tolyl methyl ketone, obtained from *o*-toluonitrile and methylmagnesium iodide, condensed readily with ethyl oxalate to form ethyl *o*-toluoylpyruvate, but in spite of the favourable structure, the requisite experimental conditions for its conversion into 4-hydroxy-2-naphthoic acid have not been discovered.

Gattermann and Liebermann (*Annalen*, 1912, **393**, 200) showed that 1-naphthol-3-sulphonic acid reacted with diazo-compounds in positions 2 and 4, coupling in position 4 being favoured by reactive diazo-compounds such as *p*-nitrobenzenediazonium salts. Diazo-compounds couple in alkaline solutions with the various 4-hydroxy-2-naphthoic acids to give red or purplish-red azo-dyes, but the products are amorphous, inseparable mixtures. Definite evidence of coupling in position 1 has been obtained by reducing the crude azo-compound from 4-hydroxy-2-naphthoic acid and benzenediazonium chloride with hydrogen in the presence of palladium-charcoal, and oxidising the crude aminohydroxynaphthoic acid with ferric chloride to a naphthaquinone-carboxylic acid mixture, which yielded α-naphthaquinone on sublimation. Similar evidence for coupling in position 3 has not been obtained; the ferric chloride oxidation represents a complex reaction which requires further investigation.

EXPERIMENTAL.

Benzylsuccinic Acid.—Benzyl chloride (20 g.) was added to ethyl sodio-α-acetosuccinate (from 30 g. of ester and 3 g. of "molecular" sodium in 100 c.c. of toluene), and the mixture heated for 18 hours in an oil-bath at 120—130°. The cooled mixture was acidified with hydrochloric acid, and the toluene layer separated. The aqueous layer was extracted with ether, the combined toluene and ethereal extracts washed and dried, and the solvents removed. The residue was distilled; the fraction, b. p. 110°/13 mm., containing unchanged reactants was discarded, and the remaining crude ethyl α-aceto-α-benzylsuccinate (30 g.) hydrolysed by boiling with 2N-sodium hydroxide (3 mols.) for 18 hours. Acidification of the cold alkaline solution precipitated benzylsuccinic acid (VI; R = H) as an oil which slowly solidified. The dried solid (16 g.) was dissolved in a small amount of warm acetone, benzene added, and the acetone removed on the steam-bath. The crystals obtained from the cold benzene were recrystallised from water, forming colourless plates, m. p. 157—160° (Fittig and Brooke, *Annalen*, 1899, **305**, 40, give m. p. 161°). Benzylsuccinic anhydride, prepared from the crude acid (14 g.) and cold acetyl chloride, crystallised from benzene–light petroleum (b. p. 60—80°) in plates (11 g.), m. p. 95—97° (Fittig and Roders, *Annalen*, 1890, **256**, 90, 96, record m. p. 102°).

4-*Keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic Acid* (VII; R = H).—A solution of anhydrous aluminium chloride (10 g.) in nitrobenzene (35 c.c.) was added to the above anhydride (7 g.), after 24 hours the mixture was decomposed with ice and concentrated hydrochloric acid, and the nitrobenzene removed in steam. The crude product was crystallised from water (charcoal), and the acid (VII; R = H) was obtained in clusters of colourless plates (5 g.), m. p. 145—147° (Derick and Kamm, *J. Amer. Chem. Soc.*, 1916, **38**, 416, give m. p. 143—145°; Attwood, Stevenson, and Thorpe, J., 1923, **123**, 1764, give m. p. 149°).

3-*Bromo*-4-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic Acid.*—To a suspension of the finely powdered dry keto-acid (5 g.) in dry chloroform (15 c.c.) a solution of bromine (1·4 c.c.) in chloroform (15 c.c.) was gradually added, and the mixture shaken until the reaction started (10—45 minutes). (It is inadvisable to warm the mixture above about 35° at this stage, since lachrymatory by-products are formed, causing a serious loss of yield.) As the bromination proceeded, a clear, almost colourless solution was obtained, the *bromo*-acid separating later as a fine white deposit, which crystallised from acetone–benzene in colourless prisms (6 g.), m. p. 177—180° (Found: C, 49·6; H, 3·7. $C_{11}H_9O_3Br$ requires C, 49·1; H, 3·4%).

4-*Hydroxy*-2-*naphthoic Acid* (I).—The above bromo-acid (6 g.) was heated on the steam-bath with diethylaniline (60 c.c.) for 6 hours. Excess of solid sodium bicarbonate was added to the cold mixture, the diethylaniline removed in steam, and the hot filtered residue cooled and acidified with concentrated hydrochloric acid. The hydroxynaphthoic acid (I) (4·1 g.) crystallised from glacial acetic acid in pale yellow, elongated prisms, m. p. 220—222°. Luce, Hofheim, Taunus, and Runne (*loc. cit.*) record m. p. 224—225°, and Cason (*loc. cit.*) 225—226° (corr.).

