*The Direct Hydroxylation of 6-Phenyl*meso*benzanthrone and Two Benzo-derivatives of* meso*Benzanthrone, and Some Related Reactions.*

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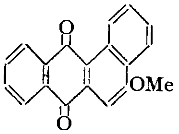
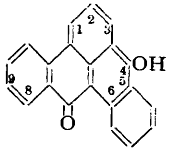
In continuation of earlier work the constitution assigned to the product of direct hydroxylation of 5 : 6-benzo*meso*benzanthrone has been confirmed. Under the same conditions 8 : 9-benzo*meso*benzanthrone affords a *mono*-hydroxy-derivative, the constitution of which has been established. 6-Phenyl*meso*benzanthrone affords the 4-hydroxy-derivative with potassium hydroxide and the 4-anilino-derivative with sodioaniline. 3-Bromo*meso*-benzanthrone yields the 6-phenyl derivative with phenylmagnesium bromide, an example of the rule that nuclear substitution is the predominant reaction when the reacting anion is highly active.

IN a previous communication (Bradley and Sutcliffe, *J.*, 1952, 1247) it was shown that 5 : 6-benzo*meso*benzanthrone gave a monohydroxy-derivative on being heated at 110° with alcoholic potassium hydroxide, and that 8 : 9-benzo*meso*benzanthrone gave a small amount of an alkali-soluble derivative with potassium hydroxide at 220—230°. The first was considered to be 4-hydroxy-5 : 6-benzo*meso*benzanthrone (II), and the correctness of this has now been shown by a synthesis from 3-methoxy-1 : 2-benzanthraquinone (I), glycerol, and sulphuric acid, the *O*-methyl substituent being eliminated. The experiments with 8 : 9-benzo*meso*benzanthrone have been extended. The addition of manganese dioxide to the alkali melt results in an increased yield of the alkali-soluble derivative from which a monohydroxy-8 : 9-benzo*meso*benzanthrone has now been isolated. The new derivative gives a monomethyl ether, but it does not form a boroacetate with Dimroth's reagent. In this, as in colour, the green fluorescence of its solution in aqueous alkalis, and the absorption spectrum of its solution in alcohol, it closely resembles 4-hydroxy*meso*benzanthrone, and the analogous constitution (III) is indicated. 4-Methoxy-8 : 9-benzo*meso*benzanthrone yields (III) on fusion with potassium hydroxide, and heating (III) with aqueous ammonia gives 4-amino-8 : 9-benzo*meso*benzanthrone (III; NH_2 for OH). There was no evidence of the formation of a violanthrone derivative in the action of potassium hydroxide on the *O*-methyl derivative, and this supports the constitution assigned.



(I)



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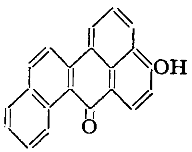
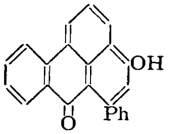


(III)

Fusion of 6-phenyl*meso*benzanthrone with potassium hydroxide and manganese dioxide gave 4-hydroxy-6-phenyl*meso*benzanthrone (IV) and 6 : 9-diphenylviolanthrone. In the absence of manganese dioxide the yield of the hydroxy-compound was lower and that of diphenylviolanthrone higher. From (IV) were derived the *O*-methyl ether (IV; OMe for OH), 4-hydroxy-6-phenyl-5-phenylazo*meso*benzanthrone (V; $R = PhN_2$), 5-amino-4-hydroxy-6-phenyl*meso*benzanthrone (V; $R = NH_2$), and the oxazole (VI). 6-Phenyl*meso*benzanthrone and sodioaniline gave 4-anilino-6-phenyl*meso*benzanthrone (IV; NHPh for OH), hydrolysed to (IV) by hot potassium hydroxide. There was no indication of the formation of a derivative of 4 : 4′-di*meso*benzanthronyl in this reaction. In contrast *meso*benzanthrone itself yields 4 : 4′-di*meso*benzanthronyl as the main product, and 4-anilino*meso*benzanthrone is formed only in minor amount (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 275).

