Reactions of 1,5-Disubstituted Naphthalenes with Phthalic Anhydride

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The products from a Friedel-Crafts reaction of 1,5-dihydroxynaphthalene with phthalic anhydride have been investigated. The reaction of 1,5-dimethoxynaphthalene with phthalic anhydride and an excess of aluminium chloride gives o- (4,8-dihydroxy-1-naphthoyl)benzoic acid and the partially demethylated compound, o- (8-hydroxy-4-methoxy-1-naphthoyl)benzoic acid, while with an excess of phthalic anhydride the main products are the dimethoxy-acid and 4,8-bis-(2-carboxybenzoyl)-1,5-dimethoxynaphthalene. The structure of the latter was confirmed by conversion into dibenzo[b,k]chrysene.

SINCE 1,5-dihydroxynaphthalene and phthalic anhydride react in the presence of aluminium chloride to give 6,14-dihydroxyhexacene-5,16:8,13-diquinone (1) only in low yield,^{1,2} we have investigated the reaction to ascertain the nature of other products. Since it was also necessary to synthesise 4- and 8-acyl-1,5-dihydroxynaphthalenes we have also studied the reaction of phthalic anhydride with O-methyl derivatives of the diol. The diquinone (1), has been prepared both in a sodium aluminium chloride melt (Method A) and in tetrachloroethane solution (Method B).^{1,2}

Reaction of a phenol or α -naphthol with an anhydride in the presence of aluminium chloride gives a keto-acid, in which substitution occurs predominantly at the position ortho to the hydroxy-group,³ presumably via a Fries rearrangement of an intermediate ester. Thus, in the preparation of (1), products such as (2a),⁴ (3),⁵ and (4)⁵ would be expected, and were indeed formed. Although 6,10-Dihydroxytetracene-5,12-diquinone (3) has been prepared by cyclisation of the keto-acid (2a) with sulphoboric acid,⁵ we obtained only poor yields of (2a); use of an aluminium chloride melt greatly improved the yield. Reaction of the quinone (3) with phthalic anhydride also gives the diquinone (1) in good yield. 2,6-Bis-(2-carboxybenzoyl)-1,5-dihydroxynaphthalene (4) was characterised by cyclisation with sulphoboric acid to give the hexacenediquinone (1); this result contrasts with a previous report that the cyclisation yields a tetracene derivative by fission of a carboxybenzoyl group.⁵

¹ E. Clar, Ber., 1939, 72, 1817.

² E. Clar, personal communication.

³ Takahito Tsunoda, J. Synthetic Org. Chem., Japan, 1954, 12, 464. R

Method B gave small amounts of a red compound which was separated from the quinone (3) by chromatography. The two compounds reacted similarly with



sulphuric acid or alkali, and upon cyclisation with sulphoboric acid the red compound gave the diquinone (1); structure (5) is assigned to the compound. It has

⁴ W. Bentley, A. Friedl, F. Thomas, and C. Weizmann, J. Chem. Soc., 1907, **91**, 424. ⁵ W. Bentley, A. Friedl, and C. Weizmann, J. Chem. Soc., 1907,

91, 1588.

an i.r. spectrum consistent with this structure, showing carboxyl as well as free and hydrogen-bonded carbonyl absorption. Partial cyclisation of the keto-acid (4) with sulphuric acid gave (5).

The residue from the 'calcium carbonate extract' of one of the fractions from Method A yielded a buff solid (<1%) on fractional crystallisation. The i.r. spectrum showed two hydroxy-peaks, and a lactone peak at 1728 cm.⁻¹ [cf. phenolphthalein (1725 cm.⁻¹) and 1-naphtholphthalein (1730 cm.⁻¹)]. The compound was also formed in a number of phthalein syntheses, e.g. the reaction of 1,5-dihydroxynaphthalene with keto-acid (2) in sulphuric acid. Treatment of 1,5-dihydroxynaphthalene with phthalic anhydride in zinc chloride also gave this compound, for which structure (6) is proposed. When treated with pyridine and acetic anhydride it gave a crystalline acetate (7), which was