4-*Methylbenzylsuccinic acid*, prepared in 45% yield from 4-methylbenzyl chloride, crystallised from carbon tetrachloride in colourless prisms, m. p. 112—115° (Found: C, 64·8; H, 6·2; equiv., 113. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%; equiv., 111). The *anhydride* crystallised from ligroin (b. p. 90—120°) in colourless plates, m. p. 88·5° (Found: C, 70·9; H, 6·2. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%), and cyclised in the presence of anhydrous aluminium chloride to give a 52% yield of 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which separated from aqueous acetic acid in colourless plates, m. p. 205—207° (Found: C, 70·3; H, 5·8; equiv., 201. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%; equiv., 204). 3-*Bromo*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid* crystallised from aqueous acetic acid in colourless elongated prisms, m. p. 167—168° (Found: C, 51·2; H, 3·9. $C_{12}H_{11}O_3Br$ requires C, 50·9; H, 3·9%). Dehalogenation gave an 11% yield of 4-*hydroxy*-6-*methyl*-2-*naphthoic acid*, which crystallised in pale yellow needles, m. p. 240—241°, from glacial acetic acid (Found: C, 71·4; H, 5·2. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

4-*Methoxybenzylsuccinic acid*, prepared from 4-methoxybenzyl chloride in 20% yield by the hydrolysis of the intermediate ethyl α-aceto-α-(4-methoxybenzyl)succinate, b. p. 175°/0·4 mm., crystallised from benzene in rosettes of colourless plates, m. p. 100—101° (Found: C, 65·3; H, 5·4; equiv., 126. $C_{12}H_{14}O_5$ requires C, 65·5; H, 5·9%; equiv., 119). 4-*Methoxybenzylsuccinic anhydride* separated from benzene–light petroleum (b. p. 60—80°) in colourless plates (yield, 92%), m. p. 92—93° (Found: C, 65·3; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%), and gave 4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which formed colourless plates (yield, 60%), m. p. 151°, from aqueous acetic acid (Found: C, 65·9; H, 5·5. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). Bromination gave a 70% yield of 3-*bromo*-4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which crystallised from acetic acid in colourless prisms, m. p. 171° (Found: C, 48·5; H, 3·5. $C_{12}H_{11}O_4Br$ requires C, 48·2; H, 3·7%). This was readily converted into 4-*hydroxy*-6-*methoxy*-2-*naphthoic acid*, crystallising from acetic acid in pale yellow prisms (yield, 20%), m. p. 238—239° (Found: C, 65·8; H, 4·8. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6%).

3-*Chlorobenzylsuccinic acid*, prepared from 3-chlorobenzyl chloride in 20% yield by hydrolysis of the intermediate ethyl α-aceto-α-(3-chlorobenzyl)succinate, b. p. 180—183°/0·6 mm., crystallised from benzene in colourless prisms, m. p. 125—127° (Found: C, 54·9; H, 4·6; equiv., 128. $C_{11}H_{11}O_4Cl$ requires C, 54·4; H, 4·5%; equiv., 121). The *anhydride* separated from benzene–ligroin in colourless elongated prisms (yield, 85%), m. p. 75·5° (Found: C, 58·3; H, 3·9. $C_{11}H_9O_3Cl$ requires C, 58·8; H, 4·0%), and gave on cyclisation 7-*chloro*-4-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which crystallised from acetic acid in colourless plates (yield, 75%), m. p. 190—191° (Found: C, 58·4; H, 4·0; equiv., 224·5). Bromination proceeded smoothly to 7-*chloro*-3-*bromo*-4-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, colourless rhombs (yield, 60%), m. p. 180—184°, from acetic acid (Found: C, 43·7; H, 2·6. $C_{11}H_8O_3ClBr$ requires C, 43·5; H, 2·6%). Loss of hydrogen bromide on treatment with diethylaniline gave 7-*chloro*-4-*hydroxy*-2-*naphthoic acid*, which crystallised from acetic acid in pale yellow, elongated prisms, m. p. 285—287° (Found: C, 59·6; H, 3·4. $C_{11}H_7O_3Cl$ requires C, 59·3; H, 3·2%), and some 6-chloro-1-naphthol as the result of partial decarboxylation. The chloronaphthol, m. p. 90°, gave a picrate which crystallised from aqueous alcohol in orange-yellow elongated prisms, m. p. 163°. Erdmann and Kirchoff (*Annalen*, 1888, **247**, 372) give m. p. 94° for the 6-chloro-1-naphthol and m. p. 165° for the picrate. The orientation of the above chlorohydroxynaphthoic acid was established by oxidation. To a warm solution of the acid (0·5 g.) in an excess of sodium bicarbonate solution a slight excess of N/2-potassium permanganate was added. The mixture was warmed for 5 minutes, and the manganese dioxide removed and washed. The concentrated filtrate and washings were acidified with concentrated hydrochloric acid, a small amount of orange-coloured impurity removed, and the filtrate extracted with ether. The extract was washed with sodium bicarbonate, the acid recovered by acidification, taken up in ether, and dried. Removal of the solvent left an oil which readily solidified on trituration with benzene and melted at 149—150° after crystallisation from acetone–benzene. The m. p. of 4-chlorophthalic acid has been variously reported as 148°, 150° and 150·5° (see Moore, Marrack, and Proud, J., 1921, **119**, 1788).

