Tetrahedron, 1958, Vol. 3, pp. 62–67. Pergamon Press Ltd., London

ANTHRAQUINONE AND ANTHRONE SERIES—XXII*

3:4:9:10-DIBENZOPYRENE AND PENTAPHENE FROM INDANTHRENE SCARLET 4G AND MAYVAT BRILLIANT RED AF

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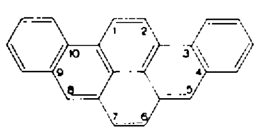
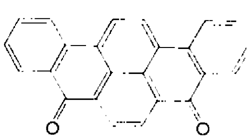
Abstract—Mayvat brilliant red AF has been identified as a halogenated derivative of 3:4:9:10-dibenzopyrene-5:8-quinone (II), the latter being obtained by dehalogenation of Mayvat brilliant red AF or Indanthrene scarlet 4G with Raney nickel, aqueous sodium hydroxide and hydrogen. Reduction of (II) with aluminium tri*cyclo*hexoxide gave 3:4:9:10-dibenzopyrene (I), a potent carcinogen, which was isolated by Bonnet and Neukomm from tobacco smoke. Oxidation of 3:4:9:10-dibenzopyrene-5:8-quinone with chromic acid in glacial acetic acid gave pentaphene-5:14:8:13-diquinone (V). Reduction of (V) with aluminium tri*cyclo*hexoxide yielded pentaphene (VI). Condensation of (V) with hydrazine gave 1:2-diaza-3:4:9:10-dibenzopyrene-5:8-quinone (VII), reduction of which with aluminium tri*cyclo*hexoxide gave 1:2-diaza-3:4:9:10-dibenzopyrene (VIII).

According to a report, Buu-Hoï isolated 3:4:9:10-dibenzopyrene (I) from tobacco smoke and found that "when the substance was injected into 4000 mice, each of them developed cancer. In some cases the growth took only 42 days to show itself. Half a mg was the amount given." The presence of 3:4:9:10-dibenzopyrene (I) in considerable quantity in the neutral fractions of tobacco tar was in fact demonstrated by Bonnet and Neukomm;[1] Lacassagne *et al.*[2] compared the carcinogenic activities of (I) and its 5-methyl and 5:8-dimethyl derivatives, and observed that, after a subcutaneous injection of 0·6 mg of one of the three compounds, (I) produced sarcoma on the 42nd day in eleven mice. The 5-methyl derivative produced sarcoma in three out of ten mice after 150 days, and the 5:8-dimethyl derivative was inactive or feebly active.



(I)



(II)

3:4:9:10-Dibenzopyrene (I) was prepared by Scholl and Neumann[3] by distilling the 5:8-quinone (II) with zinc dust; Clar[4] obtained a yield of about 85 per cent by his technique of distillation with a mixture of zinc dust, zinc chloride and sodium chloride, but Buu-Hoï and Lavit[5] have reported a yield of 53·3 per cent.

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* Part XXI *J. Sci. Ind. Res.* B **16** 392 (1957).

[1] J. Bonnet and S. Neukomm, *Helv. Chim. Acta* **39**, 1724 (1956).

[2] A. Lacassagne, F. Zaideta, N. P. Buu-Hoï and H. Chalvet, *C. R. Acad. Sci., Paris* **244**, 273 (1957).

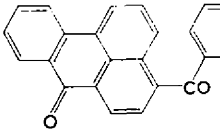
[3] R. Scholl and H. Neumann, *Ber. Dtsch. Chem. Ges.* **55**, 118 (1922).

[4] E. Clar, *Ber. Dtsch. Chem. Ges.* **72**, 1645 (1939).

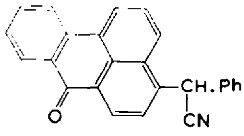
[5] N. P. Buu-Hoï and D. Lavit, *Rec. Trav. Chim. Pays-Bas* **75**, 1194 (1956).

