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RANEY NICKEL REDUCTIONS—VIII*

A SYNTHESIS OF 1:2-BENZANTHRACENE AND ITS 3'-METHYL AND 4-METHYL DERIVATIVES

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Abstract—1:2-Benzanthracene and the 3'-methyl derivative have been prepared by Raney nickel reduction of the sulphuric esters of the leuco derivatives of 1:2-benzanthraquinone and 4'-chloro-3'-methyl-1:2-benzanthraquinone, followed by dehydrogenation. 3-Hydroxy-1:2-benzanthraquinone was methylated in the 4-position by formaldehyde, sodium hydrosulphite and sodium hydroxide solution (the Marschalk reaction). Simultaneous reduction of the nuclear hydroxyl and quinone groups was effected by Raney nickel reduction of the trisulphuric ester of 3:9:10-trihydroxy-4-methyl-1:2-benzanthracene, and the resultant hexahydro-4-methyl-1:2-benzanthracene was dehydrogenated to 4-methyl-1:2-benzanthracene. The preparation of 3:4:9:10-dibenzopyrene from Mayvat brilliant red AF by Raney nickel reduction of the sulphuric ester of the leuco derivative and subsequent dehydrogenation is described.

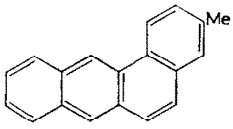
THE action of Raney alloy and sodium hydroxide solution on the sulphuric ester of the leuco derivative is a general method[1] for the conversion of quinones to the corresponding hydrocarbon derivatives, which is a useful supplement to known methods such as zinc dust distillation and reduction by zinc, zinc chloride and sodium chloride.[2] Thus 3:4:8:9-dibenzopyrene can be readily prepared from the commercially available disodium salt (Indigosol golden yellow IGK) of the disulphuric ester of the leuco derivative of 3:4:8:9-dibenzopyrene-5:10-quinone (Indanthrene golden yellow GK); treatment with Raney alloy and sodium hydroxide solution gives a mixture of hydrogenated dibenzopyrenes, which is dehydrogenated to 3:4:8:9-dibenzopyrene by iodine and sodium acetate in boiling nitrobenzene.[1] This procedure was then employed for the synthesis of 1-azanaphthacene from 2-aminoanthraquinone via 1-azanaphthacene-6:11-quinone and the disulphuric ester of its leuco derivative.[3] 1:2-Benzanthracene derivatives and 3:4:9:10-dibenzopyrene, which are of interest in connexion with carcinogenic studies, have now been similarly prepared from the appropriate quinones.

The product obtained by heating the disodium salt of the disulphuric ester of 1:2-benzanthrahydroquinone with Raney alloy and sodium hydroxide solution was an octahydrobenzanthracene, dehydrogenation of which with 2:3-dichloro-5:6-dicyanobenzoquinone[4] or chloranil gave 1:2-benzanthracene; the overall yield from benzanthraquinone was 70 per cent. Benzanthracene was also obtained in similar yield by reduction of benzanthraquinone with aluminium tri*cyclo*hexoxide in *cyclo*hexanol.[5] Elbs prepared impure benzanthracene by reduction of the quinone with

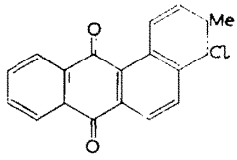
* Part VII *J. Sci. Ind. Res.* **B15**, 279 (1956).
[1] N. B. Desai, V. Ramanathan, and K. Venkataraman, *J. Sci. Ind. Res.* **B14**, 330 (1955).
[2] E. Clar, *Ber. Dtsch. Chem. Ges.* **72**, 1645 (1939).
[3] N. B. Desai, V. Ramanathan and K. Venkataraman, *J. Sci. Ind. Res.* **B15**, 279 (1956).
[4] E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.* 3569 (1954).
[5] S. Coffey and V. Boyd, *J. Chem. Soc.* 2468 (1954).

zinc and ammonia;[6] Badger and Cook[7,8] reduced the quinone successively with stannous chloride and acid to a resinous anthrol and then with zinc dust and sodium hydroxide to the hydrocarbon which required purification through the maleic anhydride adduct.

