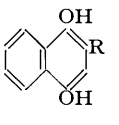
521. *Aromatic Keto-enols. Part II.* Some New 2 : 3-Dihydro-1 : 4-naphthaquinones and -anthraquinones.*

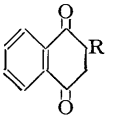
By D. B. Bruce and R. H. Thomson.

Several new 1 : 2 : 3 : 4-tetrahydro-1 : 4-diketonaphthalenes have been obtained either by fusion of the dienol or reduction of the corresponding 1 : 4-naphthaquinone with acid stannous chloride. The elimination of β-substituents, well-known in the anthraquinone series, has been observed with juglone (5-hydroxy-1 : 4-naphthaquinone) and naphthazarin derivatives: thus, in the former series elimination occurs when a 3-substituent is OH, NMe_2, NHPh, or SEt, and in the latter series when a 2-Cl group is present though a 2-Me, 2-OH, or 2-NHPh group is retained. 1 : 2 : 3 : 4-Tetrahydro-1 : 4-diketoanthracene was obtained in 50% yield by fusion of 1 : 4-dihydroxyanthracene, and the structure of certain of its hydroxy-derivatives has been investigated. No change was observed after fusion of 1 : 4-naphthylenediamine.

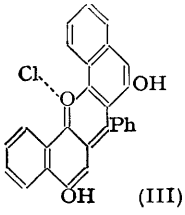
It has been shown that certain dihydroxynaphthalenes (*e.g.*, I; R = H and Me) partly isomerise in the molten state to the corresponding diketones (*e.g.*, II; R = H and Me) which can be isolated, the yield and stability being greatly increased by the presence of *peri*-hydroxyl groups as in (VI and IX; R = H) (Thomson, *J.*, 1950, 1737; 1951, 1237; Zahn and Ochwat, *Annalen*, 1928, **462**, 72). In the naphthalene series only five diketones of this type are known and we now record some attempts to extend this number.



(I)



(II)



(III)

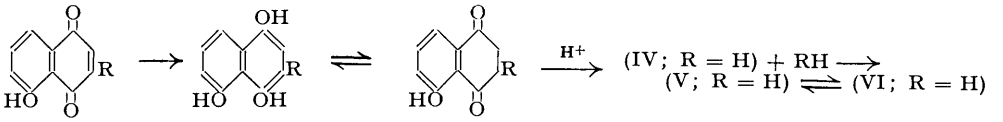
Of the simple type (II), 1 : 2 : 3 : 4-tetrahydro-1 : 4-diketo-6-methylnaphthalene was obtained in 17% yield by fusion of the dienol, but unexpectedly 1 : 4-dihydroxy-2 : 3-

* *J.*, 1950, 1737, is regarded as Part I of this series.

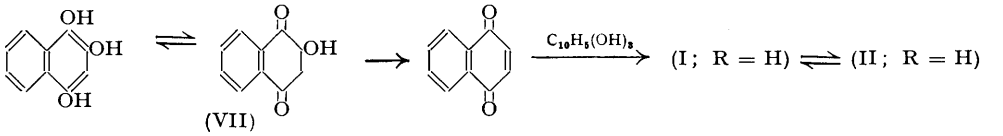
dimethylnaphthalene did not isomerise under the same conditions. 2-Chloro-1 : 4-dihydroxynaphthalene decomposes vigorously when heated, with evolution of hydrogen chloride, and does not melt. Fusion of 1 : 2 : 4-trihydroxynaphthalene gave a very low yield of (II; R = H) (see below), but no diketone was isolated from molten 1 : 2 : 4-trihydroxy-3-methylnaphthalene. All attempts to isomerise 2 : 3-dihydroxynaphthalene by fusion in a vacuum were unsuccessful.

It was stated in Part I that (II; R = H) does not condense with benzaldehyde, it being assumed that the pink tinge acquired by the mixture was due to oxidation of the dienol (I; R = H). Under different conditions the coloured material has now been isolated and is identical with the dark red pigment obtained by Wurgaft (*J. pr. Chem.*, 1894, **49**, 551) and Raudnitz and Puluj (*Ber.*, 1931, **64**, 2215) by condensing benzaldehyde with (I; R = H), shown later by Fieser and Fieser (*J. Amer. Chem. Soc.*, 1941, **63**, 1574) to be (III).