The quinone (II) can be prepared by the Scholl cyclisation of 1:4-dibenzoylnaphthalene or 4-benzoylbenzanthrone (III) with aluminium chloride.[3,6] An excellent method for the preparation of 4-benzoylbenzanthrone (III) is the condensation of benzanthrone with benzyl cyanide in presence of an alkali, followed by oxidative hydrolysis of the product (IV).[7]

Indanthrene scarlet 4G has been stated[6] to be the dibromo derivative of (II) and through the courtesy of Cassella Farbwerke, Mainkur, we obtained a sample of the dye, which contained both chlorine and bromine. It was dehalogenated by being shaken with sodium hydroxide solution, Raney nickel and hydrogen, and yielded the quinone (II). Anthraquinone undergoes reduction to 1:2:3:4-tetrahydroanthraquinone on being heated with Raney nickel and sodium hydroxide solution at water-bath temperature,[8] but the quinone (II) was unaffected under these conditions. Indanthrene scarlet 4G and Mayvat brilliant red AF were merely dehalogenated to the quinone (II) on being heated with Raney nickel and sodium hydroxide solution. Reduction of (II) with aluminium tri*cyclo*hexoxide in *cyclo*hexanol[9] readily gave the hydrocarbon (I), m.p. 281°, in 70 per cent yield. The general method for the reduction of quinones to hydrocarbons by treatment of the sulphuric ester of the leuco derivative with Raney nickel and sodium hydroxide[10] was also applicable, and will be described separately. A preliminary examination of Mayvat brilliant red AF, which dyes cotton a brilliant bluish red shade from a blood-red vat, showed that it was a halogenated quinone containing chlorine and bromine, but no nitrogen or sulphur. The dye, after removal of water-soluble matter, was found to be chromatographically homogeneous, when molten naphthalene was used as solvent and alumina as adsorbent. It crystallised from *o*-dichlorobenzene in red needles and sublimed without decomposition. Dehalogenation of the dye with sodium hydroxide, Raney nickel and hydrogen yielded the parent quinone (A), crystallising in red needles, m.p. 373°, identical with the quinone (II) obtained by dehalogenation of Indanthrene scarlet 4G.



(III)



(IV)

The dehalogenated quinones from both Mayvat brilliant red AF and Indanthrene scarlet 4G gave identical derivatives by reductive acetylation and by reductive benzoylation.

Reduction of the quinone (A) with aluminium tri*cyclo*hexoxide[9] in *cyclo*hexanol gave 3:4:9:10-dibenzopyrene, identical with the hydrocarbon obtained from (II), as shown by the analysis, m.p. and mixed m.p. and absorption spectrum. On oxidation of the hydrocarbon with boiling aqueous chromic acid, the quinone (II) was obtained.

[6] K. Venkataraman, *The Chemistry of Synthetic Dyes*, Vol. II, p. 955. Academic Press, New York (1952).

[7] *D.R.P.* 501, 082; *D.R.P.* 568, 783; N. Campbell *et al.*, *J. Chem. Soc.* 1816 (1950); *Ibid* 3429 (1953).

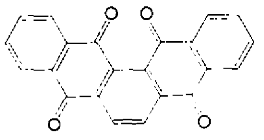
[8] V. Ramanathan, B. D. Tilak and K. Venkataraman, *Proc. Indian Acad. Sci.* A **38**, 161 (1953).

[9] S. Coffey and V. Boyd, *J. Chem. Soc.* 2468 (1954).

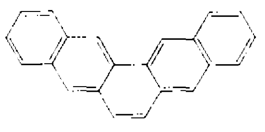
[10] N. B. Desai, V. Ramanathan and K. Venkataraman, *J. Sci. Ind. Res.* B **14**, 330 (1955); *Ibid.* B **15**, 279 (1956).

The quinone (A) from Mayvat brilliant red AF was unaffected by oxidation with chromic acid in boiling aqueous sulphuric acid or treatment with alkaline potassium permanganate; but oxidation with chromic acid in boiling acetic acid converted (A) to a yellow crystalline quinone (B), m.p. 332°, which gave an orange vat, and was identified as pentaphene-5:14:8:13-diquinone (V).[3] Reduction of (B) with aluminium tri*cyclo*hexoxide[9] gave a 91 per cent yield of pentaphene (VI), identified by its m.p. and absorption spectrum. This route to pentaphene is much more convenient than the earlier methods, such as the Elbs pyrolysis of 2:4-dibenzoyl-*m*-xylene[11] or the synthesis starting from the Grignard reaction between phthalic anhydride and *o*-tolylmagnesium bromide.[12] After the present work had been completed, Badger *et al.*[13] described a synthesis of pentaphene (VI) by cyclisation of 3:3-bisbromomethyl-2:2′-dinaphthyl, followed by dehydrogenation,[13] but this method did not give a higher yield than the earlier syntheses of Clar.[11,12] Reductive acetylation of (B) gave the tetra-acetate of the leuco compound. Interaction of (B) with hydrazine hydrate in boiling pyridine gave the reddish orange azaquinone (VII),[3,9] which dyed cotton a bright golden orange shade from a cherry-red vat. Reduction of (VII) with aluminium tri*cyclo*hexoxide gave the azahydrocarbon (VIII), lemon-yellow needles, m.p. 304°.