shown by n.m.r. to have two acetyl groups per molecule. Although the phthalein (6) failed to rearrange when treated with aluminium chloride alone in tetrachloroethane or in a sodium aluminium chloride melt, addition of phthalic anhydride to the aluminium chloride melt gave a yellow infusible product. An i.r. spectrum of this showed lactone, free carbonyl, and hydrogenbonded carbonyl absorption; no hydroxy-absorption was observed. With boroacetic anhydride it gave a crimson solution, similar to that given by the tetracene derivatives (3) and (5). The presence of a tetracene system was confirmed by reducing the compound with zinc and hydrogen to give tetracene: structure (8) is assigned to the compound.

When reduced with zinc and alkali and then heated with zinc in a stream of hydrogen, crude samples of the hexacenediquinone (1) were converted into dihydrohexacene. Small amounts of hexaphene were also isolated, and since rearrangement or cyclisation is unlikely, the evidence suggests that the hexaphenediquinone (9) must also be present, although none was



isolated. A keto-acid, isomeric with the acid (2a), was also formed in the preparation of (1). The i.r. spectrum showed carbonyl, hydrogen-bonded carbonyl, and hydroxy-absorptions, and structure (10a) is assigned to this new compound; this assignment is supported both by conversion of the compound into the known dimethyl ether (10b)⁶ and by an independent synthesis.

To effect acylation *para* to a hydroxy-group in a phenol or α -naphthol it is necessary to proceed *via* the corresponding methoxy-compound.⁷ Attempted demethylation of *o*-(4,8-dimethoxy-1-naphthoyl)benzoic acid (10b) ⁶ with hydrobromic acid gave back unchanged starting material, whilst with hydriodic acid the molecule was cleaved to give 1,5-dihydroxynaphthalene and phthalic acid. A successful reaction with aluminium chloride gave the dihydroxy-compound (10a) in 30% yield. Since this could be methylated to give (10b), no rearrangement had occurred.

Aluminium chloride was used in both the preparation and the demethylation of the ether (10b); an excess of the reagent in the reaction of 1,5-dimethoxynaphthalene and phthalic anhydride gave the dihydroxy-compound (10a) (30%) directly. A keto-acid was also formed which contained a single methoxy-group and which readily eliminated the elements of water; treatment of this with dimethyl sulphate gave the dimethyl ether (10b). We suggest that the partially demethylated compound is (10c); this structure is reasonable when it is remembered that methoxy-groups adjacent to a carbonyl group are more readily cleaved than those para to a carbonyl group.⁸ In connection with an alternative synthesis of (10c) it has been reported⁹ that Friedel-Crafts reaction of 1-hydroxy-5-methoxynaphthalene with phthalic anhydride gives two isomeric acids, (2b) and (10c); no attempt was made to distinguish between them. We have shown that one of the products is identical with (10c) while the other has an i.r. spectrum consistent with structure (2b). The acid

⁶ C. Weizmann and E. Bergmann, J. Chem. Soc., 1936, 567.

⁷ U.S.P. 2,752,390/1956 (Chem. Abs., 1957, **51**, 2868).

⁸ W. Baker, N. Brown, and A. Scott, J. Chem. Soc., 1939, 1922.

⁹ C. Weizmann, L. Haskelberg, and T. Berlin, J. Chem. Soc., 1939, 398.

(10c) upon treatment with acetic anhydride eliminated the elements of water to form a compound with strong hydroxy- and lactone absorptions in the i.r.; this suggested structure (11a). This compound is also formed as a minor product in the reaction between 1,5-dimethoxynaphthalene and phthalic anhydride in the presence of excess of aluminium chloride, while the corresponding



hydroxy-compound (11b) is formed in the reaction bewteen 1,5-dihydroxynaphthalene and phthalic anhydride; (11b) can be prepared by sublimation of the keto-acid (10a).

