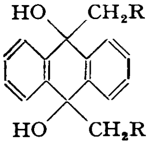
474. *Substituted Anthracene Derivatives. Part III. Further Examples of 1 : 5-Anionotropic Rearrangements.*

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

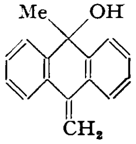
When treated with acids in the presence of an alcohol as solvent, 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (I*a*) is converted into 9-methyl-10-alkoxymethylanthracene (IV) by 1 : 5-anionotropic rearrangement of the initial product of dehydration, and alkylation with the alcohol. The structure of the product (IV; R = Me) has been confirmed by comparison with a specimen prepared by another method.

Similar treatment of 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIV) gave 9-benzyl-10-α-ethoxybenzylanthracene (XV), which has also been prepared from 9-formyl-10-benzylanthracene (XVII).

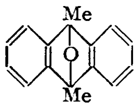
It has long been known that 9 : 10-dihydroxy-9 : 10-dialkylanthracenes (I) are particularly susceptible to dehydration, for by-products formed in this way have often been encountered after reaction of alkylmagnesium halides with anthraquinone. According to Guyot and Staehling (*Bull. Soc. chim.*, 1905, **33**, 1144) dehydration takes place in the presence of excess of the Grignard reagent, but this result was not, apparently, observed by Bachmann and Chemerda (*J. Org. Chem.*, 1939, **4**, 585), and it has not been confirmed in the present work. Dehydration is most easily effected by acids; to avoid it, the Grignard complexes must be decomposed with ammonium chloride. The structures of the dehydration products have never been established. Guyot and Staehling (*loc. cit.*) found that, when 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene (I*a*) is boiled with acetic acid, a bright yellow, sparingly soluble substance corresponding to a mono-dehydration product is formed. The structures (II) and (III) were suggested, but neither is in accord with the properties of this compound.



(I*a*, R = H; I*b*, R = Me.)



(II.)

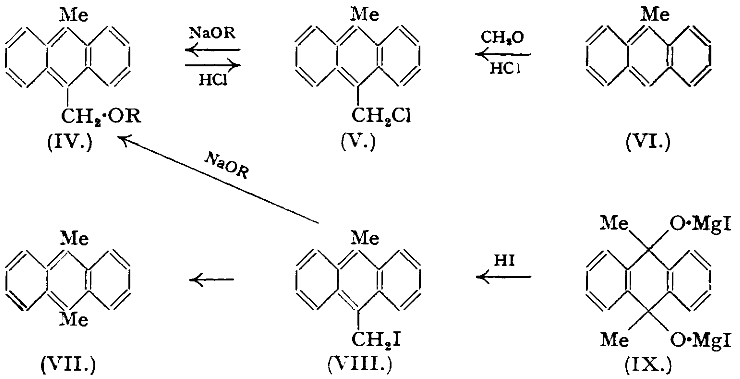


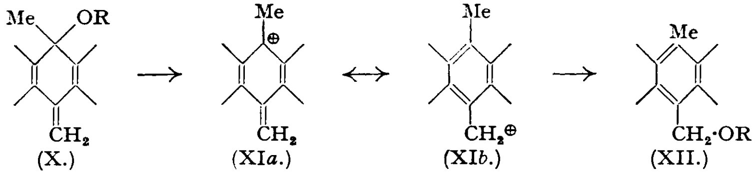
(III.)

Guyot and Staehling also isolated a product, $C_{36}H_{74}O$, after treatment of the diol (I*a*) with acetic acid containing mineral acid. Clarke and Carleton (*J. Amer. Chem. Soc.*, 1911, **33**, 1966) obtained two supposedly bimolecular compounds by dehydration of the diol (I*b*). Little systematic work has been published on the dehydration of diols of type (I). As a preliminary step, we therefore examined the nature of the products obtained by acid-catalysed dehydration in an alcohol as solvent, concurrently with the study (preceding paper) of the structure of the product obtained by similar treatment of dimethylbenzanthraquinol.