β-Hydrojuglone (1 : 2 : 3 : 4-tetrahydro-5-hydroxy-1 : 4-diketonaphthalene) (VI; R = H) may be obtained either by fusion of the α-isomer (1 : 4 : 5-trihydroxynaphthalene) or by direct reduction of juglone (IV; R = H) with sodium dithionite or acid stannous chloride in hot aqueous solution. As the fusion method failed with 3-chloro-1 : 4 : 5-trihydroxynaphthalene (which merely chars with slight evolution of hydrogen chloride) the alternative procedure was adopted in this group. When the 3-substituted juglones (IV; R = Cl, OH, NMe_2, NHPh, or SEt) were reduced with acid stannous chloride the same product was obtained in all cases, namely, β-hydrojuglone. This probably arises by the following reaction sequence :



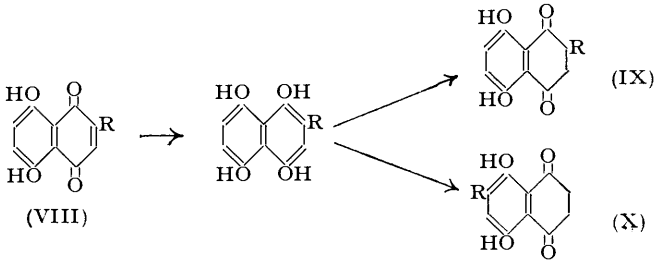
the usual reduction to (V) and isomerisation to the substituted β-hydrojuglone (VI) are followed by an acid-catalysed elimination which removes the group R with formation of the corresponding " olefin " (in this case, juglone), which is then reduced. The formation of (II; R = H) by fusion of 1 : 2 : 4-trihydroxynaphthalene could proceed in similar stages, *viz.* :



Any of the keto-alcohol (VII) formed by isomerisation would readily lose the elements of water at the temperature of fusion (*ca.* 200°) to form 1 : 4-naphthaquinone; this in turn would be reduced by the excess of 1 : 2 : 4-trihydroxynaphthalene present to (I; R = H) (since 2-hydroxy-1 : 4-naphthaquinone has a lower electrode potential than 1 : 4-naphthaquinone), which would then isomerise to the diketone (II; R = H). The formation of hydrogen chloride when 2-chloro-1 : 4-dihydroxy- and 3-chloro-1 : 4 : 5-trihydroxy-naphthalene are heated suggests that the β-substituents are eliminated in a similar manner. Reduction of 3-chloro-2-methyljuglone under the usual conditions did not yield the expected β-hydroplumbagin but plumbagin itself was isolated. This procedure eliminates two stages in the recent synthesis of plumbagin (*J.*, 1951, 1237).

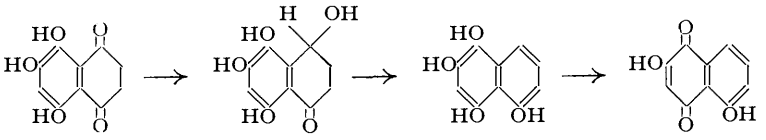
Reduction of naphthazarin (VIII; R = H) with acid stannous chloride gives rise to the diketone (IX; R = H) but from substituted naphthazarins two products, (IX and X), are possible. Four substituted naphthazarins (VIII; R = Me, OH, Cl, or NHPh) have been reduced by this method. In contrast to the 5-hydroxy-series, only chloronaphthazarin afforded 1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxy-1 : 4-diketonaphthalene, the analogues yielding

new diketones—in each case a single product. Determination of the structures of these tautomeric compounds presented some difficulty.



It was originally thought the structure of the methyl compound could be determined by preparing the two possible isomers by condensing methylsuccinic anhydride with quinol, and succinic anhydride with toluquinol. The latter pair did indeed yield the above reduction product but the conditions of condensation and subsequent working up were such that isomerisation at some stage could not be ruled out. The structure of the reduction product was established by catalytic reduction of the diketone to the corresponding di-secondary alcohol, followed by elimination of two mols. of water. This could give either 2- or 6-methyl-1 : 4-naphthaquinol according to the location of the methyl group in the original diketone. The product obtained was 2-methyl-1 : 4-naphthaquinol which could only have arisen from 1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxy-1 : 4-diketo-6-methylnaphthalene (X; R = Me).