It has been stated ⁶ that recrystallisation of the dimethoxy-acid (10b) from acetic anhydride gives the 5'-acetyl derivative, m.p. 185° . We repeated this work and found that the product did melt at $183-195^{\circ}$ when rapidly heated, but if the temperature was raised slowly a change in crystalline form occurred at about 180° , after which the compound melted at 253° . Since alkaline hydrolysis of the compound regenerated the dimethoxy-acid (10b), and the i.r. spectrum showed strong peaks at 1810 and 1740 cm.⁻¹, it is suggested that the product described is the mixed anhydride (12).



The change in crystal form at 180° is probably due to disproportionation of the mixed anhydride to symmetrical structures, following the normal behaviour of mixed anhydrides when heated.

1,5-Dimethoxynaphthalene reacted with an excess of phthalic anhydride and aluminium chloride to give, in addition to the dimethoxy-acid (10b), ca. 20% of a second product having two methoxy-groups; this was unaffected by hydriodic acid or aluminium chloride in tetrachloroethane, and is assigned structure (13). This assignment was supported by conversion of the compound into dibenzo[b,k]chrysene by (i) reduction of the carbonyl groups with zinc and alkali, (ii) cyclisation with sulphuric acid, (iii) demethylation of the cyclised product with hydriodic acid, and (iv) reduction with zinc in a stream of hydrogen.



EXPERIMENTAL

Analyses were performed by Mr. B. Saunderson, Sir John Cass College. I.r. spectra were obtained using Nujol mulls with a Perkin-Elmer 237 instrument. T.l.c. was performed using 5×20 cm. plates coated with a 0.25 mm. layer of Kieselgel 'G' nach Stahl. Melting points are uncorrected.

Reaction of 1,5-Dihydroxynaphthalene with Phthalic Anhydride.— 6,14-Dihydroxyhexacene-5,16:8,13-diquinone was prepared by the methods described by Clar.^{1,2} Method (A). 1,5-Dihydroxynaphthalene and an excess of phthalic anhydride was heated in a molten mixture of aluminium chloride and sodium chloride at 200° for 30 min.

Method (B). 1,5-Dihydroxynaphthalene and an excess of phthalic anhydride was heated with aluminium chloride in tetrachloroethane at 130° for 1 hr. The complex formed from both reactions was decomposed with hot dilute hydrochloric acid and the crude reaction product obtained as a brown solid.

Specimen Fractionation of Products.—From method (A). (a) The crude product was washed thoroughly with ether until the washings were almost colourless. The ether was evaporated off and the red-brown extract was boiled under reflux with an aqueous suspension of calcium carbonate for 4 hr. The yellow suspension was cooled and filtered, the filtrate being acidified to give a yellow resin. Repeated recrystallisation from acetic acid (charcoal) gave yellow crystals of o-(1,5-dihydroxy-2-naphthoyl)benzoic acid ⁴ (2a), m.p. 223° (lit.,⁴ 221°), ν_{max} 3180br (OH), 1720 (CO₂H), and 1630w cm.⁻¹ (hydrogen-bonded C=O) (Found: C, 70·0; H, 3·8. Calc. for C₁₈H₁₂O₅: C, 70·1; H, 3·9%).

(b) The residual solid from the calcium carbonate extraction was washed with hot water and extracted with acetone. After removal of the solvent, the residue was rinsed with a little methanol, and recrystallised several times from diethyl ketone to give a buff product which did not melt below 300° , v_{max} . 3590, 3290, and 1728 cm.⁻¹; its chromatographic behaviour was indistinguishable from that of the phthalein (6), prepared as described below.

(c) The ether-insoluble residue from (a) was boiled with excess 10% aqueous sodium hydroxide; insoluble matter was filtered off. Carbon dioxide was passed through the filtrate until no further precipitation occurred after which the precipitate was filtered off. The filtrate was acidified and the product was recrystallised from acetic acid to give yellow crystals of o-(4,8-dihydroxy-1-naphthoyl)benzoic acid (10a), m.p. 188—189°, v_{max} . 3200, 1670, and 1630 cm.⁻¹ (Found: C, 70.15; H, 3.9. C₁₈H₁₂O₅ requires C, 70.15;

H, 3.9%). The synthesis of authentic (10a) is described below.