It has now been established that when a boiling alcoholic solution of the diol (I*a*) is treated with acid, the dehydration is accompanied by 1 : 5-anionotropic rearrangement and alkylation with the alcohol used as solvent. With a little hydrochloric acid in boiling methanol the diol (I*a*) gave 9-methyl-10-methoxymethylanthracene (IV; R = Me) in good yield. In ethanol 9-methyl-10-ethoxymethylanthracene (IV; R = Et) was obtained, and in *n*-propanol 9-methyl-10-*n*-propoxymethylanthracene (IV; R = Pr^n). Mineral acid is not essential for this conversion, as picric acid is effective, giving rise to the corresponding picrates.

The mechanism of these rearrangements is of interest. It is possible that the initial step is one of alkylation by the alcohol used as solvent, and that the subsequent steps involve elimination of alcohol rather than dehydration. This seems to be indicated by the observation that 9 : 10-dimethoxy-9 : 10-dimethyl-9 : 10-dihydroanthracene, as well as the free diol, is converted into 9-methyl-10-methoxymethylanthracene when boiled with methanol and picric acid. On the other hand, with the free diol, alkylation may take place at a later stage in the rearrangement. In any case, elimination of water or alcohol would be expected to give the intermediate compound (X; R = H or alkyl). Further elimination of an hydroxyl or alkoxyl radical, under the influence of the acid, would give rise to the mesomeric ion (XI). As pointed out by Dewar ("The Electronic Theory of Organic Chemistry," 1949, p. 88) when discussing a similar rearrangement in the polyene series, the alkoxyl radical would tend to recombine with the terminal carbon atom of the mesomeric ion, so that the fully aromatic structure (XII) is formed.

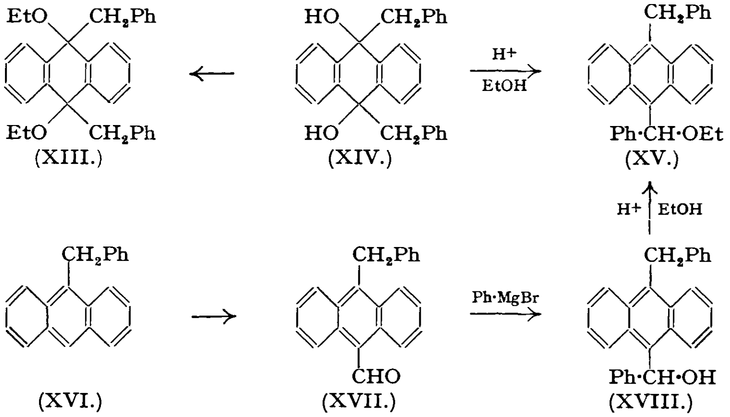




It was pointed out by Badger and Pearce (*loc. cit.*) that the preparation of 9-methyl-10-iodomethyl-1 : 2-benzanthracene by the action of hydrogen iodide on the magnesium complex from 1 : 2-benzanthraquinone and methylmagnesium iodide (Sandin and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3098) also provides an example of a similar rearrangement under the influence of an acid. The corresponding rearrangement has now been carried out in the anthracene series. Addition of hydrogen iodide to the complex from anthraquinone and methylmagnesium iodide gave 9-methyl-10-iodomethylanthracene (VIII), which was, however, too unstable to permit purification. The structure of (VIII) was established by its reduction to 9 : 10-dimethylanthracene, and as treatment with sodium methoxide gave the substance (IV; R = Me) the structure of this too is established.

To confirm its structure (IV; R = Me) was also prepared from 9-methylanthracene (VI) by conversion with paraformaldehyde and hydrogen chloride in glacial acetic acid (cf. Badger and Cook, *J.*, 1939, 802) into 9-methyl-10-chloromethylanthracene (V), which was then treated with sodium methoxide. 9-Methyl-10-chloromethylanthracene was also obtained from (IV; R = Me) by dry hydrogen chloride in benzene.