In a somewhat similar manner the structure of the stannous chloride reduction product of naphthopurpurin was established. As catalytic hydrogenation of both carbonyl groups was difficult the hydrogenation was stopped at the keto-alcohol stage. Dehydration of the product followed by oxidation yielded 2 : 5-dihydroxy-1 : 4-naphthaquinone. This could only be obtained from (X; R = OH), as follows :

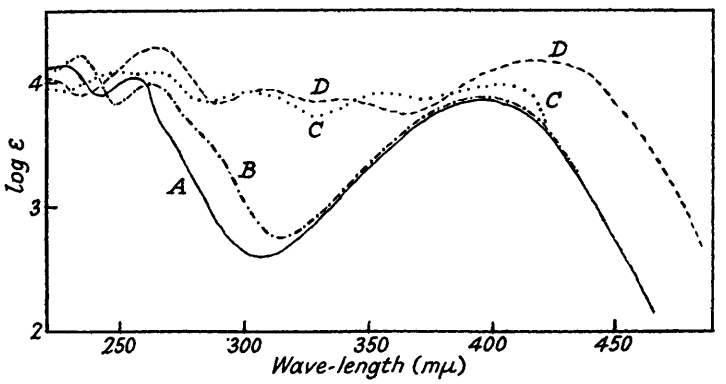


Stannous chloride reduction of naphthopurpurin therefore yields 1 : 2 : 3 : 4-tetrahydro-5 : 6 : 8-trihydroxy-1 : 4-diketonaphthalene.

It is realised that the method by which these structures were determined does not exclude the possibility of isomerisation during the first stage, but it is extremely improbable that the diketones (IX) were formed initially in boiling acid solution and then on catalytic hydrogenation at room temperature enolised and re-ketonised to (X) *before* hydrogenation commenced. Before the structure of the naphthopurpurin derivative was established the 3-μ and 6-μ regions of its infra-red spectrum were examined by Mr. T. S. Robinson who found the evidence to be consistent with either (IX or X; R = OH) but slightly in favour of the latter. By analogy the diketone obtained by reduction of anilinonaphthazarin is (X; R = NHPh) and this is supported by its ultra-violet absorption spectrum which is similar to that of the product from naphthopurpurin (see Fig.). Both show a peak at *ca.* 300 mμ not present in the curve of the product from naphthazarin.

In the tetrahydroanthracene series several diketones are known. Leucoquinizarin (XI; R = OH, R′ = H) is a well-known dyestuff intermediate (for the structure see Zahn and Ochwat, *loc. cit.*, and Flett, *J.*, 1948, 1441), and a number of derivatives with substituents in the benzenoid ring are recorded in patents. The only simple diketone (*i.e.*, without *peri*-hydroxyl groups) reported is 1 : 2 : 3 : 4-tetrahydro-1 : 4-diketo-9 : 10-diphenylanthracene (XI; R = Ph, R′ = H) obtained by reduction of 9 : 10-diphenyl-1 : 4-anthraquinone (Étienne and Bichet, *Compt. rend.*, 1949, **229**, 1154). The simplest member of the series (XI; R = R′ = H), has now been obtained in 50% yield by fusion of 1 : 4-dihydroxyanthracene.