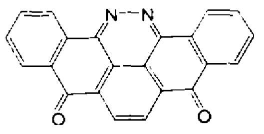
The carcinogenic properties of 3:4:9:10:dibenzopyrene (I) and 1:2-diaza-3:4:9:10-dibenzopyrene (VIII) are being examined at the Indian Cancer Research Centre. Subcutaneous injections of a ball-milled suspension of 2 mg of (I) or (VIII) in 0·2 ml of propylene glycol were given to sixteen mice; the hydrocarbon (I) produced the first tumour after 90 days, and tumours developed in all the sixteen mice after 120 days; the azahydrocarbon (VIII) produced no definite tumour in 105 days, but a specific reaction at the site of injection was noticed in ten mice after 90 days.



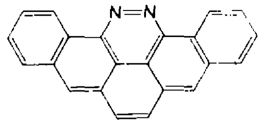
(V)



(VI)



(VII)



(VIII)

Indanthrene scarlet 4G and Mayvat brilliant red AF dye substantially different shades and they exhibit different colours in sulphuric acid; the number and position of the halogen atoms, which must be responsible for these differences, are under investigation.

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[11] E. Clar and Fr. John, *Ber. Dtsch. Chem. Ges.* 63, 2967 (1930); *Ibid.* 64, 981 (1931).

[12] E. Clar and D. G. Stewart, *J. Chem. Soc.* 3215 (1951).

[13] G. M. Badger, P. R. Jefferies and R. W. L. Kimber, *J. Chem. Soc.* 1837 (1957).

EXPERIMENTAL

Purification and properties of Mayvat brilliant red AF

Mayvat brilliant red AF double paste (50 g) was dried at 110° for 4 hr and the reddish black powder (11 g) was dissolved in sulphuric acid (200 ml). The deep olive-green solution was poured into ice and water (1 l.), and the deep-red flocculent precipitate was collected, washed free from acid and dried (10 g). The chromatographic homogeneity of the dye was examined by dissolving 150 mg in molten naphthalene (50 g) and running the solution through a jacketed column of alumina (2·5 × 30 cm) maintained at 95–100°. Development with molten naphthalene produced a deep orange-red band, which was eluted with the same solvent. The naphthalene was removed by distillation and the dye was recovered as a red powder (120 mg), which crystallised from *o*-dichlorobenzene in red needles (Found: C, 60·3; H, 1·8; Cl, 2·4; Br, 28·1. $C_{24}H_{10}O_2Cl_{0\cdot3}Br_{1\cdot7}$ requires C, 60·4; H, 2·1; Cl, 2·2; Br, 28·5 per cent). The dye before chromatography also crystallised in red needles from *o*-dichlorobenzene (Found: C, 57·9; H, 2·4; Cl, 8·7; Br, 24·9. $C_{24}H_{10}O_2Cl_{1\cdot3}Br_{1\cdot6}$ requires C, 57·3; H, 2·0; Cl, 9·2; Br, 25·2 per cent). Indanthrene scarlet 4G crystallised from the same solvent in deep orange needles (Found: C, 53·6; H, 1·7; Cl, 15·3; Br, 24·5. $C_{24}H_{10}O_2Cl_{2\cdot4}Br_{1\cdot6}$ requires C, 53·2; H, 1·7; Cl, 15·6; Br, 23·8 per cent).

Cotton yarn dyed a 2 per cent shade with Mayvat red and Indanthrene scarlet 4G gives the following colour reactions:[14] (1) alkaline hydrosulphite: bluish red, red; (2) acid hydrosulphite: both yellow-brown; (3) concentrated nitric acid: rubine, scarlet; (4) concentrated sulphuric acid: black, deep rubine. Both Mayvat red and Indanthrene scarlet 4G dissolve in organic solvents such as *o*-dichlorobenzene or xylene to form orange solutions with a strong yellow fluorescence. The solution of Mayvat red in concentrated sulphuric acid is olive green and in 16 per cent oleum straw-yellow; Indanthrene scarlet gives a deep brownish red solution in concentrated sulphuric acid and a deep red solution in 16 per cent oleum.