From Method (B). (a) After removal of the crude reaction product, a red solid precipitated from the cool tetrachloroethane layer. After being rinsed with aqueous sodium hydrogen carbonate, the red solid was dried and recrystallised from nitrobenzene to give red crystals not melting below 300°, and shown to be identical with an authentic sample of 6,10-dihydroxytetracene-5,12-quinone (3),⁵ v_{max} . 3300, 1660, and 1625 cm.⁻¹ (Found: C, 74.2; H, 3.4. Calc. for C₁₈H₁₀O₄: C, 74.5; H, 3.4%).

(b) Extraction of the tetrachloroethane mother liquor with aqueous sodium hydroxide, and acidification of the extract gave a brown product which was rinsed with ethanol and extracted with hot nitrobenzene. On addition of ligroin to the extract a red product was precipitated, which was dissolved in acetone, and eluted on a column of silica gel with acetone, the quinone (3) being readily washed through. The product remaining on the silica gel was extracted with alkali. Upon acidification 9-(2-carboxy-benzoyl)-6,10-dihydroxytetracene-6,12-quinone (5) was obtained as a red powder, and identified by comparison with a sample prepared from the keto-acid (4), v_{max} 1715, 1670, and 1630 cm.⁻¹ (Found: C, 71.0; H, 3.3. C₂₆H₁₄O₇ requires C, 71.2; H, 3.2%).

(c) The crude reaction product was extracted with hot alkali and the extract was acidified; the product was successively extracted in a Soxhlet apparatus with benzene, ether, and methanol. Addition of light petroleum to the benzene extract gave an orange precipitate which was filtered off. After evaporation of the filtrate, the residue was dissolved in acetone. Slow evaporation of the solution yielded dark red needles, m.p. 223°, ν_{max} 3270 and 1750 cm.⁻¹ identical in its chromatographic behaviour with a sample of (11b) prepared by sublimation of the keto-acid (10a) as described below.

(d) Solvent was removed from the ether extract and the residue was boiled for 2 hr. with an aqueous suspension of calcium carbonate. After filtration, the yellow extract was acidified to give a dirty yellow solid. Extraction with hot acetic acid gave a dirty yellow solution and a yellow residue of 2,6-bis-(2-carboxybenzoyl)-1,5-dihydroxynaphthalene (4), not melting below 300°, ν_{max} 1680 (CO₂H) and 1625 cm.⁻¹ (weak, hydrogen-bonded C=O), identical in chromatographic behaviour and colour reactions with authentic (4) prepared by the method of Bentley et al.4 (sulphuric acid gave a dark green solution which turned blue on warming; boroacetic anhydride gave a red solution which exhibited an orange fluorescence). The acetic acid extract was concentrated and the product, after recrystallisation from acetic acid (charcoal) gave yellow crystals of o-(1,5dihydroxy-2-naphthoyl)benzoic acid (2a), m.p. 231° (lit.3,9 221°, 231°) ν_{max} 3180br (OH), 1720 (CO2H), and 1630w cm.⁻¹ (hydrogen-bonded C=O) (Found: C, 70.0; H, 3.8. Calc. for $C_{18}H_{12}O_5$: C, 70.1; H, 3.9%), identical in chromatographic behaviour and colour reactions with authentic (2a) prepared by the method of Bentley et al.⁴ (sulphuric acid gave a red-brown solution which slowly turned green and then blue when warmed).

6,10-Dihydroxytetracene-5,12-quinone (3).—Method (1). By the method of Bentley et al.⁵ the quinone was obtained as a red solid in 6% yield.

Method (2). To a molten mixture of aluminium chloride (40 g.) and sodium chloride (8 g.) at 120° was added the

keto-acid (2a) (8 g.). The mixture was stirred and heated at 180–200° for 40 min. The cooled mixture was decomposed with ice and hydrochloric acid and the product was filtered off, and washed with water and methanol, and dried to give the quinone as a red-brown solid (7.5 g.). Sublimation or recrystallisation of this from nitrobenzene gave a red solid which did not melt below 300°, ν_{max} . 3300 (OH), 1660 (C=O), and 1625 cm.⁻¹ (weak hydrogen-bonded C=O) (Found: C, 74.2; H, 3.4. Calc. for C₁₈H₁₀O₄: C, 74.5; H, 3.4%). Sulphuric acid gave a blue-green solution, while aqueous alkalis gave a blue solution which turned olive-green with sodium dithionite. Boroacetic anhydride ¹⁰ gave a scarlet solution which exhibited an orange fluorescence. Solutions of the quinone in organic solvents also exhibited an orange fluorescence.

