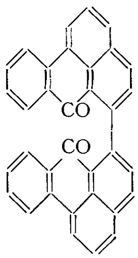
353. *Kationoid Reactivity of Aromatic Compounds. Part VIII. The Action of Fused Potassium Hydroxide on* 6 : 6'-*Di*meso*benzanthronyl and a Note on the Properties of* 6- *and* 8-*Chloro*meso*benzanthrones.*

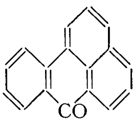
By W. Bradley and G. V. Jadhav.

6 : 6'-Di*meso*benzanthronyl reacts with potassium hydroxide at 240—250° to form a mixture of acids together with some violanthrone and an unidentified product. At 260—270° the principal product is violanthrone, the mode of formation of which is discussed. A further illustration of the ease of transmission of effects through the naphthalene nucleus of *meso*benzanthrone has been encountered in the reactivity of 6-chloro*meso*benzanthrone towards sodium methoxide and amines in circumstances which leave 8-chloro*meso*benzanthrone unaltered.

In continuation of previous work further experiments have been carried out on the properties of 6 : 6'-di*meso*benzanthronyl (I). Unlike *meso*benzanthrone (II) which yields 4 : 4'-di*meso*benzanthronyl (III) (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259), 6 : 6'-di*meso*benzanthronyl is completely stable towards concentrated alcoholic potassium hydroxide at 100—105°. It is unaffected by concentrated aqueous potassium hydroxide at 180—190°, but at 240—250° a mixture of acids is formed together with a smaller proportion of violanthrone and another unidentified product. The most abundant constituent, which is also the acid of highest melting point, is easily separable because of its sparing solubility in glacial acetic acid. Its elementary composition and melting point suggest the molecular composition, $C_{34}H_{22}O_4$. The structure may be (IV) in agreement with the known mode of scission of analogous ketones, but a dihydroxy-derivative of (I) is not improbable on present evidence. 1 : 1'-Dianthraquinonyl (V) forms a mixture of benzoic and diphenyl-3 : 3'-dicarboxylic acids when it is fused with potassium hydroxide at 200° (Eckert, *Ber.*, 1925, **58**, 321), and both α- and β-benzoylnaphthalene yield naphthalene and benzoic acid when they are heated with soda–lime at 350° (Grucarevic and Merz, *Ber.*, 1873, **6**, 1246). A mixture of α- and β-chrysenic acids (VII and VIII, respectively) is obtained by the alkali fusion of chrysoketone (VI), the α-form having the higher melting point and the lower solubility in aqueous acetic acid (Graebe, *Ber.*, 1900, **33**, 680).



(I.)



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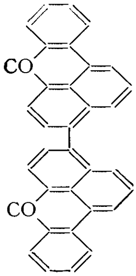

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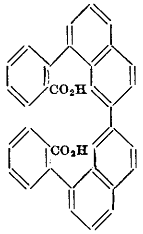

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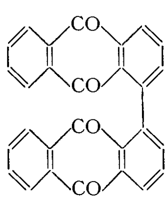
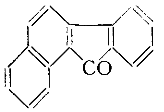


(V.)

Unsuccessful efforts have been made to cyclise the acid by treatment with sulphuric acid, oleum, and phosphorus pentachloride followed by aluminium chloride, procedures which serve to convert α- and β-chrysenic acid into chrysoketone or *o*-(1-naphthyl)benzoic acid into *meso*benzanthrone (Graebe, *loc. cit.*; Schaarschmidt and Georgeacopol, *Ber.*, 1917, **50**, 1082).

Crystallisation of the acetic acid-soluble portion of the acidic product gives a *substance*, m. p. 258—260°, the composition of which approximates to $C_{34}H_{22}O_5$. It may be a hydroxy-derivative of (IV), or a trihydroxy-derivative of (I). Its most characteristic property is that of dissolving in cold potassium hydrogen carbonate solution, forming a yellow solution with a green fluorescence.

At 260—270° the yield of acids is much smaller than at 240—250° and the product now contains violanthrone (IX) as a principal constituent. The formation of this colouring matter has considerable interest since it involves the breaking of the 6 : 6′-linkage of the di*meso*benzanthronyl. The reconstruction of the molecule is not a purely thermal phenomenon because boiling with quinoline or diphenyl sulphone (b. p. 375°) for several hours leaves 6 : 6′-di*meso*benzanthronyl completely unchanged. Anhydrous aluminium chloride reacts to form a red oxonium salt, but there is no formation of violanthrone at 232° or at a lower temperature.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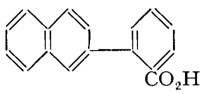
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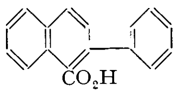
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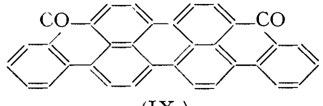
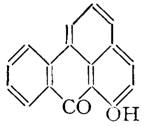
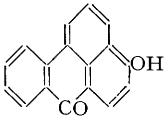

(IX.)

