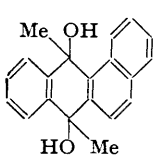
473. *Substituted Anthracene Derivatives. Part II. An Example of 1 : 5-Anionotropic Rearrangement.*

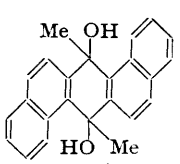
By G. M. Badger and R. S. Pearce.

The acid-catalysed dehydration of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (I), in the presence of an alcohol, has been shown to give 9-methyl-10-alkoxymethyl-1 : 2-benzanthracene (VI). The formation of this substance involves a 1 : 5-anionotropic rearrangement of the initial product of dehydration (V), and alkylation with the alcohol used as solvent.

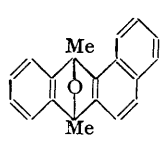
When a solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (I) in warm methanol was treated with a little sulphuric acid, a mixture of the expected methyl ether and a dehydration product was obtained (Badger, Goulden, and Warren, *J.*, 1941, 18). A similar product of dehydration was obtained by treatment of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (II) with boiling alcoholic picric acid. The dehydration products were tentatively assigned the structures of endocyclic monoxides (III and IV), by analogy with that proposed by Enderlin (*Compt. rend.*, 1936, **202**, 669, 1188) for the product of thermal dehydration of 6 : 12-dihydroxy-6 : 12-diphenyl-5 : 11-di-*p*-bromo-



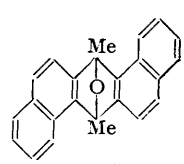
(I.)



(II.)



(III.)



(IV.)

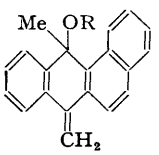
phenyl-6 : 12-dihydronaphthacene. Structures involving transannular monoxide bridges have also been proposed for the compound obtained by reduction of rubrene photo-oxide with zinc and acetic acid, for the isomerisation product of the same photo-oxide (Bergmann and McLean, *Chemical Reviews*, 1941, **28**, 367), and for the dehydration product of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (Guyot and Staehling, *Bull. Soc. chim.*, 1905, **33**, 1144). None of these structures is at all probable for these compounds. Although models of transannular *per*-oxides can be constructed without strain (Dufraisse, *Bull. Soc. chim.*, 1939, **6**, 422), dihydro-aromatic structures having a *mono*-oxide bridge involve very considerable distortion of the normal valency angles for both oxygen and carbon.

The study of the structures of these supposed *endo*monoxides has now been undertaken, and the present paper records the results of an investigation into the nature of the product obtained from the diol (I) by warm methanol and sulphuric acid. Satisfactory conditions for the preparation of this product in good yield by the addition of a little concentrated hydrochloric acid to a boiling methanolic solution of the diol have been devised.

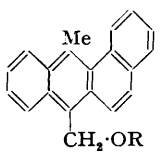
It soon became evident that this product cannot have the *endo*monoxide structure (III) as its properties are not consistent with its being a dihydrobenzanthracene derivative. Even when highly purified it is faintly yellow, and its solutions show a strong blue fluorescence. Moreover, it forms a dark red picrate. When tested for carcinogenic activity (under the name "9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene 9 : 10-oxide") it was found to be moderately active, although the corresponding *endo*peroxide (photo-oxide) is inactive, as expected (Badger *et al.*, *Proc. Roy. Soc.*, 1940, *B*, **129**, 445). These properties are those expected of a fully aromatic *meso*-substituted benzanthracene derivative; this structure was also indicated by the rate of addition of osmium tetroxide, which was intermediate between those for 1 : 2-benzanthracene and 9 : 10-dimethyl-1 : 2-benzanthracene (cf. Badger, *J.*, 1949, 456).

The endocyclic monoxide structure (III) was finally rejected when it was found that the product obtained by dehydration of the diol (I) in ethanol is similar to, but not identical with, that obtained in methanol. It has now been established that dehydration of the diol (I) in methanol gives 9-methyl-10-methoxymethyl-1 : 2-benzanthracene (VI; R = Me), and that dehydration in ethanol gives the 10-ethoxymethyl analogue (VI; R = Et). These products can only be formed if the initial dehydration product (V; R = H) or its alkyl ether (V; R = Me or Et) suffers 1 : 5-anionotropic rearrangement.

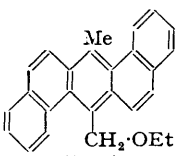
The structure of the product (VI; R = Me) has been confirmed by direct comparison with a specimen obtained by iodomethylation of 9-methyl-1 : 2-benzanthracene, followed by treatment with sodium methoxide (Sandin and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3098). Similarly,



(V.)