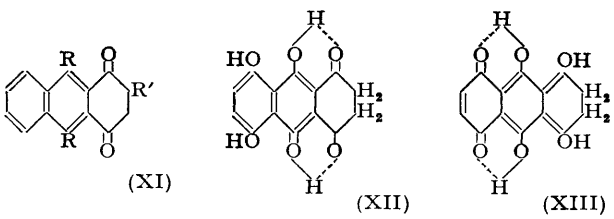
The diketone is much more stable than the dienol. When melted in a vacuum and allowed to cool slowly the product was substantially the diketone with only a small amount of dienol. The diketone slowly dissolves in dilute alkali, forming a red solution from which the dienol is precipitated by acid. The elimination of β-substituents observed when certain substituted 5-hydroxy- and 5 : 8-dihydroxy-1 : 4-naphthaquinones are reduced has long been known to occur with substituted quinizarins and other *peri*-hydroxy- and -amino-anthraquinones. The elimination of β-sulphonic acid groups, in particular, has proved useful in the preparation of a number of anthraquinone dyes (*e.g.*, Marschalk, *Bull. Soc. chim.*, 1927, **41**, 943). On the other hand, Meyer and Sander (*Annalen*, 1920, **420**, 124) found that the pentahydroxyanthracene, obtained by reduction of purpurin with zinc and acetic acid in the cold, rearranged in hot glacial acetic acid in absence of air to the diketone (XI; R = R′ = OH) without elimination of the β-hydroxyl group. Subsequent treatment of the diketone with sulphuric acid or sodium hydroxide yielded quinizarin. We have confirmed this; if the heating is carried out in the presence of hydrochloric acid quinizarin is obtained directly. In contrast, 2-chloroquinizarin is reduced to leucoquinizarin by zinc and acetic acid even in the cold. It may well be that β-substituted diketones can also be



Reduction products of (*A*) *naphthazarin,* (*B*) *methylnaphthazarin,* (*C*) *naphthopurpurin, and* (*D*) *anilinonaphthazarin.*

obtained in the 5-hydroxy- and 5 : 8-dihydroxy-1 : 4-naphthaquinone series under suitable conditions.

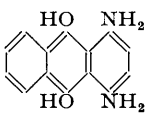
An interesting compound in this group is leuco-1 : 4 : 5 : 8-tetrahydroxyanthraquinone for which a number of plausible structures can be written. The substance forms a dimethyl ether with diazomethane, and, under conditions which do not normally induce enolisation of these diketones, a tetra-acetate. This indicates the presence of four hydroxyl groups, two of which form hydrogen bonds as in (XII). The compound was too insoluble for determination of active hydrogen, and experience has shown that it is extremely difficult to prepare and purify polycarbonyl derivatives from compounds of this type. The infra-red absorption spectrum of the crystalline leuco-compound shows a fairly strong broad band



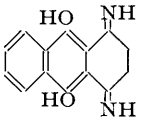
at 3392 cm.$^{-1}$, indicating the presence of a hydroxyl group with intermolecular (or weak intramolecular) hydrogen bonding. In the 6-μ region a strong band at 1606 cm.$^{-1}$ corresponds to a carbonyl stretching mode of vibration in which the oxygen atom is very

strongly hydrogen-bonded. The infra-red evidence is thus strongly in favour of structure (XII) or (XIII) but does not differentiate between them. In both cases the absorption in the 3-μ region due to the strongly hydrogen-bonded hydroxyl groups would be suppressed (cf. Flett, *loc. cit.*). The chemical evidence indicates that the leuco-compound has structure (XII), which would be expected since (XII) contains two benzenoid rings and (XIII) none.

peri-Aminoanthraquinones analogous to quinizarin also form stable leuco-compounds. The simplest example, leuco-1 : 4-diaminoanthraquinone (XV) (see Flett, *loc. cit.*), is



(XIV)



(XV)

generally prepared by the action of ammonia on leucoquinizarin but can also be obtained by hydrogenation of the diaminoquinone in the cold to form (XIV), which rearranges to (XV) when warmed in absence of air. Reduction of the diaminoquinone with acid stannous chloride eliminates the imino-groups with the formation of leucoquinizarin (G.P. 148,792). The structural features of leuco-1 : 4-diaminoanthraquinone favour the di-imino-configuration but the stable existence of simple di-imines analogous to (II) is unlikely. In fact no detectable change was observed after fusion and rapid cooling of 1 : 4-naphthylenediamine in a vacuum.

Experimental

Fusion of 1 : 2 : 4-*Trihydroxynaphthalene.*—1 : 2 : 4-Trihydroxynaphthalene (4 g.) was placed in a flask (previously flushed with nitrogen) which was evacuated and heated in a bath at 205° for 10 minutes, and then plunged into ice-water and swirled until the melt had solidified. The solid was extracted with warm benzene (thrice) and chloroform, and the combined extracts were treated with charcoal and evaporated under reduced pressure. The dark residue was extracted with hexane (charcoal) from which crystals, m. p. 90° (0·21 g.), separated. Recrystallisation from hexane afforded leaflets of 2 : 3-dihydro-1 : 4-naphthaquinone, m. p. and mixed m. p. 97°. Acetylation gave 1 : 4-diacetoxynaphthalene, m. p. and mixed m. p. 130°.