Cyclisation of the Keto-acid (4).—Method (1). A mixture of the keto-acid (4) (0.25 g.) and boric acid (0.5 g.) was treated with sulphuric acid sufficient to give a clear, red solution. Upon addition of an equal volume of oleum the solution turned deep blue. After 15 min. the mixture was poured into ice-water and the red-brown precipitate was filtered off and washed with water and methanol. The crude product was treated with hot aqueous sodium hydroxide and the blue precipitate was filtered off, washed thoroughly with alkali and water, and acidified. Recrystallisation of the product from nitrobenzene gave red-brown crystals (0.04 g.) of 6,14-dihydroxyhexacene-5,16:8,13-diquinone (1), not melting below 300° (Found: C, 74.5; H, 3.0. Calc. for $C_{26}H_{12}O_6$: C, 74.3; H, 2.9%); i.r. and u.v. spectra identical with those of authentic (1).1,2

Method (2). A solution of the keto-acid (4) (0.22 g)in sulphuric acid (4 ml) was heated on a steam-bath for 5 min. When cool, the blue solution was poured into icewater and the red precipitate was filtered off and washed with water and methanol, it was dried to give an orangebrown solid (0.11 g.) which recrystallised from nitrobenzene to give 9-(2-carboxybenzoyl)-6,10-dihydroxytetracene-5,12-quinone (5) as an orange powder (0.03 g.) which did not melt below 300°, ν_{max} 1715 (CO₂H), 1670 (C=O), and 1630 cm.⁻¹ (hydrogen-bonded C=O) (Found: C, 71·1; H, 3·3: C₂₆H₁₄O₇ requires C, 71·2; H, 3·2%). Sulphuric acid gave a blue solution, while aqueous alkali gave a blue solution which turned mauve with sodium dithionite. Boroacetic anhydride gave a crimson solution which exhibited a deep scarlet fluorescence. A sample of this compound was cyclised with oleum and boric acid as previosuly described. The product was shown to be identical with an authentic sample of 6,14-dihydroxyhexacene-5,16:8,13-diquinone (1) by i.r., u.v., spectroscopy and colour tests.

Phthalein (6). A mixture of phthalic anhydride (8 g.), 1,5-dihydroxynaphthalene (16 g.), and zinc chloride (25 g.) was stirred and heated at 140° for 2 hr. The product was repeatedly extracted with hot water, to leave a black residue of the phthalein (6). A sample was extracted with ethanol, solvent was removed from the extract, and the residue was washed with ether. Repeated recrystallisation from diethyl ketone gave a small quantity of pink solid, which did not melt below 300°, ν_{max} 3590 and 3290 (OH) and 1728 cm.⁻¹ (lactone). Sulphuric acid gave a red solution, while aqueous alkali gave a blue solution. Aqueous acids gave a purple colour.

¹⁰ O. Dimroth and T. Faust, Ber., 1921, 54, 3020.

A sample of the phthalein, was acetylated with an excess of acetic anhydride in pyridine on a steam bath for 1 hr. Work up and repeated recrystallisation of the product from xylene gave crystals of the *diacetate* (7) m.p. 268— 269°, $\nu_{\rm max}$ 1760 and 1745 cm.⁻¹ (lactone and acetate) (Found: C, 74·15; H, 4·0. C₃₂H₂₀O₇ requires C, 74·4; H, 3·9%). Sulphuric acid gave a crimson solution. The n.m.r. spectrum in deuteriochloroform showed a ratio of methyl to aromatic protons of 6:14.