3′-Methyl-1:2-benzanthracene (I) was first synthesised by Cook[9] in 5–10 per cent yield by the pyrolysis of 1-benzoyl-2:6-dimethylnaphthalene, and subsequently by Newman and Gaertner[8] by a laborious process involving several steps. Hydrogenolysis of the disulphuric ester of the leuco derivative of 4′-chloro-3′-methyl-1:2-benzanthraquinone (II), followed by dehydrogenation, provides a much more convenient route to (I) in an overall yield of 40 per cent calculated on the phthalic anhydride used. 1-Chloro-2-methylnaphthalene condensed with phthalic anhydride in presence of aluminium chloride in the unsubstituted ring in the 6-position, as Scholl[10] has shown in the case of 2-chloro-1-methylnaphthalene, and cyclisation with sulphuric acid gave (II).



I

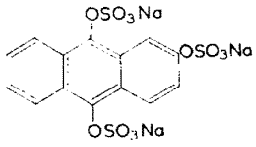


II

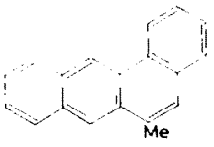
Since our projected synthesis of 4-methyl-1:2-benzanthracene (IV) involved the reduction of a β-hydroxyl group in an anthraquinone derivative, the reduction of 2-hydroxyanthraquinone to anthracene was first studied. The action of copper bronze on 2-hydroxyanthraquinone in chlorosulphonic acid and pyridine, followed by sodium hydroxide solution, gave a quantitative yield of the trisodium salt (III) of the trisulphuric ester of 2-hydroxyanthrahydroquinone. Treatment of (III) with Raney alloy and sodium hydroxide solution and dehydrogenation of the product with selenium gave anthracene in a yield of about 85 per cent. 3-Hydroxy-4-methylbenzanthraquinone (V) was then reduced to (IV) via the trisulphuric ester of the leuco derivative and dehydrogenation of the hexahydro-4-methylbenzanthracene obtained by hydrogenolysis with Raney alloy and alkali. For the preparation of (V) we used the Marschalk reaction,[11] condensing 3-hydroxybenzanthraquinone with formaldehyde and aqueous sodium hydroxide. An improvement in Fieser's procedure for the preparation of 3-hydroxybenzanthraquinone,[12] starting from 1-methoxynaphthalene and phthalic anhydride, is to oxidise 3-methoxy-1:2-benz-10-anthrone to 3-methoxybenzanthraquinone with sodium dichromate and acetic acid and demethylate with alumunium chloride–sodium chloride at 130–140°. The formation of (IV) by pyrolysis of 1-benzoyl-2:3-dimethylnaphthalene was first described by Fieser and Peters;[13] (IV) was synthesised later by Fieser and Jones[14,8] from 6-methyltetralin and phthalic anhydride. More recent syntheses of (IV) involve the

[6] K. Elbs, *Ber. Dtsch. Chem. Ges.* **19**, 2209 (1886).
[7] G. M. Badger and J. W. Cook, *J. Chem. Soc.* 802 (1939).
[8] M. S. Newman and V. R. Gaertner, *J. Amer. Chem. Soc.* **72**, 264 (1950).
[9] J. W. Cook, *J. Chem. Soc.* 456 (1932).
[10] R. Scholl, C. Seer and A. Zinke, *Monatshchrift* **41**, 583 (1921).
[11] C. Marschalk, *Bull. Soc. Chim.* **3**, 1545 (1936).
[12] L. F. Fieser and E. M. Dietz, *J. Amer. Chem. Soc.* **51**, 3141 (1929).
[13] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.* **54**, 3742 (1932).
[14] L. F. Fieser and R. N. Jones, *J. Amer. Chem. Soc.* **60**, 1940 (1938).

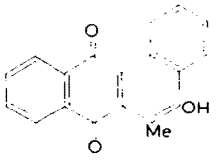
condensation of 9-methyl-1:2:3:4-tetrahydrophenanthrene with succinic anhydride[15] and the condensation of 2-allyl*cyclo*hexanone with tetralin.[16] The present procedure utilises more readily available intermediates; it is also applicable to the synthesis of other 4-alkylbenzanthracenes.