The readiness with which diols of type (I) undergo the dehydration and rearrangement evidently depends on the nature of the alkyl or aralkyl group. With boiling alcoholic picric acid 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIV) gave only 9 : 10-diethoxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (XIII), but prolonged boiling with ethanol and mineral acid gave the expected dehydration product, 9-benzyl-10-α-ethoxybenzylanthracene (XV). In order to establish the structure of this transformation product, a series of reactions analogous to those used by Julian, Cole, Diemer, and Schafer (*J. Amer. Chem. Soc.*, 1949, **71**, 2058) was carried out. 9-Benzylanthracene was converted by Fieser's formanilide method (*Org. Synth.*, 1940, **20**, 11) into 9-formyl-10-benzylanthracene (XVII) and thence by phenylmagnesium bromide into 9-benzyl-10-α-hydroxybenzylanthracene (XVIII). With ethanol and a trace of sulphuric acid, this gave 9-benzyl-10-α-ethoxybenzylanthracene (XV).



The structures of several of our compounds have been confirmed by their ultra-violet absorption spectra (Figs. 1 and 2). 9-Methyl-10-ethoxymethyl- and 9-benzyl-10-α-ethoxybenzylanthracene and the carbinol (XVIII) show typical anthracene spectra, very similar to that of 9 : 10-dimethylanthracene. On the other hand, the photo-oxide of 9-methyl-10-ethoxymethylanthracene and 9 : 10-diethoxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene, show spectra of dihydroanthracene type as expected.

FIG. 1.

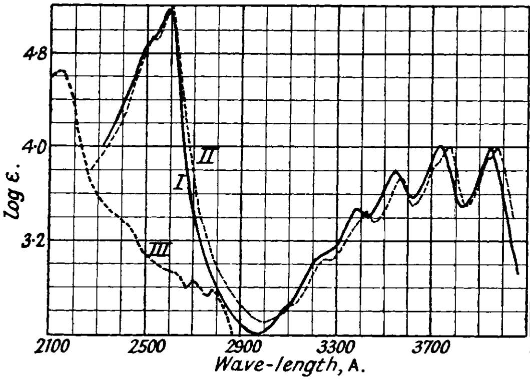


FIG. 2.

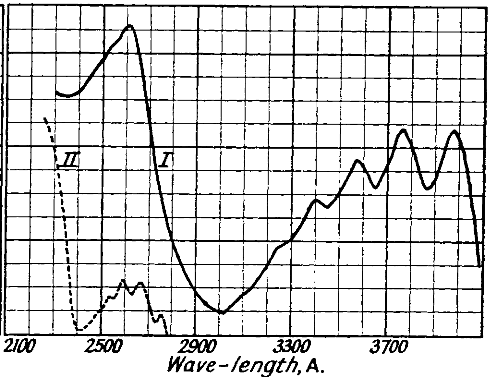


FIG. 1.—*I, 9-Methyl-10-ethoxymethylanthracene (in alcohol). Max. (and log* ε*) at* 2520 (4·93), 2590 (5·24), (3100, 2·69), (3250, 3·08), 3390 (3·48), 3550 (3·80), 3740 (4·01), (3870, 3·71), and 3950 (3·98). *II,* 9 : 10-*Dimethylanthracene (after Jones,* J. Amer. Chem. Soc., 1945, **67**, 2127). *III, 9-Methyl-10-ethoxymethylanthracene photo-oxide (in alcohol).*

FIG. 2.—*I. 9-Benzyl-10-α-ethoxybenzylanthracene (in alcohol). Max. and log* ε *at* (2550, 4·90), 2610 (5·20), (3110, 2·74), (3250, 3·18), 3400 (3·56), 3570 (3·90), 3760 (4·16), and 3980 (4·16). *II.* 9 : 10-*Diethoxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (in alcohol). Max. and log* ε *at* (2490, 2·49), 2540 (2·74), 2595 (2·86), 2655 (2·84), and 2750 (2·57).

EXPERIMENTAL.