6-*Methyl*-1 : 4-*naphthaquinone* (by J. M. Lyons).—This compound was first reported in B.P. 324,661 (no analysis or m. p.) and has recently been prepared by Bendz (*Acta Chem. Scand.*, 1951, **5**, 489) but no details are given. A mixture of benzoquinone (10·8 g.) and isoprene (6·8 g.) in glacial acetic acid (60 c.c.) was set aside at room temperature with occasional shaking. After 3 days the solution was treated with charcoal, filtered, warmed to 60°, and oxidised by the addition of a solution of potassium dichromate (25 g.) in water (250 c.c.) containing concentrated sulphuric acid (25 c.c.). The quinone separated on cooling and a further amount was isolated by dilution of the mother-liquor and ether-extraction. Recrystallisation from aqueous acetic acid afforded yellow needles, m. p. 91° (63%). Reductive acetylation yielded 1 : 4-*diacetoxy*-6-*methylnaphthalene*, minute leaflets, m. p. 105° (from aqueous alcohol) (Found : C, 69·9; H, 5·6. $C_{15}H_{14}O_4$ requires C, 69·75; H, 5·5%). The *quinol* was obtained by heating the quinone (0·5 g.) under reflux with stannous chloride (2 g.), concentrated hydrochloric acid (5 c.c.), and water (45 c.c.) for 20 minutes. The solution was filtered (charcoal) and cooled in ice. 1 : 4-Dihydroxy-6-methylnaphthalene separated and was recrystallised from water (containing a little sodium dithionite), forming needles, m. p. 170° (decomp.) (75%) (Found : C, 75·5; H, 5·75. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%).

1 : 2 : 3 : 4-*Tetrahydro*-6-*methyl*-1 : 4-*diketonaphthalene.*—1 : 4-Dihydroxy-6-methylnaphthalene (3 g.) was fused in a vacuum in a bath at 190—200°. After 5 minutes the melt was cooled rapidly in ice and extracted with warm chloroform (3 × 10 c.c.), the extract cooled and filtered, and the solvent removed under diminished pressure. The residue was extracted with boiling light petroleum (b. p. 50—60°; 3 × 20 c.c.), and the combined extracts were concentrated to 15 c.c. The diketone separated on cooling and recrystallised from the same solvent in needles, m. p. 92° (17%) (Found : C, 75·5; H, 5·8. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%). The *bis*-p-*nitrophenylhydrazone* formed brick-red crystals, m. p. 267° (decomp.) (from aqueous dioxan) (Found : C, 62·4; H, 4·5; N, 18·6. $C_{23}H_{30}O_4N_6$ requires C, 62·15; H, 4·55; N, 18·9%).

Condensation of 1 : 2 : 3 : 4-*Tetrahydro*-1 : 4-*diketonaphthalene with Benzaldehyde.*—Dry hydrogen chloride gas was passed into a refluxing solution of the diketone (0·32 g.) and benzaldehyde (0·21 g.)

in ether (20 c.c.) for 2 hours. The ether was then removed under reduced pressure and the crystalline residue recrystallised from glacial acetic acid, forming dark red crystals with a bronze lustre. Its reactions, as described by Fieser and Fieser (*loc. cit.*), were identical with a sample prepared by their method.

Reduction of 3-Substituted 5-Hydroxy-1 : 4-naphthaquinones.—The substituted quinone (0·5 g.) was added to a hot solution of stannous chloride (2·5 g.) in hydrochloric acid (120 c.c.; 4N). After refluxing for 30 minutes the solution was filtered and, while still warm, extracted with chloroform (3 × 5 c.c.). The extract was dried ($CaCl_2$), the solvent removed *in vacuo*, and the residue crystallised from light petroleum (b. p. 50—60°). 1 : 2 : 3 : 4-Tetrahydro-5-hydroxy-1 : 4-diketonaphthalene crystallised in light yellow leaflets, m. p. and mixed m. p. 96—97° (average yield, 30%). Hot acetylation gave 1 : 4 : 5-triacetoxynaphthalene, m. p. and mixed m. p. 130°. Reduction with sodium dithionite gave lower yields. In certain cases it was convenient to dissolve the quinone in a little solvent.