Methyl 7-chloro-4-hydroxy-2-naphthoate after crystallisation from methyl alcohol and benzene separated from the latter in colourless elongated prisms, m. p. 218—220°, and 7-chloro-4-methoxy-2-naphthoic acid crystallised from ethyl alcohol in rosettes of colourless prisms, m. p. 251—258°.

4-*Hydroxy*-1-*phenyl*-2-*naphthoic Acid.*—4-Keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid, which crystallised in colourless plates, m. p. 208—209°, from glacial acetic acid, was prepared as described by Hewett (J., 1936, 596). Bromination gave 3-*bromo*-4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which after two crystallisations from acetone–benzene separated in colourless prisms, m. p. 199—202° (Found : C, 58·8; H, 3·7. $C_{17}H_{13}O_3Br$ requires C, 59·1; H, 3·8%). 4-Hydroxy-1-phenyl-2-naphthoic acid, obtained in 70% yield by dehalogenation with diethylaniline, crystallised from aqueous acetic acid in colourless needles, m. p. 205—208°, undepressed by a sample of the acid prepared by Borsche's method (*loc. cit.*). Some 4-phenyl-1-naphthol, m. p. 136—138° (Borsche, *loc. cit.*, gives m. p. 140°), was isolated from the bicarbonate-insoluble fraction.

4-*Hydroxy*-1-*methyl*-2-*naphthoic Acid.*—Some particulars of this preparation kindly supplied by Imperial Chemical Industries Ltd. were modified, and the following method adopted.

Phenylmethylitaconic acid (III; R = Me) was prepared from acetophenone (7·2 g.), ethyl succinate (19 g.), and sodium ethoxide (8·3 g.) by a method similar to that of Stobbe (*Annalen*, 1899, **308**, 114). The crude acid (9 g.), m. p. 125—140°, probably a mixture of isomers (see Stobbe, *loc. cit.*), was refluxed with freshly distilled acetyl chloride (30 c.c.) for 2—3 hours, and the excess of chloride then removed by distillation under reduced pressure. The oily product (8 g.) was dissolved in nitrobenzene (8 c.c.) and a solution of aluminium chloride (8 g.) in nitrobenzene (30 c.c.), previously cooled in ice, was added. After 48 hours concentrated hydrochloric acid was added, and the nitrobenzene removed in steam. The brown semi-solid was dried and triturated with cold benzene, leaving a bright yellow solid. From this, boiling benzene extracted a yellow material, probably an indone derivative, which crystallised from the benzene and melted at 125—145°, leaving 4-*hydroxy*-1-*methyl*-2-*naphthoic acid* (4·5 g.) as a pale brown solid which, after repeated crystallisation from glacial acetic acid, gave colourless plates, m. p. 203—207° (Found : C, 71·1; H, 5·0. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·9%). The naphthoic acid structure (I) was confirmed by conversion into the following derivatives by the use of standard methods. The *methyl* ester crystallised from benzene in rhombic prisms, m. p. 171—174° (Found : C, 72·9; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%). The *ethyl* ester, crystallised similarly, had m. p. 127—129° (Found : C, 73·2; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). The *methyl* ether separated from ligroin (b. p. 90—120°) in clumps of needles, m. p. 158—160° (Found : C, 72·1; H, 5·3. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%), and *methyl* 4-*methoxy*-1-*methyl*-2-*naphthoate* after crystallisation from methyl alcohol was obtained in colourless rhombs, m. p. 99·5° (Found : C, 73·0; H, 6·1. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

o-*Methylacetophenone.*—*o*-Toluonitrile (12 g.) in toluene (30 c.c.) was treated with methylmagnesium iodide (magnesium, 2·4 g.; methyl iodide, 14 g.; ether, 60 c.c.), and the mixture kept overnight. The ether was removed on a water-bath, and the residue boiled for 3 hours. Dilute sulphuric acid was added to the cold mixture, the toluene layer separated, and the aqueous layer extracted with ether. The combined toluene and ethereal extracts were washed and dried, and after the removal of the solvents through a column the residual oil was distilled. The ketone (9 g.) distilled at 93—95°/13 mm. and gave a semicarbazone, m. p. 209° (Mercer, Robertson, and Cahn, J., 1935, 999, give b. p. 93—95°/15 mm. for the ketone and m. p. 210° for the semicarbazone; cf. also Baker, J., 1938, 447).