Treatment of 3-bromo*meso*benzanthrone with phenylmagnesium bromide gave 3-bromo-6-phenyl*meso*benzanthrone (VII), an instance of nuclear substitution by an anion, without replacement of halogen. The constitution of this compound was proved by debromination to 6-phenyl*meso*benzanthrone by Busch, Wiher, and Zink's method (*J. prakt. Chem.*, 1940, **155**, 163). Heating (VII) with alcoholic potassium hydroxide gave 6 : 13-diphenyl*iso*violanthrone.



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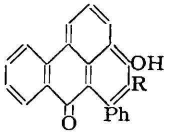
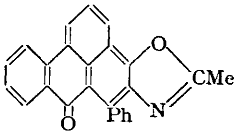
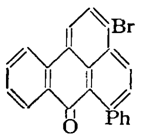


(V)



(VI)



(VII)

The occurrence of nuclear substitution when the reagent is the active anion of the Grignard reagent, and of self-coupling when it is the less active hydroxyl ion, is a further instance of the relation between substitution and self-coupling processes discussed by Bradley and Sutcliffe (*J.*, 1954, 708).

The formation of *mono*hydroxy-derivatives of the *mono*ketones, 5 : 6- and 8 : 9-benzo*meso*benzanthrone and 6-phenyl*meso*benzanthrone, on fusion with an alkali hydroxide, supports the conclusion (Bradley and Sutcliffe, *J.*, 1951, 2118) that the number of hydroxyl groups introduced equals the number of activating carbonyl groups present.

EXPERIMENTAL

*Action of Potassium Hydroxide on 6-Phenyl*meso*benzanthrone.*—6-Phenyl*meso*benzanthrone was prepared by Allen and Overbaugh's method (*J. Amer. Chem. Soc.*, 1935, **57**, 740); the purified product had m. p. 185—186°, as recorded.

*4-Hydroxy-6-phenyl*meso*benzanthrone.*—An intimate mixture of 6-phenyl*meso*benzanthrone (10 g.) and manganese dioxide (10 g.) was added during 0·5 hr. to a stirred melt of potassium hydroxide (100 g.) and potassium acetate (10 g.) at 220°, and then the temperature was raised to 240° for 1 hr. The product was cooled and added to water (1·5 l.) and the resulting suspension was filtered. The residue was extracted with water and the combined alkaline solutions were acidified. The precipitate which formed was collected, washed, dried, and crystallised from chlorobenzene; it afforded 7·5 g. of yellow crystals, m. p. 274—276° (Found: C, 85·3; H, 4·3. $C_{23}H_{14}O_2$ requires C, 85·7; H, 4·4%). *4-Hydroxy-6-phenyl*meso*benzanthrone* gave a yellow solution in aqueous sodium hydroxide, and a deep yellow solution with a slight greenish-yellow fluorescence in concentrated sulphuric acid. There was no colour change in acetic anhydride on the addition of boroacetic anhydride.

6 : 9-*Diphenylviolanthrone*.—The alkali-insoluble material obtained in the above preparation was heated with acidified sodium sulphite solution to remove manganese dioxide, then collected, washed, dried, dissolved in hot trichlorobenzene, and chromatographed at 150° on alumina using a jacketed column. A blue zone formed and this was extracted with trichlorobenzene. Concentration of the extract gave 1 g. of blue-violet needles which did not melt below 400° or dissolve in aqueous alkaline sodium dithionite. They dissolved in pyridine with a deep bluish-violet colour, changed to bluish-red on the addition of aqueous alkaline sodium dithionite. The light absorption of a solution of the product in concentrated sulphuric acid ($\lambda_{max.}$ at 390, 530, 570, 740, 790, and 870 mμ) resembled that of violanthrone ($\lambda_{max.}$ at 390, 570, 760, and 850 mμ).

When manganese dioxide was omitted from the reactants in the above preparation the yield of 4-hydroxy-6-phenyl*meso*benzanthrone, m. p. 274—276°, was 0·65 g., and that of 6 : 9-diphenylviolanthrone was 3·5 g.