III



IV



V

The preparation of the potent carcinogen, 3:4:9:10-dibenzopyrene, from the 5:8-quinone by reduction with aluminium tri*cyclo*hexoxide[5] was described in a recent communication.[17] An alternative and equally convenient method is to convert Mayvat brilliant red AF, which is mainly a dibromo-3:4:9:10-dibenzopyrene-5:8-quinone, into the sulphuric ester of the leuco derivative, reduce this ester with Raney alloy and sodium hydroxide solution, and dehydrogenate the mixture of hydrogenated hydrocarbons thus obtained with selenium.

EXPERIMENTAL

Hydrogenolysis of the disodium salt (VI) *of the disulphuric ester of benzanthrahydroquinone.* Chlorosulphonic acid (5 ml) was slowly run into pyridine (50 ml) below 20°. The mixture was heated to 60°, 1:2-benzanthraquinone (5 g) was added, followed by an equal weight of copper bronze. After stirring at 60–65° for 3 hr, the mixture was poured into 150 ml of 10% NaOH solution and filtered from copper. From the filtrate, pyridine was removed by steam distillation, the residue was cooled, just acidified (Congo Red) with HCl, and filtered. The filtrate, which exhibited a violet fluorescence on dilution, contained the theoretical amount of (VI), as determined by ceric sulphate oxidation.[18] An aliquot part of this solution, containing 6·2 g of (VI), corresponding to 3·5 g of the quinone, was made up to 620 ml, and sodium hydroxide (62 g) added. The alkaline solution was heated on a boiling water-bath and Raney alloy (62 g) added in the course of 2 hr. After stirring for 2 hr more, the mixture was cooled, filtered, the nickel residue deactivated with HCl and extracted with alcohol. Removal of the solvent gave 2·7 g of a pale yellow viscous oil, b.p. 175–8°/0·7 mm (Found: C, 91·3; H, 8·3. $C_{18}H_{20}$ requires: C, 91·5; H, 8·5%).

1:2-*Benzanthracene.* The above hydrogenated hydrocarbon (1 g) was dissolved in benzene (25 ml), 2:3-dichloro-5:6-dicyanobenzoquinone (5 g) in 50 ml benzene was added, and the mixture refluxed for 2 hr. After dilution with petroleum ether, the precipitated quinol was filtered and the filtrate run through a short column of alumina. The colourless percolate, which had a blue fluorescence, on removal of the solvent, gave the aromatic hydrocarbon, which crystallised from alcohol in shining leaflets (0·9 g), m.p. 159° (Found: C, 94·6; H, 5·3. $C_{18}H_{12}$ requires: C, 94·7; H, 5·3%). The m.p. quoted in the literature[7] is 158–159°.

Reduction of 1:2-*benzanthraquinone with aluminium tri*cyclo*hexoxide.* 1:2-Benzanthraquinone (1 g) was refluxed with a solution of aluminium (1 g) in *cyclo*hexanol (20 ml) for 40 hr. The solvent was distilled off, the residue poured into 3% NaOH solution, and filtered. The alkali-insoluble residue was extracted with alcohol. The alcohol extract, on concentration and cooling, gave pale yellow plates (0·7 g), m.p. 151–2°. Recrystallisation from alcohol gave almost colourless, shining plates, m.p. 159°, undepressed when mixed with 1:2-benzanthracene obtained in the previous experiment.

2-(5′-*Chloro*-6′-*methyl*-2′-*naphthoyl*)*benzoic acid.* To a clear solution of phthalic anhydride

[15] W. E. Bachman, M. W. Cronyn and W. S. Struve, *J. Org. Chem.* **12**, 596 (1947).
[16] O. P. Vig, S. V. Kessar and S. M. Mukherji, *Nature, Lond.* **174**, 834 (1954).
[17] B. D. Tilak, M. K. Unni and K. Venkataraman, *Tetrahedron* **3**, 62 (1958).
[18] K. Venkataraman, *The Chemistry of Synthetic Dyes* Vol. II, p. 1058. Academic Press, New York (1952).