5-Hydroxy-2-methyl-1 : 4-naphthaquinone (Plumbagin).—3-Chloro-5-hydroxy-2-methyl-1 : 4-naphthaquinone (1·1 g.) was heated for 30 minutes with a boiling solution of stannous chloride (5·5 g.)in hydrochloric acid (240 c.c.; 4N). The solution was filtered and, while still warm, extracted repeatedly with chloroform. Hydrogen peroxide (10 c.c.; 100-vol.) was added to the aqueous layer which was then extracted with ether. The ethereal and chloroform extracts were dried ($CaCl_2$) and evaporated separately, and the residues crystallised from aqueous alcohol. Each gave plumbagin as orange-yellow needles, m. p. 77° (0·19 g. by chloroform extraction; 0·15 g. from the ether extract; total yield, 37%).

Reduction of Substituted Naphthazarins.—A mixture of the quinone (1 g.), stannous chloride (5 g.), and hydrochloric acid (150—200 c.c.; 4N) was refluxed until the initial red colour was discharged (15—30 minutes), the solution filtered if necessary and allowed to cool, and the crystalline product collected (yield, 50—90%). In the case of methyl- and anilino-naphthazarin the acid stannous chloride solution was added gradually to a refluxing solution of the quinone in glacial acetic acid (75 c.c.).

1 : 2 : 3 : 4-Tetrahydro-5 : 8-dihydroxy-1 : 4-diketonaphthalene.—Obtained from chloronaphthazarin in yellow needles, this had m. p. and mixed m. p. with an authentic specimen, 152°, and light-absorption maxima at 228, 255, and 294·5 mμ (log ε 4·15, 4·04, and 3·86, respectively) in 95% alcohol.

1 : 2 : 3 : 4-Tetrahydro-5 : 8-dihydroxy-1 : 4-diketo-6-methylnaphthalene.—This was prepared as recorded above or as follows: An intimate mixture of succinic anhydride (5 g.) and toluquinol (6·4 g.) was added in portions to a molten mixture of aluminium chloride (50 g.) and sodium chloride (15 g.), stirred under nitrogen at 180—200°. Heating was continued until the evolution of hydrogen chloride ceased. The melt was allowed to cool (under nitrogen) and dissolved in 4N-hydrochloric acid. The mixture was heated to the b. p., filtered, and allowed to cool. The diketone which separated crystallised from light petroleum (b. p. 100—120°) (charcoal) in orange needles, m. p. 161·5° (6%) (Found: C, 58·9; H, 4·8. $C_{11}H_{10}O_4$ requires C, 59·1; H, 4·9%). Light absorption: Max. at 234, 263, and 394·5 mμ (log ε 4·22, 3·99, and 3·88 respectively) in 95% alcohol. Acetylation with 10 parts of acetic anhydride and a trace of concentrated sulphuric acid in an ice-bath (cf. Zahn and Ochwat, *loc. cit.*) afforded a *diacetate* which separated from methanol in very pale yellow needles, m. p. 169—171° (Found: C, 62·55; H, 5·1. $C_{15}H_{14}O_6$ requires C, 62·2; H, 4·8%).

Determination of structure. The diketone (1·06 g.) in ethyl acetate (100 c.c.; "AnalaR") with platinum oxide (0·1 g.) was hydrogenated until 2 mols. of hydrogen had been taken up. After filtration the solvent was removed at 30° under reduced pressure and the residue, a light brown solid, refluxed for 1 hour with a solution of potassium hydroxide (200 c.c.; 15%), under nitrogen. The resulting solution was kept overnight, then acidified with hydrochloric acid, and an excess of ferric chloride solution added. An orange precipitate of 2-methyl-1 : 4-naphthaquinone appeared, was collected, and dried (m. p. 102°; 78%). Reductive acetylation yielded 1 : 4-diacetoxy-2-methylnaphthalene, m. p. 113° alone or mixed with an authentic specimen. The experiment was repeated with a solution of alcohol (50 c.c.) and hydrochloric acid (200 c.c.; 5N) as dehydrating agent. After 1 hour's boiling the bulk of the alcohol was removed and the residual solution thrice extracted with ether. The combined extracts were dried (Na_2SO_4) and evaporated, to yield a greenish-white solid. This was extracted with boiling light petroleum (b. p. 50—60°). The extract on cooling deposited 2-methylnaphthaquinol, m. p. *ca.* 153° (decomp.), which on acetylation gave 1 : 4-diacetoxy-2-methylnaphthalene, m. p. and mixed m. p. 113° (0·2 g.).