*4-Methoxy-6-phenyl*meso*benzanthrone*.—4-Hydroxy-6-phenyl*meso*benzanthrone (2 g.) was refluxed for 4 hr. with methyl toluene-*p*-sulphonate (2 g.) and potassium carbonate (2 g.) in chlorobenzene (100 c.c.). The resulting suspension was filtered, and the cooled filtrate was washed with aqueous sodium hydroxide, then with water, and finally concentrated. Greenish-yellow needles (2 g.) separated which, after crystallisation from ethanol, had m. p. 175—176° (Found: C, 85·5; H, 4·7; OMe, 9·2. $C_{23}H_{13}O{\cdot}OMe$ requires, C, 85·7; H, 4·8; OMe, 9·2%). In concentrated sulphuric acid *4-methoxy-6-phenyl*meso*benzanthrone* gave a deep yellow solution with a faint greenish-yellow fluorescence. It was recovered unaltered after 4 hours' refluxing with acetic anhydride.

*4-Acetoxy-6-phenyl*meso*benzanthrone* resulted (0·9 g.) when the 4-hydroxy-derivative (1 g.) was refluxed with acetic anhydride for 3 hr. It separated from alcohol in greenish-yellow crystals, m. p. 187—189° (Found: C, 81·8; H, 4·5. $C_{25}H_{16}O_3$ requires C, 82·4; H, 4·4%).

*4-Hydroxy-6-phenyl-5-phenylazo*meso*benzanthrone* was obtained when aniline (0·93 g.) was diazotized in hydrochloric acid, and the resulting solution was added slowly and below 8° to a stirred solution of 4-hydroxy-6-phenyl*meso*benzanthrone (3·22 g.) in water (20 c.c.) containing sodium hydroxide (0·5 g.) and sodium carbonate (2·5 g.). The red precipitate of *4-hydroxy-6-phenyl-5-phenylazo*meso*benzanthrone* which formed was collected after 1 hr., dried, and purified from alcohol. Red crystals (3 g.), m. p. 226—228° (Found: C, 81·4; H, 4·3; N, 6·5. $C_{29}H_{18}O_2N_2$ requires C, 81·6; H, 4·3; N, 6·7%), were obtained.

2′-Methyl-6-phenyloxazolo(5′ : 4′-4 : 5)meso*benzanthrone* (VI).—The above azo-compound (2 g.) was dissolved in ethanol (150 c.c.), sodium dithionite (5 g.) was added, and then water at such a rate that none of the azo-compound was precipitated. The colour changed from bluish-red to orange. After 1 hour's refluxing the resulting solution was cooled, then acidified with acetic acid, and finally extracted continuously with benzene. The concentrated extract afforded 1 g. of red-brown crystals, m. p. 185—188°. A portion of the product (0·5 g.) was refluxed for 1 hr. with an excess of acetic anhydride. The yellow solution which formed was concentrated and cooled. It gave yellow crystals, which after purification from ethanol were obtained as fine needles (0·4 g.), m. p. 279—280° (Found: C, 82·6; H, 4·2; N, 4·2. $C_{25}H_{15}O_2N$ requires C, 83·0; H, 4·2; N, 3·9%). *2′-Methyl-6-phenyloxazolo*(5′ : 4′-4 : 5)meso*benzanthrone* was insoluble in aqueous acid or alkali. It was unaffected by prolonged refluxing with methanolic potassium hydroxide.

*3-Bromo-6-phenyl*meso*benzanthrone*.—3-Bromo*meso*benzanthrone (100 g.) was added during 30 min. to a stirred solution of the Grignard reagent prepared from bromobenzene (150 g.), magnesium (25 g.), and ether (700 c.c.). Stirring was continued for 5 hr. and then 30% acetic acid (370 c.c.) was added. After distillation in steam the residual aqueous solution was separated from a solid, and this was dried, dissolved in benzene (350 c.c.), and kept at 0° for several days. A solid separated and this was crystallised three times from benzene (charcoal). *3-Bromo-6-phenyl*meso*benzanthrone* (25·5 g.) forms yellow crystals, m. p. 202—203° (Found: C, 71·3; H, 3·3; Br, 21·3. $C_{23}H_{13}OBr$ requires C, 71·7; H, 3·4; Br, 20·8%).