Diphthaloyl Derivative (8).—A mixture of the crude phthalein (6) (2 g.) and phthalic anhydride (1.5 g.) was heated in a melt of aluminium chloride (10 g.) and sodium chloride (2 g.) at 200° for 30 min. to give a deep blue liquid. The cool complex was decomposed with ice-hydrochloric acid and the product was washed with hot water, ethanol, and acetone. Recrystallisation of the product gave yellow crystals (1.7 g) of the diphthaloylated derivative (8) which did not melt below 300°, and which did not sublime in vacuo, ν_{max} 1760 (lactone), 1670 (C=O), and 1630 $\rm cm^{-1}$ (weak hydrogen-bonded C=O) (Found: C, 76.4; H, 2.8. C44H20O9 requires C, 76.3; H, 2.9%). Sulphuric acid gave a blue solution, while aqueous sodium hydroxide gave a red solid which dissolved to a dark-green solution with sodium dithionite. Boroacetic anhydride gave a red solution which exhibited an orange fluorescence.

A small sample of this compound when heated with zinc in a stream of hydrogen gave an orange product. Recrystallisation for xylene gave orange crystals, identified as tetracene by the u.v. spectrum, $\lambda_{max.}$ 470, 440, 414, 392, 374, 293, 274, and 264.5 nm. in ethanol (lit.,¹¹ 471, 441, 415, 393, 373, 293, 274, and 264.5 nm.).

1,5-Dimethoxynaphthalene.—This compound was prepared by a literature method.¹²

o-(4,8-Dimethoxy-1-naphthoyl)benzoic Acid (10b). This compound was prepared by a literature procedure ⁷ as pale green crystals (75%), m.p. 274-275° (lit.,⁷ 263°), v_{max} 1685 (CO₂H), 1650 (C=O), and 1068 cm.⁻¹ (OCH₃) (Found: C, 71·2, H, 4·6; OCH₃, 19·1. Calc. for C₂₀H₁₆O₅: C, 71·4; H, 4·8; OCH₃, 18·5%). Sulphuric acid gave a dark green solution, while aqueous sodium hydroxide gave a colourless sodium salt which was soluble in hot water, but sparingly soluble in cold water.

Recrystallisation of the acid (10b) from acetic anhydride gave pale yellow crystals of o-(4,8-dimethoxy-1-naphthoyl)benzoic acetic anhydride (12), m.p. 184° (rapid heating), 252-253° (slow heating) (lit.,⁶ 185°). ν_{max} 1810 and 1740 (anhydride) and 1655 cm.⁻¹ (C=O) [Found: C, 69·7; H, 4·7; OCH₃, 16·7. Calc. for C₂₀H₁₂O₄(OCH₃)₂. C, 69·8; H, 4·8; OCH₃, 16·4%].

A sample of the anhydride was heated under reflux with an excess 10% aqueous sodium hydroxide for 30 min. The solution was diluted with an equal volume of water, filtered, and acidified. Recrystallisation from acetic acid gave the product as buff crystals m.p. $273-275^{\circ}$, identical with the acid (10b).

o-(4,8-Dihydroxy-1-naphthoyl)benzoic acid (10a).—A stirred suspension of the dimethoxy-acid (10b) (1·15 g) in benzene (40 ml.) was treated with powdered aluminium chloride (3·8 g.), under reflux for 45 min. Decomposition of the red oil which formed with ice-dilute hydrochloric acid gave a yellow resin which was heated with 2N-aqueous sodium carbonate containing a little decolourising charcoal. The yellow solution was filtered and acidified, and the solid

¹¹ E. Clar, 'Polycyclic Hydrocarbons,' Springer-Verlag, Berlin, 1964, Vol. 1, 391. product recrystallised from acetic acid to give the *di*hydroxy-acid (10a) as yellow rhombic plates (30%), m.p. 188—198°, ν_{max} 3200 (intermolecularly-bonded OH), 1670 (CO₂H), and 1630 cm.⁻¹ (weak: hydrogen-bonded C=O) (Found: C, 70·15; H, 3·9. C₁₈H₁₂O₅ requires C, 70·15; H, 3·9%). Sulphuric acid gave a yellow-green, fluorescent solution.