Naphthopurpurin.—The following procedure was found to give better yields than those

quoted by Fieser (*J. Amer. Chem. Soc.*, 1928, **50**, 460). Chloronaphthazarin (1·5 g.) in alcohol (150 c.c.) was heated under reflux with a solution of potassium hydroxide (1·9 g.) in water (100 c.c.) until the colour, originally royal-blue, became cherry-red. Most of the alcohol was removed on the steam-bath and the crude naphthopurpurin (55%) isolated by acidification with dilute sulphuric acid. As Fieser (*loc. cit.*) stated, purification of naphthopurpurin by recrystallisation from benzene or by vacuum-sublimation is difficult, but crude material is satisfactory for reduction to the leuco-compound.

1 : 2 : 3 : 4-*Tetrahydro*-5 : 6 : 8-*trihydroxy*-1 : 4-*diketonaphthalene*.—This reduction *product* crystallised from benzene in yellowish-orange needles, m. p. 223° (Found : C, 57·8; H, 4·0. $C_{10}H_8O_5$ requires C, 57·7; H, 3·85%). Light absorption : Max. at 250, 263·5, 303, 356, and 399 mμ (log ε 4·09, 4·09, 3·93, 3·91, and 3·98 respectively) in 95% alcohol. The infra-red spectrum shows a hydroxyl band at 3493 cm.$^{-1}$ and a carbonyl band at 1637 cm.$^{-1}$.

Determination of structure. The diketone (0·4 g.) in ethyl acetate (50 c.c.; "AnalaR") with platinum oxide (0·1 g.) was hydrogenated until 1 mol. of hydrogen was taken up. At this stage the solution was yellow with an intense green fluorescence. After filtration the solvent was removed at 30° under reduced pressure, leaving a light brown solid. This was immediately heated in a boiling solution of potassium hydroxide (15 g.) in water (100 c.c.) for 30 minutes. The solution, at first yellow, became blood-red very rapidly. When cool, it was acidified with dilute sulphuric acid and extracted with chloroform. Removal of the solvent gave an orange solid, m. p. 195—200° (decomp.) (40%), not depressed by admixture with 2 : 5-dihydroxy-1 : 4-naphthaquinone; its diacetate had m. p. 151·5° alone or mixed with an authentic specimen.

6-*Anilino*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dihydroxy*-1 : 4-*diketonaphthalene*.—Anilinonaphthazarin was prepared according to Fierz-David and Stockar (*Helv. Chim. Acta*, 1943, **26**, 95), who did not record the m. p. Our material crystallised from chlorobenzene in dark green small plates, m. p. 233° (Found : C, 68·2; H, 3·9; N, 5·4. Calc. for $C_{16}H_{11}O_4N$: C, 68·3; H, 3·9; N, 5·0%). The *diketone* obtained on reduction crystallised from light petroleum (b. p. 100—120°) in yellow needles, m. p. 173—173·5° (Found : C, 67·6; H, 4·25; N, 5·0. $C_{16}H_{13}O_4N$ requires C, 67·8; H, 4·6; N, 4·95%). Light absorption : Max. at 265, 307·5, 339, and 417 mμ (log ε 4·29, 3·94, 3·86, and 4·16 respectively) in 95% alcohol.

1 : 4-*Dihydroxyanthracene*.—1 : 4-Anthraquinone (1·5 g.) in ether (30 c.c.) was reduced by shaking it with sodium dithionite (3 g.) in water (40 c.c.). The ethereal layer was dried ($CaSO_4$), the solvent removed, and the residue crystallised from aqueous alcohol (containing a little dithionite), forming pale yellow needles, m. p. 190° (decomp.; darkening from 175°) (84%) of the *dihydroxy*-compound (Found : C, 79·5; H, 5·1. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%).