Ethyl o-*Methylbenzoylpyruvate.*—A mixture of *o*-methylacetophenone (2 g.) and ethyl oxalate (2·2 g.) was added to an ice-cold solution of sodium (0·34 g.) in dry alcohol (5 c.c.). After 24 hours the sodium salt deposited was collected, dissolved in water, and treated with carbon dioxide. The oil liberated was extracted with ether, washed, and dried, and the solvent removed. The unpurified ethyl *o*-methylbenzoylpyruvate (1 g.) was added to a cold solution of sodium (0·23 g.) in dry alcohol (2·5 c.c.), and after several hours the deposit of sodium salt was collected, dissolved in water, and acidified. The dry solid crystallised from benzene in clusters of pale buff plates, m. p. 118° (Found : C, 64·7; H, 4·9%). It dissolved readily in aqueous sodium bicarbonate and is probably *o*-methylbenzoylpyruvic acid ($C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

The addition of diazotised amines to solutions of the hydroxynaphthoic acids in sodium hydroxide gave the colour reactions tabulated below. An asterisk denotes the formation of a precipitate. In each experiment two drops of a dilute solution of the diazotised amine were added to ten drops of a solution of the hydroxynaphthoic acid containing 0·5 mol. of the acid per litre of N-sodium hydroxide.

2-Naphthoic acid.	Aniline.	*p*-Toluidine.	*p*-Nitroaniline.	α-Naphthylamine.	Benzidine.	Sulphanilic acid.
4-Hydroxy-	Dark cherry-red*	Cherry-red*	Brilliant purplish-red	Cherry-red	Bright crimson	Bright cherry red
4-Hydroxy-6-methyl-	Ruby-red	Dark red	Purple	Purplish-red*	Bluish-purple	Bright red
4-Hydroxy-6-methoxy-	Ruby-red	Dark red	Purplish-red*	Purplish-red*	Purplish-red	Bright red
7-Chloro-4-hydroxy-	Brownish-red*	Bright red*	Purplish-red*	Cherry-red	Purplish-red*	Light red
4-Hydroxy-1-phenyl-	Ruby-red	Bright red*	Purplish-red*	Purplish-red	Deep blue*	Crimson-red
4-Hydroxy-1-methyl-	Ruby-red	Crimson-red	Purplish-red*	Cherry-red	Deep blue*	Bright red

Coupling of Diazotised Aniline with 4-*Hydroxy*-2-*naphthoic Acid.*—The diazo-solution, prepared from aniline (0·5 g.), 4% hydrochloric acid (10 c.c.), and 0·32% sodium nitrite solution (12·4 c.c.), was added to 4-hydroxy-2-naphthoic acid (1·0 g.) dissolved in 10·6% sodium hydroxide solution (12 c.c.). After 15 minutes the solution was acidified with concentrated hydrochloric acid and the dark red azo-compound (1·3 g.) was collected, washed, and dried on porous plate. The azo-compound (0·5 g.), which could not be crystallised and was apparently a mixture, was dissolved in absolute alcohol and shaken with hydrogen in the presence of 5% palladium–charcoal (0·2 g.) until absorption ceased (80 c.c.). Filtration and removal of the alcohol in a vacuum left amino-4-hydroxy-2-naphthoic acid as a brown residue. This (0·2 g.) was dissolved in hot dilute hydrochloric acid, filtered, and treated with a solution of anhydrous ferric chloride (0·6 g.) and a few drops of concentrated hydrochloric acid. After 10 minutes the precipitated naphthaquinonecarboxylic acids were collected, washed, and dried. The nitrogen-free precipitate, m. p. 153—160° (decomp.), which was soluble in sodium bicarbonate solution, was slowly sublimed at 1 mm. The bright yellow needles, m. p. 120—123°, which sublimed at 100—140° (bath temperature) were identified as α-naphthaquinone by colour tests and direct comparison with an authentic specimen. The red or orange-red product, m. p. 130—150°, which sublimed at 140—200° could not be purified or identified.

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