9 : 10-*Dihydroxy-9 : 10-dimethyl-9 : 10-dihydroanthracene.*—To obtain this diol it is of advantage to prepare the Grignard complex in the presence of anthraquinone, rather than to add the anthraquinone to the preformed alkylmagnesium halide (cf. Guyot and Staehling, *Bull. Soc. chim.*, 1905, **33**, 1144; Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583; Davies and Kipping, *J.*, 1911, 296). A mixture of anthraquinone (10 g.), magnesium (5 g.), methyl iodide (15 c.c.), benzene (120 c.c.), and ether (60 c.c. was boiled under reflux on the steam bath for 2 hours. The reaction was not unduly vigorous. After cooling, the mixture was decomposed with ice and ammonium chloride. Part of the product separated,

and a further quantity was obtained by evaporation of the ether–benzene layer. The diol (7·2 g.) crystallised from alcohol in colourless prisms, m. p. 185—190°.

9-*Methyl*-10-*methoxymethylanthracene*.—A solution of the above diol (1 g.) and picric acid (2 g.) in methanol (100 c.c.) was boiled under reflux for 2 hours. After concentration and cooling of the mixture, the *picrate* (1·75 g.) separated. Recrystallisation from methanol gave reddish-brown needles, m. p. 124—125° (Found: C, 59·2; H, 4·2. $C_{17}H_{16}O,C_6H_3O_7N_3$ requires C, 59·3; H, 4·1%). Decomposition of the picrate in benzene with dilute alkali gave 9-*methyl*-10-*methoxymethylanthracene* as long pale yellow blades, m. p. 108—109° (from methanol) (Found: C, 86·4; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%). The same product was obtained when a boiling solution of the diol (0·5 g.) in methanol (20 c.c.) was treated with dilute hydrochloric acid (5 c.c.).

9-*Methyl*-10-*ethoxymethylanthracene*.—Similarly prepared, but recrystallised from ethanol the *picrate* formed small reddish-brown needles, m. p. 117—118° (Found: C, 60·4; H, 4·5. $C_{18}H_{18}O,C_6H_3O_7N_3$ requires C, 60·1; H, 4·4%). Decomposition in the usual way gave 9-*methyl*-10-*ethoxymethylanthracene*, which sublimed without decomposition in a high vacuum and formed pale yellow blades, m. p. 106—107°, from ethanol (Found: C, 86·7; H, 7·1. $C_{18}H_{18}O$ requires C, 86·4; H, 7·3%). The *photo-oxide*, prepared by exposure of a benzene solution of the above product to air and indirect sunlight, formed colourless silky needles, m. p. 153—154° (after sintering), from alcohol (Found: C, 76·9; H, 6·7. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

9-*Methyl*-10-*propoxymethylanthracene*.—Similarly prepared, 9-*methyl*-10-n-*propoxymethylanthracene* formed small pale yellow blades or plates, m. p. 101—102°, from methanol (Found: C, 86·5; H, 7·4. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). The *picrate* formed reddish-brown needles, which decomposed to an amorphous powder on prolonged drying at 90°. When heated rapidly, it melted indefinitely at *ca.* 120° (Found: C, 61·1; H, 4·5. $C_{19}H_{20}O,C_6H_3O_7N_3$ requires C, 60·8; H, 4·7%).

9-*Methyl*-10-*iodomethylanthracene*.—A mixture of anthraquinone (10 g.), magnesium (5 g.), methyl iodide (15 c.c.), dry benzene (120 c.c.), and dry ether (60 c.c.) was boiled under reflux on the steam-bath for 2 hours. After cooling, the product was gradually added to a solution of hydriodic acid (120 c.c.) and methanol (400 c.c.) at 0°. Acetic acid (400 c.c.) was then added, and the yellow crystalline product (9·5 g.) collected and dried in air. This product, evidently 9-methyl-10-iodomethylanthracene, liberated iodine on attempted recrystallisation, and on heating, and could not be purified for analysis (cf. Sandin and Fieser, *loc. cit.*).