(VI.)

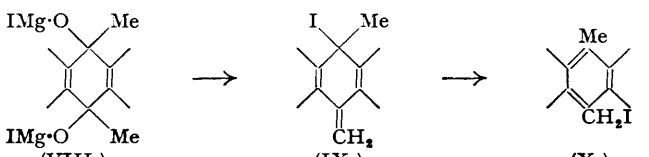


(VII.)

dehydration of the diol (I) with boiling ethanolic picric acid gave 9-methyl-10-ethoxymethyl-1 : 2-benzanthracene (as the picrate) identical with a specimen prepared as above but with sodium ethoxide. The ultra-violet absorption spectrum of this compound resembled that of 9 : 10-dimethyl-1 : 2-benzanthracene (Fig. 1).

There can be no doubt that 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (II) also suffers dehydration and rearrangement with alkylation when heated with alcoholic picric acid (Badger, Goulden, and Warren, *loc. cit.*). The compound previously regarded as 9 : 10-dimethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene 9 : 10-oxide (IV) must therefore be 9-methyl-10-ethoxymethyl-1 : 2 : 5 : 6-dibenzanthracene (VII), and the ultra-violet absorption spectrum is consistent with this conclusion (Fig. 2).

1 : 5-Anionotropic shifts are by no means unknown in the anthracene series. For example, Julian, Cole, Diemer, and Schafer (*ibid.*, 1949, **71**, 2058) found that 9-hydroxy-10-benzylidene-9 : 10-dihydroanthracene is readily rearranged to 9-α-hydroxybenzylanthracene by brief boiling in acetone solution with a little sulphuric acid. Similarly, 9-hydroxy-9-phenyl-10-benzylidene-



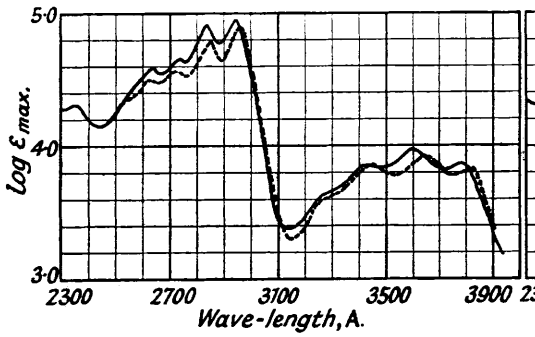
(VIII.) (IX.) (X.)

9 : 10-dihydroanthracene is isomerised to 9-phenyl-10-α-hydroxybenzylanthracene (Julian and Cole, *ibid.*, 1935, **57**, 1609, who give references to earlier work by Barnett and Cook). It is also noteworthy that Sandin and Fieser (*loc. cit.*) have prepared 9-methyl-10-iodomethyl-1 : 2-benzanthracene (X) by addition of hydrogen iodide to the magnesium complex (VIII) from

1 : 2-benzanthraquinone and methylmagnesium iodide. The intermediate (IX) evidently undergoes anionotropic rearrangement to give the iodomethyl compound (X).

Absorption spectra.

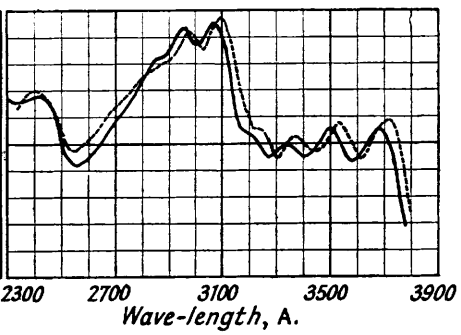
FIG. 1.



——— 9-*Methyl*-10-*ethoxymethyl*-1 : 2-*benzanthracene* (*in alcohol*) : *Maxima at* 2650 (4·59); 2745 (4·66); 2835 (4·91); 2945 (4·97); (3280, 3·83); 3440 (3·87); 3600 (3·98) 3765 A. (3·88) (*log* ε *in parentheses*).

– – – – 9 : 10-*Dimethyl*-1 : 2-*benzanthracene* (*after Jones*, J. Amer. Chem. Soc., 1945, **67**, 2127).

FIG. 2.



——— 9-*Methyl*-10-*ethoxymethyl*-1 : 2 : 5 : 6-*dibenzanthracene* (*in alcohol*) : *Maxima at* 2420 (4·36); (2860, 4·64); 2955 (4·87); 3070 (4·93); (3200, 4·08); 3350 (4·0); 3500 (4·11); 3680 A. (4·11) (*log* ε *in parentheses*).