Debromination. Palladium chloride (0·18 g.) was dissolved in water (10 c.c.) and added with vigorous stirring to a suspension of calcium carbonate (10 g.) in water (10 c.c.). The resulting pale brown precipitate was collected, washed, and dried. A portion (2 g.) of the catalyst so prepared was heated in a sealed tube at 140—145° for 1·5 hr. with 3-bromo-6-phenyl*meso*benzanthrone (3 g.), methanol (50 c.c.), and 100% hydrazine hydrate (1·4 c.c.). The product was stirred with an excess of hydrochloric acid, and the solid collected, dried, and chromatographed on alumina from chlorobenzene at 100° using a jacketed column. Two bands formed. The more strongly adsorbed was blue; elution with chlorobenzene gave 6 : 9-diphenylviolanthrone (1·3 g.) having the same absorption spectrum in concentrated sulphuric acid as the same compound prepared by heating 6-phenyl*meso*benzanthrone with potassium hydroxide. The less strongly absorbed was yellow; elution with chlorobenzene gave 6-phenyl*meso*benzanthrone (0·5 g.; m. p. 186—188°) identical (mixed m. p.) with the compound prepared from *meso*benzanthrone and phenylmagnesium bromide.

6 : 13-*Diphenyl*iso*violanthrone*.—3-Bromo-6-phenyl*meso*benzanthrone (5 g.) was added during 10 min. at 150° to a stirred melt of potassium hydroxide (48 g.) in ethanol (30 g.). After 2 hours' stirring the product was cooled and added to water (1 l.), and the resulting suspension was filtered. The residue, after being washed until neutral, was dried, and recrystallised from trichlorobenzene. Violet needles (2·5 g.) which did not melt below 400° were obtained. They dissolved in pyridine forming a violet solution which changed to blue on the addition of aqueous alkaline sodium dithionite. The absorption spectrum of the compound in concentrated sulphuric acid, like that of *iso*violanthrone, exhibited light absorption maxima at 390 and 735 mμ. Presence of some of a violanthrone derivative was not excluded.

4-*Anilino-6-phenyl*meso*benzanthrone*.—A solution of sodioaniline was prepared from aniline (75 g.), sodium (3 g.), copper bronze (0·1 g.), and nickel oxide (0·1 g.). 6-Phenyl*meso*benzanthrone was added at 40—45° to the solution which was stirred for 2 hr., then cooled, and added to 5% hydrochloric acid (1 l.). The precipitate was collected, extracted with hot dilute hydrochloric acid, washed, dried, and purified from chlorobenzene. 4-*Anilino-6-phenyl*meso*benzanthrone* crystallised in red needles (4 g.), m. p. 264—265° (Found: C, 87·7; H, 4·5; N, 3·9. $C_{29}H_{19}ON$ requires C, 87·7; H, 4·8; N, 3·5%). There was no indication of the formation of 6 : 6′-diphenyldi-(4-*meso*benzanthronyl) in the reaction of 6-phenyl*meso*benzanthrone with sodioaniline.

Hydrolysis. 4-Anilino-6-phenyl*meso*benzanthrone (0·5 g.) was heated in a sealed tube at 250° for 5 hr. with potassium hydroxide (5 g.) and water (10 c.c.). After addition to water, the precipitated solid was collected and washed with dilute sodium hydroxide, and the combined alkaline solutions were acidified with hydrochloric acid. A yellow precipitate formed which, after purification from chlorobenzene, afforded yellow crystals (0·3 g.), m. p. 274—276°, not depressed on admixture with 4-hydroxy-6-phenyl*meso*benzanthrone prepared from 6-phenyl*meso*benzanthrone and potassium hydroxide.