Methylation of the dihydroxy-acid with aqueous methanolic potassium hydroxide and dimethyl sulphate, on a steam-bath for 30 min. gave a pale yellow solid on acidification. Recrystallisation from acetic acid gave pale brown crystals, m.p. $272-274^{\circ}$, shown to be identical with the dimethoxy-acid (10b).

Sublimation of o-(4,8-Dihydroxy-1-naphthoyl)benzoic Acid. —A sample of the dihydroxy-acid (10a) was heated in a sublimation apparatus at 260° under reduced pressure, to give a pale yellow sublimate which crystallised from benzene as pale yellow crystals (10%), m.p. 223—224° v_{max} 3270 (OH), 1750 (lactone), and 1630 cm.⁻¹ (weak: C=O?). Sulphuric acid gave a yellow green fluorescent solution.

o-(8-Hydroxy-4-methoxy-1-naphthoyl)benzoic Acid (10c).---Aluminium chloride (20 g.) was added in portions during 1 hr., to a stirred mixture of phthalic anhydride (7.5 g.) and 1,5-dimethoxynaphthalene (9.4 g.) in tetrachloroethane (100 ml.) heated on a steam-bath. The mixture was heated and stirred for a further 2 hr. the initially dark red solution, slowly becoming dark fluorescent green. When cool, the mixture was treated with ice-hydrochloric acid to give a black tarry product. Solvent was steamed distilled off and the product was extracted with boiling 20% aqueous sodium carbonate (2 \times 5 ml), the solution being filtered hot. The cold solution gave a dirty vellow precipitate which was filtered off, and recrystallised from from hot water. A further crop of product was obtained by concentration of the mother liquor to 50 ml., and addition of a saturated solution of sodium chloride (50 ml.). The recrystallised product was dissolved in boiling water and acidified. The yellow product, after recrystallisation from acetic acid gave the monomethoxy acid (10c) (3.4 g.) as yellow rhombic plates, m.p. 199° [Found: C, 70.7; H, 4·4; OCH₃, 10·0. C₁₈H₁₁O₄(OCH₃) requires C, 70·8; H, 4.4; OCH₃, 9.6%], ν_{max} 1710 (CO₂H) and 1630 cm.⁻¹ (weak: hydrogen-bonded C=O). Sulphuric acid gave a yellow-green fluorescent solution, while aqueous sodium hydroxide gave a colourless sodium salt, sparingly soluble in cold water, readily soluble in hot water.

The black mother liquors from the above reaction after treatment with charcoal, acidification, and repeated recrystallisation from acetic acid gave yellow crystals of the dihydroxy-acid (10a) (4.5 g.), m.p. 187—188°.

Extraction of the brown resin obtained by acidification of the mother liquors from the above reaction with benzene (3×10 ml.) gave a yellow solution, which was washed with aqueous sodium carbonate and dried (Na₂SO₄). Removal of the solvent left a yellow resin which gave on trituration with cold benzene a colourless residue (*ca.* 0.05 g.), m.p. 219-220°; ν_{max} 1770 cm⁻¹ (lactone) and 1630 cm⁻¹ (weak: C=O?).

Reaction of the Keto-acid (10c) with Acetic Anhydride.—A suspension of the keto-acid (10c) (0.5 g.) in acetic anhydride (10 ml.) was heated on a steam-bath for 20 min. The solution was poured into cold water and allowed to solidify.

¹² W. Bentley, R. Robinson, and C. Weizmann, J. Chem. Soc., 1907, **91**, 106.

The solid product (11a), recrystallised from acetic acid to give pale buff crystals (0.4 g.), m.p. 219–220° (Found: C, 74.6; H, 4.0. $C_{19}H_{12}O_4$ requires C, 75.0; H, 4.1%). v_{max} . 1770 (lactone) and 1630 cm.⁻¹ (weak: C=O?). An n.m.r. spectrum in deuteriochloroform showed the presence of a single methyl group. Sulphuric acid gave a yellow-green fluorescent solution.

