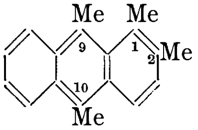
5. *Polycyclic Aromatic Hydrocarbons. Part XXVII.*

By G. M. Badger, F. Goulden, and F. Ll. Warren.

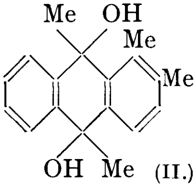
9 : 10-Dimethyl-9 : 10-dihydro-1 : 2-benzanthraquinol and 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthraquinol have been dehydrated to endo-*oxides*, which are easily reduced to the completely aromatic hydrocarbons. This reaction furnishes an alternative route to the highly carcinogenic 9 : 10-dimethyl-1 : 2-benzanthracene. Unsuccessful attempts have been made to transform 1 : 2 : 9 : 10-tetramethyl-9 : 10-dihydroanthraquinol into 1 : 2 : 9 : 10-tetramethylanthracene (I).

Two unsuccessful attempts to synthesise 1 : 2 : 9 : 10-tetramethylanthracene (I) have been recorded (Badger, Cook, and Goulden, J., 1940, 16; Fieser and Webber, *J. Amer. Chem. Soc.*, 1940, **62**, 1360). Our interest in this unknown hydrocarbon, which lies in its relationship to the actively carcinogenic 9 : 10-dimethyl-1 : 2-benzanthracene and the feebly carcinogenic 9 : 10-dimethylanthracene, has led us to renew our efforts to prepare it.

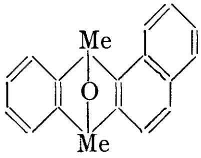
Reduction of 1 : 2 : 9 : 10-tetramethyl-9 : 10-dihydroanthraquinol (II) with hydriodic acid in acetic acid, a procedure whereby Cook (J., 1931, 495) prepared *meso*-dialkyl and -diaryl derivatives of 1 : 2 : 5 : 6-dibenzanthracene, gave a yellow amorphous product. Cook found that dihydroanthraquinols of the dibenzanthracene series were reduced to dihydrides of the aromatic hydrocarbons by hydriodic acid and red phosphorus in acetic acid. With the diol (II) this reaction led to the formation of a crystalline *compound* having the composition of 1 : 2 : 9 : 10-tetramethyl-9 : 10-dihydroanthracene, and its ultraviolet absorption spectrum, examined by Dr. E. Roe, is consistent with the formulation of a dihydroanthracene derivative. However, dehydrogenation to 1 : 2 : 9 : 10-tetramethylanthracene could not be accomplished.



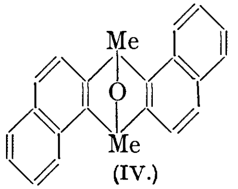
(I.)



(II.)



(III.)



(IV.)

For comparison, 9 : 10-*dimethyl*-9 : 10-*dihydroanthracene* was prepared, and its dehydrogenation examined. 9 : 10-Dimethylanthracene was smoothly formed when the dihydride was heated with sulphur at 230°. 9 : 10-Dimethylanthracene, and not its dihydride, was obtained when 9 : 10-dimethyl-9 : 10-dihydroanthraquinol was reduced with hydriodic acid and phosphorus in acetic acid. The dihydro-compound required for the dehydrogenation experiment was obtained by the action of methyl iodide on the disodio-compound of anthracene, a method introduced by Hugel and Lerer (*Bull. Soc. chim.*, **1933**, **53**, 1498).

In the case of *meso*-dialkyldihydroanthraquinols loss of two molecules of water may occur following treatment with acetic acid containing a trace of mineral acid. However, Enderlin (*Compt. rend.*, 1936, **202**, 1188) obtained an endocyclic oxide by thermal dehydration of 1 : 10-diphenyl-4 : 9-bis-*p*-bromophenyl-9 : 10-dihydro-2 : 3-benzanthraquinol. Conditions have now been found for the facile monodehydration of 9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthraquinol and 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthraquinol to compounds which are doubtless endo-*oxides* (III and IV). These oxides were reduced, the former by hydriodic acid and the latter by methylmagnesium iodide, to the 9 : 10-dimethyl derivatives of 1 : 2-benzanthracene and 1 : 2 : 5 : 6-dibenzanthracene, respectively.

EXPERIMENTAL.

1 : 2 : 9 : 10-*Tetramethyl*-9 : 10-*dihydroanthracene*.—A Grignard solution was prepared from methyl iodide (2·5 c.c.), magnesium (0·9 g.), ether (15 c.c.), and benzene (15 c.c.), most of the ether distilled off on the water-bath, and benzene (15 c.c.) added. 1 : 2-Dimethylanthraquinone (2·3 g.) (Badger, Cook, and Goulden, *loc. cit.*), suspended in a Soxhlet thimble underneath the condenser (compare Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583), dissolved after the solution had been refluxed for 4 hours. After decomposition with ice-cold ammonium chloride solution, the organic layer was evaporated, and the resulting oil boiled in acetic acid (50 c.c.) with red phosphorus (1·5 g.) and hydriodic acid (5 c.c., *d* 1·9) for 2 hours and poured into water. An alcoholic solution of the solid was decolourised with charcoal and evaporated to small volume. The *product*, probably 1 : 2 : 9 : 10-tetramethyl-9 : 10-dihydroanthracene, formed colourless needles (0·9 g.), m. p. 100—101°, from alcohol (Found : C, 91·4; H, 8·35. $C_{18}H_{20}$ requires C, 91·45; H, 8·55%).