This compound (1 g.) was treated with sodium methoxide (from 2 g. of sodium) in methanol (40 c.c.), and the mixture boiled for 15 minutes. Water was added and the product collected. The resulting solid was extracted with boiling methanol, and the solution filtered from sparingly soluble material (0·2 g.) and treated with excess of picric acid. Decomposition of the resulting picrate (m. p. 120—124°) in the usual way gave 9-methyl-10-methoxymethylanthracene, m. p. 106—107°, not depressed on admixture with a specimen prepared as described above. The insoluble by-product was identified as anthraquinone by m. p. and mixed m. p.

9 : 10-*Dimethylanthracene*.—(i) A solution of the above iodomethyl compound (5 g.) in dioxan (300 c.c.) and concentrated hydrochloric acid (15 c.c.) was added to stannous chloride (50 g.) in dioxan (250 c.c.) and concentrated hydrochloric acid (150 c.c.). The mixture was boiled for 5 minutes and then set aside for 1 hour. Water (2½ l.) was then added. Next morning, the product was collected and recrystallised from benzene–alcohol. A sparingly soluble by-product, 1′ : 2′-*di*-(10-*methylanthranyl*)-*ethane* (0·5 g.), was first obtained. It formed very small colourless prisms, m. p. >300°, from benzene (Found: C, 93·7; H, 6·2. $C_{32}H_{26}$ requires C, 93·6; H, 6·4%). 9 : 10-Dimethylanthracene (2·4 g.) crystallised from benzene in bright yellow prisms, m. p. 179—180°, not depressed on admixture with a specimen prepared by the method of Bachmann and Chemerda (*loc. cit.*).

(ii) A mixture of 9-methyl-10-ethoxymethylanthracene (0·5 g.), acetic acid (8 c.c.) and hydriodic acid (1 c.c.) was boiled for 10 minutes. After cooling, the mixture was diluted with water, and sulphur dioxide was passed into the suspension for a few minutes. The product was collected and recrystallised from benzene. It formed yellow crystals, m. p. 178°, not depressed on admixture with an authentic specimen.

(iii) 9 : 10-Dimethylanthracene (0·25 g.) was also obtained by treatment of the diol (I*a*) (0·5 g.) with acetic acid (15 c.c.) and hydriodic acid (2 c.c.), followed by sublimation of the product and recrystallisation from alcohol.

9-*Methyl*-10-*chloromethylanthracene*.—(i) A suspension of 9-methylanthracene (7·5 g.) in glacial acetic acid (45 c.c.) was added to a solution prepared by passing hydrogen chloride into paraformaldehyde (3 g.) suspended in glacial acetic acid. The mixture was kept at 45° for 2 hours and then left at room temperature overnight. After addition of water, the product was collected and recrystallised from benzene. 9-*Methyl*-10-*chloromethylanthracene* (5·5 g.) formed yellow needles, which charred and melted at 192° (Found: C, 80·0; H, 5·5. $C_{16}H_{13}Cl$ requires C, 79·8; H, 5·4%). This compound (1 g.) was boiled with methanol (40 c.c.) and sodium methoxide (from 2 g. of sodium) for 15 minutes. The product, purified by way of the picrate, had m. p. 106—107°, not depressed on admixture with specimens of 9-methyl-10-methoxymethylanthracene prepared by either of the methods described above.

(ii) A stream of hydrogen chloride was passed into a solution of 9-methyl-10-ethoxymethylanthracene (2 g.) in benzene (50 c.c.), for ½ hour. Yellow crystals gradually separated and were collected and added to the material obtained by evaporation of the washed benzene solution. Recrystallisation of the crude material from benzene gave 9-methyl-10-chloromethylanthracene (1·6 g.), identical with that obtained by the first method.