1 : 2 : 3 : 4-*Tetrahydro*-1 : 4-*diketoanthracene*.—1 : 4-Dihydroxyanthracene (1·2 g.) was heated for a few minutes at 210—220° in a vacuum and the melt cooled rapidly in ice. The solid was extracted with hot chloroform (3 × 10 c.c.), the solvent removed under reduced pressure, and the residue crystallised first from alcohol and then from light petroleum (b. p. 80—90°). The *diketone* separated in pale yellow leaflets, m. p. 170—171° (50%) (Found : C, 79·8; H, 4·7. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%). The *bis*-p-*nitrophenylhydrazone* crystallised from aqueous dimethylformamide in rust-red needles, m. p. 295° (decomp.) (Found : C, 64·5; H, 4·3; N, 17·7. $C_{26}H_{20}O_4N_6$ requires C, 65·0; H, 4·2; N, 17·5%).

Reduction of Purpurin.—Zinc dust (10 g.) was stirred into a suspension of purpurin (0·5 g.) in glacial acetic acid (50 c.c.) and stirring was continued until no further lightening of colour was apparent. Subsequent operations were carried out under nitrogen. The mixture was filtered directly into concentrated hydrochloric acid (50 c.c.), and the filtrate refluxed for 30 minutes, cooled, and poured into cold water. The orange precipitate (0·35 g.) which formed crystallised from ethyl alcohol in orange-red needles, m. p. 195° alone or mixed with an authentic specimen of quinizarin.

Reduction of 2-*Chloroquinizarin*.—2-Chloroquinizarin (1 g.), suspended in glacial acetic acid (50 c.c.), was stirred with zinc dust (10 g.) at room temperature until all the quinone had dissolved. After filtration the solution was diluted with cold water, whereupon flocculent yellow material was precipitated. This crystallised from light petroleum in yellow-orange needles, m. p. 157°, identical with leucoquinizarin.

Leuco-1 : 4 : 5 : 8-*tetrahydroxyanthraquinone*.—Commercial material was recrystallised from dioxan, forming bronze leaflets m. p. *ca.* 300°. The *tetra-acetate* was obtained by stirring the leuco-compound (0·3 g.) into an ice-cold mixture formed by slow addition of acetyl chloride (0·9 c.c.) to pyridine (5 c.c.) with cooling. After 15 minutes' stirring the yellow suspension was set aside for 1 hour in the ice-bath and then collected. The product crystallised from glacial acetic acid in minute yellow needles, m. p. 266° (decomp.) (Found : C, 59·7; H, 3·8; Ac, 40·85.

$C_{22}H_{18}O_{10}$ requires C, 59·7; H, 4·1; Ac, 38·9%). The *dimethyl ether*, formed by treating a suspension of the leuco-compound (0·5 g.) in chloroform (100 c.c.) with ethereal diazomethane (from 1·2 g. of nitrosomethylurea) at −10°, crystallised from alcohol in dark reddish-brown crystals, m. p. 200° (decomp.) (Found: C, 63·25; H, 4·6; OMe, 18·5. $C_{16}H_{14}O_6$ requires C, 63·55; H, 4·7; OMe, 20·5%).

1 : 4-*Naphthylenediamine*.—4-Nitro-1-naphthylamine (8 g.) in ethyl acetate (500 c.c.) was hydrogenated with Raney nickel as catalyst. After filtration the solution was concentrated, to 80 c.c., diluted with light petroleum (200 c.c.), and cooled in ice. The diamine separated in light yellow needles, m. p. 121° (80%).

Leuco-1 : 4-*diaminoanthraquinone*.—1 : 4-Diaminoanthraquinone (0·5 g.) in dimethylformamide (15 c.c.) was hydrogenated over Adams's catalyst, the purple solution becoming brownish-red. When 1 mol. of hydrogen was absorbed, the hydrogen in the flask was displaced by nitrogen and the mixture warmed for 30 minutes on the steam-bath and then filtered into cold water (100 c.c.). After cooling in ice, the product was collected as dark crystals with a green lustre, m. p. 271° (decomp.) not depressed by a sample prepared from leucoquinizarin.

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