Reaction of 1-Hydroxy-5-methoxynaphthalene with Phthalic Anhydride.—This reaction was performed as described in the literature.⁹ Fractional recrystallisation of the product gave two compounds: (a) a yellow crystalline compound, m.p. 199°, shown to be identical with a sample of o-(8-hydroxy-4-methoxy-1-naphthoyl)benzoic acid (10c), and (b) a solid obtained as brown needles, m.p. 222—224°, ν_{max} . 1680 (CO₂H) and 1627 cm.⁻¹ (hydrogen-bonded C=O). Sulphuric acid gave a red solution which turned dark green on warming.

Methylation of the Monomethoxy Acid (10c).—A sample of the monomethoxy acid (10c) was methylated by the same procedure as was used for the dihydroxy acid. The product, m.p. $274-275^{\circ}$, had an i.r. spectrum identical with that of the dimethoxy-acid (10b).

4,8-Bis-(2-carboxybenzoyl)-1,5-dimethoxynaphthalene (13). —Powdered aluminium chloride (7.3 g.) was stirred into a suspension of 1,5-dimethoxynaphthalene (5.2 g.) and aluminium chloride (8.5 g.) was added in portions, the mixture then being stirred for 24 hr. The red resinous complex was decomposed with ice-hydrochloric acid to give a yellow resin. Tetrachloroethane was distilled off in steam, and the residue was washed with water, then hot alcohol. By boiling the product with aqueous sodium carbonate, and fractional crystallisation of the sodium salts, removal of most of the monosubstituted product (10b) was effected. The colourless sodium salt was dissolved in hot water, and acidified, the white product being extracted with hot acetic acid to remove any residual monosubstituted product. The diacid (13) (19%) was obtained as a white powder, not melting below 300°, and which was insoluble in most common organic solvents [Found: C, 69.5; H, 4.25; OCH₃, 12.6. $C_{26}H_{14}O_6(OCH_3)_2$ requires C, 69.5; H, 4.2; OCH₃, 11.9%], ν_{max} at 1695 (CO₂H) and 1660

cm.⁻¹ (C=O). Sulphuric acid gave a deep red solution, while aqueous sodium hydroxide gave a colourless sodium salt, sparingly soluble in cold water, more soluble in hot water.

Conversion into Dibenzo[b,k]chrysene.-A solution of the diacid (13) (3 g.) in 5% aqueous sodium hydroxide (40 ml.) was heated under reflux with zinc dust (3 g.) activated with cuprammonium sulphate, for ca. 24 hr. The reaction was followed by acidifying samples of the solution and studying the i.r. spectrum of the product; the peak at 1660 cm.⁻¹ disappeared rapidly and was replaced by a strong peak at 1760 cm.⁻¹ (phthalide). When the reaction was complete, this latter peak also disappeared, leaving the peak at 1680 cm.⁻¹ (CO₂H). The solution was filtered whilst hot and the residue was washed with hot water. As the filtrate cooled, a white precipitate formed and was filtered off. A further quantity of product could be obtained by the addition of a little solid sodium chloride to the mother liquors. The white product was dissolved in hot water and acidified to give 4.8-bis-(2-carboxybenzyl)-1.5-dimethoxynaphthalene (2.3 g.) as a white powder which did not melt below 300°. The reduced product thus obtained (0.4 g.) was dissolved in sulphuric acid (8 ml.) and the red solution was stirred at room temperature for 10 min. The solution was then poured into cold water and the yellow precipitate was filtered off, washed with water, and dried in air to give a yellow powder (0.35 g.). This product (0.14 g) was boiled under reflux with hydriodic acid (5 ml.) for 1 hr. The solution was diluted with water, and the black product was filtered off, and washed with water and sodium thiosulphate solution; it was dried to give a black amorphous solid (0.13 g.). A sample of this (0.21 g.) mixed with zinc dust (6 g.) was heated in a stream of hydrogen at 390° for 4 hr. The orange crystals which formed gave, after recrystallisation from xylene, orangevellow crystals (0.008 g.) of dibenzo[b,k]chrysene, identified by its u.v. spectrum, λ_{max.} 420, 397, 376, 357, 330, 308, and 294 nm. in benzene (lit., 13 420, 396, 377, 358, 329, 307, and 294 nm.).

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¹³ Ref. 11, p. 377.