(8·5 g) and 1-chloro-2-methylnaphthalene (9·8 g) in acetylene tetrachloride (50 ml) was added anhydrous aluminium chloride (15 g) in four lots in 1 hr at room temp. The mixture was stirred for 8 hr, left overnight, poured into ice-cold HCl, and the solvent removed by steam distillation. The resinous residue was washed with water, dissolved in Na_2CO_3 solution and reprecipitated with acid, when the keto acid was obtained as a granular mass (16 g), m.p. 90–100° after softening at 60°. The substance was uncrystallisable, but cyclisation yielded a readily crystallisable anthraquinone derivative. When the acid was purified by running the dark brown solution in benzene through a short column of Florex, recovering the pale yellow product from the percolate, diluting the alcoholic solution with water, and letting stand in a refrigerator for a few days; it was obtained as a buff coloured powder, melting indefinitely at about 120° (Found: C, 70·1; H, 4·6; Cl, 9·4. $C_{19}H_{13}O_3Cl$ requires: C, 70·4; H, 4·0; Cl, 11·0%). Fieser and Peters[13] encountered similar difficulty in crystallising the condensation products of phthalic anhydride and methylnaphthalenes.

4′-Chloro-3′-methylbenzanthraquinone (II). A solution of 2-(5′-chloro-6′-methyl-2′-naphthoyl)-benzoic acid (10 g) and boric acid (10 g) in conc. H_2SO_4 (100 ml) was stirred at 60–70° for 4 hr. On pouring into water the greenish yellow precipitate was filtered, washed with dilute NaOH solution and dried (6·5 g). It crystallised from benzene in elongated yellow needles, m.p. 227° (Found: C, 74·4; H, 3·5; Cl, 11·2. $C_{19}H_{11}O_2Cl$ requires: C, 74·3; H, 3·6; Cl, 11·6%).

Disodium salt of the disulphuric ester of 4′-chloro-3′-methylbenzanthrahydroquinone. The reduction and esterification were carried out as in the case of benzanthraquinone; 6·5 g of the quinone (II) gave a solution containing 8·7 g of the disodium salt of the ester (80% yield), as determined by the ceric sulphate method.[18]

Hydrogenolysis of the disodium salt of the disulphuric ester of 4′-chloro-3′-methylbenzanthrahydroquinone. A solution containing the ester (8 g) was made up to 800 ml and sodium hydroxide (80 g) added. The alkaline solution was heated on a water-bath and Raney alloy (80 g) added in 2 hr. After stirring for 3 hr more, the mixture was cooled and filtered, and the nickel residue, after deactivation with acid, extracted with alcohol. The alcohol extract yielded 3·6 g of a viscous oil, b.p. 205–10°/2 mm (Found: C, 91·8; H, 8·3. $C_{19}H_{20}$ repuires: C, 91·9; H, 8·1%).

3′-Methyl-1:2-benzanthracene (I). A mixture of the hydrogenated hydrocarbon (2 g) and 2:3-dichloro-5:6-dicyanobenzoquinone (7·5 g) was refluxed with benzene (100 ml) for 2 hr. The precipitated quinol was filtered off and the filtrate run through a short column of alumina. The pale yellow percolate on removal of the solvent gave yellow plates, which crystallised from alcohol in shining pale yellow plates (1·75 g), m.p. 160° (Found: C, 93·8; H, 6·1. $C_{19}H_{14}$ requires: C, 94·2; H, 5·8%). The picrate crystallised from alcohol in red needles, m.p. 144°. Cook[9] quotes m.p. 160° for the hydrocarbon and 144–45° for the picrate.

Hydrogenolysis of the trisodium salt of the trisulphuric ester of 2-hydroxyanthrahydroquinone. Chlorosulphonic acid (6·5 ml) was slowly run into a mixture of 2-hydroxyanthraquinone (5 g) and pyridine (60 ml) below 20°. After stirring the paste at 20° for 30 min, the temp. was raised to 60° and copper bronze (5 g) added. Stirring was continued at this temp. for 3 hr, the reaction mixture then poured into 10% NaOH solution (250 ml) and filtered. From the filtrate pyridine was removed by steam distillation and the solution filtered again to remove the precipitated impurities. The filtrate was made up to 1100 ml, made alkaline with 110 g NaOH, and heated on a water-bath with Raney alloy (110 g) added in the course of 2 hr. After heating for a further 2 hr, the mixture was filtered, the nickel residue deactivated with acid and extracted with alcohol. The alcohol extract on removal of solvent gave a colourless product (3·3 g) which crystallised from aqueous acetic acid in colourless plates, m.p. 93° (Found: C, 92·1; H, 8·0. $C_{14}H_{14}$ requires: C, 92·3; H, 7·7%). The tetrahydroanthracene (3 g) was mixed with selenium (10 g) and heated to 300° gradually. The product was extracted with alcohol leading to colourless plates (2·7 g), m.p. 216°, undepressed when mixed with anthracene.