Dehalogenation of Mayvat brilliant red AF

The finely powdered dye (1 g) was precipitated from sulphuric acid and washed free from acid. It was suspended in 5% sodium hydroxide solution (100 ml) in a pressure bottle, Raney nickel (1 g) was added, and the mixture was shaken with hydrogen at 38 lb pressure for 6 hr. The mixture was filtered, the nickel residue was washed with 2% sodium hydroxide solution containing a little glucose, and the combined deep-red filtrate was air-oxidised. The red precipitate was collected, washed and dried. The quinone (A; 0·58 g), which was halogen-free, crystallised from *o*-dichlorobenzene in deep red shining needles, m.p. 373° (Found: C, 85·9; H, 3·5. Calc. for $C_{24}H_{12}O_2$; C, 86·2; H, 3·6 per cent). The m.p. of 3:4:9:10-dibenzopyrene-5:8-quinone quoted in the literature[3] is 365°. This parent quinone, by the halogenation of which both Mayvat red and Indanthrene scarlet 4G are prepared, gives the same colourations as Mayvat red in *o*-dichlorobenzene, concentrated sulphuric acid and 16% oleum.

Reductive benzoylation of (A). The quinone (A) (50 mg) was shaken with 5% sodium hydroxide solution (20 ml) and sodium hydrosulphite (0·2 g) at 70–80° for

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[14] H. B. Bradley and D. A. Derrett-Smith, *J. Soc. Dyers Col.* **56**, 97 (1940).

10 min. Benzoyl chloride (0·3 ml) was then added to the clear red vat and the mixture was shaken vigorously for 5 min, when a pale yellow granular precipitate separated (60 mg). Crystallisation from benzene gave pale-yellow needles, m.p. 343° (Found: C, 84·4; H, 4·1. $C_{38}H_{22}O_4$ requires C, 84·1; H, 4·0 per cent).

Reductive acetylation of (A). A mixture of the quinone (A) (100 mg), acetic anhydride (15 ml) and zinc dust (1 g) was heated under reflux for 2 hr and then filtered hot. The residue was extracted with hot acetic anhydride (10 ml) and the combined filtrates were concentrated to small bulk and poured into crushed ice with stirring. The precipitate (100 mg) crystallised from benzene in pale yellow needles, m.p. 310–15° (dec.) (Found: C, 79·7; H, 4·2. $C_{28}H_{18}O_4$ requires C, 80·3; H, 4·3 per cent).

Reduction of the quinone (A) to 3:4:9:10-dibenzopyrene (I). Aluminium turnings (1 g) were heated under reflux with *cyclo*hexanol (20 ml) after the addition of a few milligrams of mercuric chloride as catalyst. The quinone (A) (0·5 g) was added to the opalescent solution and the mixture was heated under reflux for 48 hr. *Cyclo*hexanol was removed by distillation and the pasty mass was stirred into 5% sodium hydroxide solution (200 ml). The last traces of *cyclo*hexanol were removed by steam-distillation, and the solution was then treated with sodium hydrosulphite (1 g) to dissolve any unconverted quinone. The mixture was filtered and the residual dark brown powder (0·7 g) was dissolved in warm benzene (250 ml) and chromatographed on alumina. The yellow fluorescent percolate was collected, concentrated to small bulk and cooled. Pale yellow plates of the hydrocarbon (I) were obtained (0·32 g). After recrystallisation from benzene–hexane the substance had m.p. 281° (Found: C, 94·9; H, 4·6. Calc. for $C_{24}H_{14}$. C, 95·4; H, 4·6 per cent). The hydrocarbon dissolves in benzene to an orange-yellow solution with a blue fluorescence. The solution in concentrated sulphuric acid is greenish blue, changing rapidly to blue and finally to violet; the solution first exhibits a blue fluorescence, which immediately changes to red, and disappears in a minute.

Scholl and Neumann[3] give m.p. 281·5–282°. Identity with 3:4:9:10-dibenzopyrene was proved by the absorption spectrum, which was identical with that recorded by Clar.[15]

Oxidation of the hydrocarbon (50 mg) by heating under reflux with chromic acid (500 mg) in water (10 ml) gave a product that crystallised from *o*-dichlorobenzene in red needles, m.p. 373°, alone or mixed with quinone (A) (Found: C, 86·6; H, 3·7. $C_{24}H_{12}O_2$ requires C, 86·2; H, 3·6 per cent).

Oxidation of quinone (A). The quinone (0·5 g) was heated under reflux with glacial acetic acid (20 ml), and a solution of chromic acid (2 g) in glacial acetic acid (20 ml) was added in five equal lots, each at the end of 8 hr. After the solution had been heated under reflux for 40 hr, it was diluted with water, and the yellow crystalline precipitate was collected, washed and dried (440 mg). Crystallisation from chlorobenzene gave yellow needles of quinone (B), m.p. 332° (Found: C, 78·3; H, 3·1. $C_{22}H_{10}O_4$ requires C, 78·1; H, 3·0 per cent). Scholl and Neumann[3] give m.p. 325° for pentaphene-5:14:8:13-diquinone (V). The substance gives an orange vat, which has no affinity for cotton. The solution in *o*-dichlorobenzene is yellow, and in concentrated sulphuric acid lemon-yellow.