– – – – 9 : 10-*Dimethyl*-1 : 2 : 5 : 6-*dibenzanthracene* (*after Mayneord and Roe*, Proc. Roy. Soc., 1935, *A*, **152**, 299).

EXPERIMENTAL.

9 : 10-*Dihydroxy*-9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*.—The following modified method (cf. Davies and Kipping, *J.*, 1911, 296) was more satisfactory than the published procedure (Bachmann and Chemerda, *J. Amer. Chem. Soc.*, 1938, **60**, 1023). A mixture of benzanthraquinone (5 g.), magnesium (2·5 g.), methyl iodide (6 c.c.), dry benzene (30 c.c.), and dry ether (30 c.c.) was allowed to react. After 40 minutes, the reflux was maintained for a further hour by gentle heating. After cooling, the complex was poured into an ice-cold saturated solution of ammonium chloride. The ether–benzene layer deposited the diol (3·0 g.) when kept in the refrigerator overnight, and a further quantity (1·0 g.) was obtained by evaporation.

9-*Methyl*-10-*methoxymethyl*-1 : 2-*benzanthracene*.—(i) The formation of this compound, as a by-product in the preparation of 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene, was first described (under the name " 9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene 9 : 10-oxide ") by Badger, Goulden, and Warren (*loc. cit.*). The published analytical figures are in good agreement with the structure now established (Found : C, 88·2; H, 6·3. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%).

(ii) A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (2 g.) in boiling methanol (40 c.c.) was treated with concentrated hydrochloric acid (8 c.c.). After 3 minutes, the solution was poured into water, and the product collected. 9-Methyl-10-methoxymethyl-1 : 2-benzanthracene crystallised from alcohol in pale yellow blades, m. p. 120—121°, alone or mixed with a specimen prepared by the first method.

(iii) The *picrate* of 9-methyl-10-methoxymethyl-1 : 2-benzanthracene was prepared from the diol by 2 hours' boiling with methanol and excess of picric acid. It formed small red needles, m. p. 108—109°, after recrystallisation from benzene (Found : C, 63·2; H, 3·9. $C_{21}H_{18}O,C_6H_3O_7N_3$ requires C, 62·9; H, 4·1%). Decomposition of the picrate in the usual way gave methylmethoxymethylbenzanthracene, m. p. 120—121°, alone or mixed with a specimen prepared by method (i).

(iv) 9-Methyl-10-methoxymethyl-1 : 2-benzanthracene was also prepared from 9-methyl-1 : 2-benzanthracene by iodomethylation to 9-methyl-10-iodomethyl-1 : 2-benzanthracene, followed by treatment with sodium methoxide (Sandin and Fieser, *loc. cit.*). A specimen, m. p. 120—121°, thus prepared showed no depression of the m. p. when mixed with specimens prepared by methods (i) and (ii). The same product was also obtained by treatment of the Grignard complex between 1 : 2-benzanthraquinone and methylmagnesium iodide with hydriodic acid, followed by treatment of the resulting iodomethyl compound with sodium methoxide (Sandin and Fieser, *loc. cit.*).

9-*Methyl*-10-*methoxymethyl*-1 : 2-*benzanthracene Photo-oxide*.—A solution of the above methylmethoxymethylbenzanthracene in benzene was set aside in diffuse sunlight in an open beaker for 3 days. Purification of the resulting dark brown sticky solid by recrystallisation from alcohol (charcoal) gave the *photo-oxide* as small colourless plates, m. p. 147—149° (Found : C, 79·0; H, 5·95. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

9-*Methyl*-10-*ethoxymethyl*-1 : 2-*benzanthracene*.—A solution of 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (5 g.) and picric acid (10 g.) in absolute alcohol (1 l.) was boiled under reflux for 2 hours. After concentration and cooling, the picrate separated. This dissociated to some

extent on recrystallisation from alcohol and a pure specimen could not be obtained for analysis. The crude material had m. p. 83°. The picrate, in benzene, was decomposed by shaking it with aqueous sodium carbonate solution. 9-Methyl-10-ethoxymethyl-1 : 2-benzanthracene formed pale yellow blades, m. p. 126—127°, after recrystallisation from benzene (Found : C, 88·35; H, 6·7. Calc. for $C_{22}H_{20}O$: C, 88·0; H, 6·7%). The m. p. was not depressed by admixture with a specimen prepared by refluxing 9-methyl-10-iodomethyl-1 : 2-benzanthracene with sodium ethoxide in ethanol, according to the method of Sandin and Fieser (*loc. cit.*).

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