3-Methoxy-1:2-benzanthraquinone. 3-Methoxy-1:2-benz-10-anthrone was prepared according to Fieser and Dietz, starting from 1-methoxynaphthalene and phthalic anhydride.[12] The anthrone (40 g) was suspended in glacial acetic acid (200 ml) and treated with sodium dichromate (40 g) dissolved in water (20 ml). The mixture was stirred on a water-bath for 15 min, during which the reaction mixture boiled vigorously. Dilution with cold water gave a bright orange-brown precipitate of the quinone (33 g). Crystallisation from benzene gave brown needles, m.p. 188° (Fieser and Dietz, m.p. 188·5°).

3-Hydroxy-1:2-benzanthraquinone. An intimate mixture of aluminium chloride (50 g) and sodium

chloride (10 g) was melted on a free flame. 3-Methoxybenzanthraquinone (10 g) was quickly added to the melt and the mixture stirred with a thermometer at 140–45° for 2 min. The melt was poured into ice-cold 5% HCl, when the hydroxy compound separated as an orange-brown precipitate (9·5 g). The product dissolved in alkali with a deep purple colour, which changed to orange-red on adding sodium hydrosulphite. The acetyl derivative, prepared by refluxing with acetic anhydride and a drop of H_2SO_4, crystallised from benzene in stout yellow needles, m.p. 232° (Fieser and Dietz, m.p. 232°). The acetyl derivative was hydrolysed by dissolving in cold conc. H_2SO_4 and pouring into water. The hydroxy compound crystallised from dioxane in orange-red plates, decomposing at about 250° (Found: C, 78·6; H, 3·8. $C_{18}H_{10}O_3$ requires: C, 78·8; H, 3·7%). Fieser and Dietz have not recorded the m.p. or analysis of this compound.

3-*Hydroxy*-4-*methyl*-1:2-*benzanthraquinone* (V). 3-Hydroxybenzanthraquinone (6 g) was dissolved in NaOH solution (600 ml) and vatted with 15 g of sodium hydrosulphite at 40–45° for 10 min in a nitrogen atmosphere. The solution was treated with 37·5% formalin (4·2 ml) and stirred on a water-bath for 1 hr. The mixture was cooled and air-oxidised; acidification gave an orange-brown precipitate (4·8 g). The acetyl derivative crystallised from benzene-hexane in thin yellow needles, m.p. 203° (Found: C, 76·7; H, 4·1. $C_{21}H_{14}O_4$ requires: C, 76·4; H, 4·3%). The methyl ether, prepared by the action of dimethyl sulphate and NaOH solution, crystallised from alcohol in thin yellow needles, m.p. 146° (Found: C, 79·3; H, 4·5. $C_{20}H_{14}O_3$ requires: C, 79·5; H, 4·6%). The acetyl derivative was hydrolysed by cold conc. H_2SO_4; the hydroxy compound (V) crystallised from dioxane in orange-brown platelets, m.p. 228° (Found: C, 79·1; H, 4·4. $C_{19}H_{12}O_3$ requires: C, 79·2; H, 4·2%).