Reductive acetylation of quinone (B). The quinone (B) (70 mg), acetic anhydride

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[15] E. Clar, *Ber. Dtsch. Chem. Ges.* **69**, 1677 (1936).

(15 ml) and zinc dust (1 g) were heated under reflux for 2 hr and treated as described above. The product crystallised from benzene–hexane in pale yellow needles, m.p. 295–300° (dec.) (Found: C, 71·2; H, 4·2. $C_{30}H_{22}O_8$ requires C, 70·6; H, 4·3 per cent).

1:2-*Diaza*-3:4:9:10-*dibenzopyrene*-5:8-*quinone* (VII) *from quinone* (*B*). A mixture of quinone (B) (100 mg), 85% hydrazine hydrate (1 ml) and pyridine (10 ml) was heated under reflux for 1 hr. The mixture was diluted with water and aerated, and the orange-yellow precipitate was collected (100 mg). Crystallisation from *o*-dichlorobenzene gave reddish orange needles, m.p. above 360° (dec.) (Found: C, 79·0; H, 3·4; N, 8·7. Calc. for $C_{22}H_{10}O_2N_2$: C, 79·1; H, 3·0; N, 8·7 per cent). Scholl and Neumann[3] describe this compound as orange-red needles, decomposing ca. 440°. The substance dyes cotton an orange-yellow shade from a cherry-red vat.

Reduction of the azaquinone (VII) *to* 1:2-*diaza*-3:4:9:10-*dibenzopyrene* (VIII). On heating a mixture of the quinone (VII) (1 g) and a solution of aluminium turnings (1 g) in *cyclo*hexanol (20 ml) under reflux overnight and isolating the product as described above, an unvattable product (0·8 g) was obtained; after chromatography on alumina and crystallisation from benzene, the azahydrocarbon (VIII) was obtained as lemon-yellow needles (0·6 g), m.p. 304° (Found: C, 87·0; H, 4·2; N, 9·1. $C_{22}H_{12}N_2$ requires C, 86·8; H, 4·0; N, 9·2 per cent).

Reduction of quinone (*B*) *to pentaphene* (VI). Quinone (B) (0·2 g) was heated under reflux with a solution of aluminium turnings (0·5 g) in *cyclo*hexanol (10 ml) for 12 hr and the product was isolated as described above. Chromatography on alumina and crystallisation from benzene–hexane gave pale yellow needles (0·15 g), m.p. 262° (Clar and John[11] give m.p. 257° and Badger *et al.*[13] m.p. 255–257°) (Found: C, 94·8; H, 5·4. $C_{22}H_{14}$ requires C, 95·0; H, 5·0 per cent). The absorption spectrum of the hydrocarbon was determined in heptane solution, and was identical with that of pentaphene.[16] The substance dissolves in benzene to a very pale yellow solution with a blue fluorescence, and in concentrated sulphuric acid to a pale red solution on warming.

Dehalogenation of Indanthrene scarlet 4G

The purified dye (5 g) was dehalogenated by means of Raney nickel (3 g) and hydrogen at 40 lb pressure, as described for Mayvat brilliant red AF. The halogen-free quinone (3 g) crystallised from *o*-dichlorobenzene in red needles, m.p. 373°, undepressed by quinone (A) (Found: C, 86·0; H, 3·6. $C_{24}H_{12}O_2$ requires C, 86·2; H, 3·6 per cent). The quinone (0·3 g), on reduction with aluminium tri*cyclo*hexoxide (1 g of aluminium turnings in 20 ml of *cyclo*hexanol), gave the hydrocarbon (160 mg), pale yellow needles or plates from benzene–hexane mixture, m.p. 281°, undepressed by 3:4:9:10-dibenzopyrene prepared from Mayvat brilliant red AF (Found: C, 95·1; H, 4·5. $C_{24}H_{14}$ requires C, 95·4; H, 4·6 per cent).

Acknowledgements—This work was carried out under the auspices of the Council of Scientific and Industrial Research, to whom our thanks are due. We are indebted to the Otto B. May Co. Inc. and Cassella Farbwerke for gifts of dyes, and to Dr. T. S. Gore and Dr. G. D. Shah for the microanalyses recorded in the paper.

[16] E. Clar, *Ber. Dtsch. Chem. Ges.* **65**, 508 (1932).