4-*Hydroxy*-5 : 6-*benzo*meso*benzanthrone*. (II).—A mixture of 3-methoxy-1 : 2-benzanthraquinone (1 g.), glycerol (1 g.), aniline sulphate (1 g.), concentrated sulphuric acid (13·5 c.c.), and water (3·9 c.c.) was stirred and heated at 140° for 1·25 hr. The resulting solution was cooled and added to water, and the dark brown precipitate was collected and washed (0·95 g.). It dissolved almost completely in dilute sodium hydroxide solution with a pink colour and a yellow fluorescence. The filtered solution was acidified, and the resulting precipitate was washed, dried, and crystallised from nitrobenzene. Light brown needles, m. p. 322—324°, were obtained, the m. p. of which was not depressed on admixture with the hydroxy-compound, m. p. 324—326°, prepared by the action of ethanolic potassium hydroxide on 5 : 6-benzo*meso*benzanthrone. Acetylation of the material, m. p. 322—324°, with hot acetic anhydride and pyridine, and crystallisation of the product from acetic acid gave pale yellow needles, m. p. 276—278° (decomp.), not depressed on mixing with the acetyl derivative, m. p. 280—281° (decomp.), of the hydroxy-compound, m. p. 324—326°.

4-*Hydroxy*-8 : 9-*benzo*meso*benzanthrone*.—8 : 9-Benzo*meso*benzanthrone was prepared by the method of Scholl (G.P. 239,671) and Cook (*J.*, 1939, 268). After distillation at 210—230°/10^{-4} mm. and subsequent crystallisation from toluene it was obtained as bright orange-yellow needles, m. p. 184—188°. An intimate mixture of the ketone (3 g.) and manganese dioxide (3 g.) was added during 10 min. at 210° to potassium hydroxide (30 g.) and potassium acetate (3 g.). The melt was then stirred for 1 hr. at 240°, during which it became grey-brown and viscous. After cooling and addition to water (600 c.c.), the resulting suspension was filtered, and the dark reddish-yellow filtrate, which exhibited a very strong green fluorescence, was acidified with hydrochloric acid. The precipitate which formed was collected, washed, and dried (1·35 g.).

Sublimation at 250° *in vacuo* gave a single band of bright yellow needles, m. p. 302—304° (Found : C, 84·9; H, 4·2. $C_{21}H_{12}O_2$ requires C, 85·2; H, 4·1%). 4-*Hydroxy*-8 : 9-*benzo*meso*benzanthrone* gave a yellow solution in acetic anhydride, unchanged on the addition of boroacetic anhydride. It gave a yellow solution and a green fluorescence in concentrated sulphuric acid.

4-*Methoxy*-8 : 9-*benzo*meso*benzanthrone*.—The 4-hydroxy-derivative (0·3 g.), methyl toluene-*p*-sulphonate (0·6 g.), and potassium carbonate (0·6 g.) were refluxed 5 hr. in chlorobenzene (50 c.c.). The resulting suspension was filtered, and the cooled filtrate washed with dilute sodium hydroxide, then water, and chromatographed on alumina. A yellow band formed and this was extracted with chlorobenzene. Concentration gave yellow crystals of 4-*methoxy*-8 : 9-*benzo*meso*benzanthrone* (0·17 g.), m. p. 199—201° (Found : OMe, 12·0. $C_{21}H_{11}O{\cdot}OMe$ requires OMe, 10·5%).

Hydrolysis. 4-Methoxy-8 : 9-benzo*meso*benzanthrone (0·1 g.) was stirred for 1 hr. at 240° with potassium hydroxide (1 g.) and potassium acetate (0·1 g.). On addition to water (150 c.c.) a yellow solution formed, and this was filtered and acidified. A yellow precipitate resulted and this was collected, washed, dried (0·09 g.), and sublimed *in vacuo* at 250°. Bright yellow needles, m. p. 302—304°, were obtained which did not depress the m. p. of 4-hydroxy-8 : 9-benzo*meso*benzanthrone.

4-*Amino*-8 : 9-*benzo*meso*benzanthrone*.—4-Hydroxy-8 : 9-benzo*meso*benzanthrone (0·6 g.) and aqueous ammonia (20 c.c. of S.G. 0·88) were heated at 220—230° for 7 hr. After being cooled, the dark red crystals were collected, washed with dilute sodium hydroxide, then water, and finally they were sublimed at 250° *in vacuo*. Bright red needles of 4-*amino*-8 : 9-*benzo*meso-*benzanthrone* (0·32 g.), m. p. 283—286° (Found : C, 85·0; H, 4·3; N, 4·7. $C_{21}H_{13}ON$ requires C, 85·4; H, 4·4; N, 4·8%), were obtained.

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