Hydrogenolysis of the trisodium salt of the trisulphuric ester of 3-*hydroxy*-4-*methylbenzanthrahydroquinone.* Chlorosulphonic acid (6 ml) was slowly run into a mixture of 3-hydroxy-4-methylbenzanthraquinone (V, 5 g) and pyridine (50 ml) below 20°. The paste was stirred at 20° for 30 min, the temp. then raised to 60° and copper bronze (5 g) added. After stirring the mixture at this temp. for 3 hr, it was poured into 200 ml of 10% NaOH solution and filtered. The filtrate, after removal of pyridine, was cooled, just acidified and filtered from brown impurities. The filtrate, which was almost colourless with a blue fluorescence, was used for hydrogenolysis. The solution was made up to 1040 ml, and heated at 70° with sodium hydroxide (104 g) and Raney alloy (104 g) gradually added during 3 hr. The mixture was then stirred on a boiling water-bath for 3 hr, cooled and filtered. The nickel residue was deactivated with dilute HCl and extracted with alcohol. The brown viscous oil, obtained after the removal of alcohol, was dissolved in hexane and run through a short column of alumina. The colourless percolate on removal of solvent gave an almost colourless oil (3·2 g), b.p. 205–8°/2 mm (Found: C, 91·9; H, 8·1. $C_{19}H_{20}$ requires: C, 91·9; H, 8·1%).

4-*Methyl*-1:2-*benzanthracene* (IV). The hydrogenated hydrocarbon (0·44 g), 2:3-dichloro-5:6-dicyanobenzoquinone (0·6 g) and benzene (40 ml) were refluxed for 30 min. More quinone (0·6 g) was added, the mixture refluxed for 2 hr, filtered, and the brown filtrate run through a short column of alumina. The clear yellow percolate on removal of solvent gave a brown oil, which was dissolved in alcohol. The alcoholic solution was concentrated and treated with picric acid. On cooling red-brown needles of the picrate crystallised. After two crystallisations from the same solvent it melted at 148° (Found: C, 64·2; H, 3·6; N, 9·2. $C_{25}H_{17}N_3O_7$ requires: C, 63·7; H, 3·6; N, 8·9%). The picrate was decomposed with dilute ammonia and the hydrocarbon crystallised from alcohol containing a little benzene; the colourless needles had m.p. 124° (Found: C, 94·0; H, 6·2. $C_{19}H_{14}$ requires: C, 94·2; H, 5·8%). Fieser and Jones[14] cite m.p. 124–124·6°.

Sulphuric ester of the leuco derivative of Mavvat brilliant red AF. Chlorosulphonic acid (5 ml) was slowly run into pyridine (50 ml) below 20°. The temp. was then raised to 50° and the finely divided dye (5 g) added to it, followed by copper bronze (5 g). After stirring the mixture at 60–65° for 3 hr, it was poured into 200 ml of water containing 20 g NaOH and filtered. The solution obtained after the removal of pyridine by steam distillation of the filtrate contained ester corresponding to 4·5 g of the dye. The estimation was carried out by oxidising an aliquot part with ceric sulphate and weighing the precipitated dye.[18]

Reduction of the sulphuric ester of the leuco derivative of Mavvat brilliant red AF. The solution containing ester (sodium salt) corresponding to 3·0 g of the dye was made up to 500 ml and sodium hydroxide (50 g) added. The alkaline solution was heated on a water-bath and Raney alloy (50 g) added in the course of 2 hr. After stirring for 2 hr more, the reaction mixture was filtered. The nickel was deactivated and extracted with benzene. The benzene extract, after running through a

short column of alumina, gave on concentration and cooling pale yellow plates (1·4 g). The product (1 g) was dissolved in hexane and chromatographed on alumina. The chromatogram was developed and eluted with hexane–benzene mixture. The first fraction, colourless with a faint blue fluorescence, gave colourless needles (0·16 g), m.p. 175° (Found: C, 93·5; H, 7·1. $C_{24}H_{22}$ requires: C, 92·9; H, 7·1%). The second fraction, colourless with a blue fluorescence, gave colourless shining plates (0·76 g), m.p. 223° (Found: 93·8; H, 5·7. $C_{24}H_{18}$ requires: C, 94·1; H, 5·9%). The product (0·6 g) was mixed with selenium (1·2 g) and heated at 290–300° for 3 hr. The mass was cooled and extracted with benzene. The benzene extract, after running through a short column of alumina, led to shining yellow plates (0·45 g), m.p. 281° (Found: C, 94·9; H, 4·7. $C_{24}H_{14}$ requires: C, 95·3; H, 4·7%). Identity with 3:4:9:10-dibenzopyrene was proved by its absorption spectrum and mixed m.p. with the hydrocarbon obtained by the reduction of 3:4:9:10-dibenzopyrene-5:8-quinone with aluminium tri*cyclo*hexoxide.[17]

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