Dehydrogenation with sulphur at 230° for ½ hour gave a product which decomposed on attempted distillation. In another experiment, 1 g. of the dihydro-compound was heated at 265° for ½ hour with a palladium catalyst (0·2 g.). The product was extracted with acetic acid, the solution concentrated (a portion of it did not give a coloration with picric acid), and a few drops of water added. The yellow amorphous precipitate decomposed at 130° and could not be crystallised (Found : C, 92·25; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

9 : 10-*Dimethylanthracene*.—(i) A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (2 g.) (Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583) in acetic acid (100 c.c.) was treated with red phosphorus (3 g.) and hydriodic acid (5 c.c., *d* 1·9) and boiled for 2 hours. The reaction mixture was worked up as above. After sublimation at 110°/0·2 mm., and recrystallisation from benzene, the product (0·45 g.) formed pale yellow crystals, m. p. 180—181°, alone or mixed with authentic 9 : 10-dimethylanthracene.

(ii) A suspension of anthracene (40 g.), powdered sodium (20 g.), and broken glass in ether (400 c.c.) was shaken for 48 hours. A blue colour developed after the first ½ hour and gradually became very intense. The mixture was cooled in ice, and methyl iodide added dropwise through a reflux condenser until the solution had become decolourised. After filtration, the ether was evaporated, and the residue cooled in a freezing mixture. The unchanged anthracene which crystallised was removed, and the filtrate distilled. The fraction (16 g.), b. p. 180—185°/25 mm., solidified and was recrystallised from alcohol, the pure 9 : 10-*dimethyl*-9 : 10-*dihydroanthracene* forming colourless crystals, m. p. 101—102° (Found : C, 92·0; H, 7·9. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%).

The above dihydro-compound (3·3 g.) was heated at 230° for ½ hour with sulphur (0·55 g.). The product (2·8 g.) was purified through the picrate (m. p. 173—175°) and finally by recrystallisation from benzene. It formed pale yellow blades, m. p. 180—182°, alone or mixed with authentic 9 : 10-dimethylanthracene.

9 : 10-*Dimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene* 9 : 10-*Oxide*.—This oxide was obtained by a method similar to that described by Bachmann and Chemerda (*J. Amer. Chem. Soc.*, 1938, **60**, 1023) for the preparation of 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene. A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (10 g.) in benzene (30 c.c.) and methyl alcohol (40 c.c.) was warmed and then treated with concentrated sulphuric acid (0·5 c.c.). After several hours, the methyl ether which had crystallised was removed, and the filtrate evaporated to small volume, giving 9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene* 9 : 10-*oxide* (5·5 g.), which, recrystallised from benzene, formed plates, m. p. 120—121° (Found : C, 88·2; H, 6·3. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%).

Reduction of the oxide. A solution of the oxide (11 g.) in glacial acetic acid (150 c.c.), at 30°, was treated with a solution of hydriodic acid (11 c.c., *d* 1·9) in acetic acid (20 c.c.). The mixture was shaken for a few minutes and then boiled for 10 minutes. Sulphur dioxide was passed into the slightly diluted solution in order to decolorise it; the hydrocarbon which crystallised was recrystallised from acetic acid (yield, 7 g.). It formed plates, m. p. 122° alone or mixed with authentic 9 : 10-dimethyl-1 : 2-benzanthracene but depressed by the original oxide.

9 : 10-*Dimethyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracene* 9 : 10-*Oxide*.—A solution of 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthraquinol (1·4 g.) and picric acid (2·8 g.) in absolute alcohol (280 c.c.) was refluxed for 2 hours. After concentration, the picrate which separated was collected and dissociated by treatment with boiling alcohol, the *oxide* (1·0 g.) separating on cooling. Recrystallisation from *cyclo*hexane and from alcohol gave pale yellow needles, m. p. 140—141° (Found : C, 89·0; H, 6·1. $C_{24}H_{18}O$ requires C, 89·4; H, 5·6%).

The *picrate*, prepared from the pure oxide, formed deep red needles, m. p. 107—108° (Found : C, 65·5; H, 4·2. $C_{24}H_{18}O,C_6H_3O_7N_3$ requires C, 65·3; H, 3·8%).

Action of methylmagnesium iodide. The oxide (0·5 g.) was added to a Grignard solution prepared from methyl iodide (1 c.c.), magnesium (0·4 g.), and ether (10 c.c.). The orange-red solution was boiled for 2 hours and decomposed with ice and ammonium chloride, and the product recrystallised from benzene. The pale yellow leaflets gave an intense reddish-purple solution in concentrated sulphuric acid, and had m. p. 208—210°, not depressed by authentic 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene (J., 1931, 495) (Found : C, 93·5; H, 5·8. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%).

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The Chester Beatty Research Institute,
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