9 : 10-*Dihydroxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene*.—This diol was prepared by the interaction of benzyl chloride with magnesium in the presence of anthraquinone as described above for the corre-

sponding dimethyl diol. After recrystallisation from alcohol, 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene formed small colourless transparent crystals, m. p. 185°, which became opaque when dried (Found: C, 85·9; H, 6·1. Calc. for $C_{28}H_{24}O_2$: C, 85·7; H, 6·2%). Padova (*Ann. Chim.*, 1910, **19**, 353) gives m. p. 184°.

9 : 10-*Diethoxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene*.—In an unsuccessful attempt to carry out the anionotropic rearrangement with picric acid, a solution of the above diol (0·5 g.) and picric acid (1 g.) in absolute ethanol was boiled for 1 hour. After cooling, the colourless crystals which had separated were collected and washed free of picric acid. Alcoholic solutions of the crude material had an intense blue fluorescence, showing the presence of traces of rearranged product, but the fluorescence was removed by repeated recrystallisation. 9 : 10-*Diethoxy*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthracene* was obtained as colourless plates, m. p. 248—250° (Found: C, 85·7; H, 7·1. $C_{32}H_{32}O_2$ requires C, 85·7; H, 7·2%).

9-*Formyl*-10-*benzylanthracene*.—A mixture of 9-benzylanthracene (Cook, *J.*, 1926, 2160; 35 g.), methylformanilide (35 g.), phosphorus oxychloride (35 g.), and chlorobenzene (20 c.c.) was heated on a steam-bath for 1½ hours. Crystalline sodium acetate (140 g.), dissolved in water (250 c.c.), was added to the cooled mixture, which was then rapidly steam-distilled. The residue was washed with a little alcohol and recrystallised from acetic acid. 9-*Benzylanthracene*-10-*aldehyde* (30·6 g.) formed bright yellow blades, m. p. 158—160° (Found: C, 89·2; H, 5·55. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%).

9-*Benzyl*-10-*α-hydroxybenzylanthracene*.—A warm benzene solution of 9-formyl-10-benzylanthracene (4 g.) was added to the Grignard solution prepared from bromobenzene (16 c.c.) and magnesium (2·5 g.) in ether. After 2 hours at room temperature, the mixture was decomposed with ice and ammonium chloride. 9-*Benzyl*-10-*α-hydroxybenzylanthracene* (3·2 g.) crystallised from benzene–light petroleum in very small pale yellow prisms, m. p. 170—172° (rapid heating) (Found: C, 89·7; H, 5·9. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%). The *photo-oxide*, prepared by exposure of a benzene–light petroleum solution of the above compound to air and diffuse sunlight for several days, formed colourless silky needles, m. p. 206—208° (Found: C, 82·8; H, 5·4. $C_{28}H_{22}O_3$ requires C, 82·7; H, 5·5%).

9-*Benzyl*-10-*α-ethoxybenzylanthracene*.—(i) A solution of 9-benzyl-10-α-hydroxybenzylanthracene (1 g.) in absolute ethanol was treated, at room temperature, with 3 drops of concentrated sulphuric acid in a little ethanol. Next morning the crystals which had deposited were collected and recrystallised from alcohol. 9-*Benzyl*-10-*α-ethoxybenzylanthracene* was obtained in almost quantitative yield and formed colourless small plates, m. p. 190—191° (Found: C, 89·5; H, 6·3. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%.

(ii) A boiling ethanol solution of 9 : 10-dihydroxy-9 : 10-dibenzyl-9 : 10-dihydroanthracene (5 g.) was treated with concentrated hydrochloric acid (5 c.c.), and the mixture boiled for 6 hours. 9-Benzyl-10-α-ethoxybenzylanthracene was obtained in almost quantitative yield and had m. p. 190—191°, alone or mixed with a specimen prepared as described in the first method.

We are grateful to the Director of Chemistry (Mr. S. D. Shield), South Australian Government Department of Chemistry, for permission to use the Beckman spectrophotometer, and to Mr. R. T. Howard for the microanalyses. This work was supported by a maintenance grant (to R. S. P.) from the Commonwealth Research Fund.

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