It is probable that the formation of violanthrone involves the intermediate production of 4 : 4′-di*meso*benzanthronyl which then undergoes cyclisation. We have confirmed that 4 : 4′-di*meso*benzanthronyl readily yields violanthrone at 200—210° (Lüttringhaus and Neresheimer, *loc. cit.*, state that the reaction begins at 170°), which is well below the temperature of the formation of the colouring matter from the 6 : 6′-isomeride. An idea that 6 : 6′-di*meso*benzanthronyl is first hydrolysed to a mixture of *meso*benzanthrone and its 6-hydroxy-derivative (X), the former of which then yields violanthrone, is untenable because 6-hydroxy*meso*benzanthrone, although very stable to alkalis (*J.*, 1937, 1791), is not encountered. Further, the reaction product contains no trace of 4-hydroxy*meso*benzanthrone (XI), which is easily recognised by the strong green fluorescence of its alkaline solution. This phenol invariably accompanies the products of transformation of *meso*benzanthrone in hot alkaline solution; in our experiments 5 mg. of *meso*benzanthrone were detected quite readily by this test.


(X.)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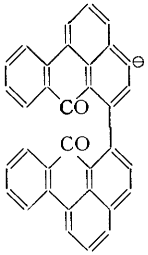
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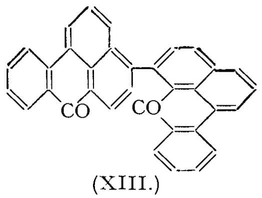

(XIII.)

The need of a strong alkali and a high temperature suggests that 6 : 6′-di*meso*benzanthronyl, like *meso*benzanthrone (see Part VII), is a very weak acid yielding the anion (XII), and that 4 : 4′-di*meso*benzanthronyl is formed from this by a cationotropic change in which the migrating *meso*benzanthronyl group either yields 4 : 6′-di*meso*benzanthronyl (XIII) at an intermediate stage or, more probably, rearranges during migration and forms 4 : 4′-di*meso*benzanthonyl directly.

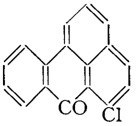
The mobility of a group attached to the 6-position of *meso*benzanthrone is a further consequence of the great intensity of the effect transmitted from the carbonyl group through the naphthalene unit of the structure. The same effect is responsible for the unusual ease with which *meso*benzanthrone undergoes substitution by electron-donating agents (see Part VI), for the ease with which the acyl derivatives of 3-, 4-, and 6-amino*meso*benzanthrone form salts with alkalis (Bradley, *J. Soc. Dyers Col.*, 1942, **58**, 4), and for the facile hydrolysis of 6 : 6′-di*meso*benzanthronylamine (Part VI).

This property of *meso*benzanthrone has been studied further by comparing the ease of replacement of chlorine when substituted at the 6- and the 8-position successively. It has been found that, whilst the halogen of 6-chloro*meso*benzanthrone can be replaced quite readily by treatment with sodium methoxide or with a variety of aliphatic and aromatic amines, including *p*-nitroaniline, yet that of 8-chloro*meso*benzanthrone is stable towards these reagents.

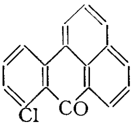
All the 6-arylamino*meso*benzanthrones form salts when 20% ethyl-alcoholic potassium hydroxide is added to their solutions in pyridine (cf. *ibid.*, p. 2), an additional illustration of the strong electron-attracting properties of the *meso*benzanthrone structure at the 6-position.

6-Chloro*meso*benzanthrone (XIV) has already been described and oriented (Part VII). 8-Chloro*meso*benzanthrone (XV) was prepared by reaction of 1-chloroanthr-9-one (Barnett and Matthews, *J.*, 1923, **123**, 2549) with glycerol and sulphuric acid, a method which might yield either

6- or 8-chloro*meso*benzanthrone or both of these. Actually, a homogeneous chloro*meso*benzanthrone, m. p. 178—179°, was obtained together with a substance, m. p. 120—121°, which appeared to be a eutectic mixture of the two isomers. The compound of m. p. 178—179° was different from 6-chloro*meso*benzanthrone, and its identity as 8-chloro*meso*benzanthrone was established by its conversion by oxidation into 5-chloroanthraquinone-1-carboxylic acid (XVI), m. p. 312—313° (Heilbron, Heslop, and Irving, *J.*, 1936, 784, give m. p. 312—313°, and Cahn, Jones, and Simonsen, *J.*, 1933, 444, m. p. *ca.* 306°, varying with the rate of heating).



(XIV.)



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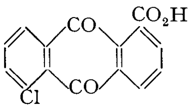

(XVI.)

A compound, m. p. 183°, has been referred to as 8-chloro*meso*benzanthrone (B.P. 301,197) but no proof of structure is given.

Experimental.

Fusion of 6 : 6′-*Di*meso*benzanthronyl with Potassium Hydroxide at* 240—250°.—6 : 6′-Di*meso*benzanthronyl (1·0 g.) was added portionwise to a stirred melt of potassium hydroxide (20 g.) and water (4 c.c.) at 240—250°, and the heating was then continued for 2 hours. The cooled melt, added to water, gave a solid and a red solution. The filtered solution showed a slight green fluorescence, and when acidified gave a yellow precipitate. This was collected, washed, and extracted by means of warm sodium hydrogen carbonate solution, and the acids were reprecipitated, giving 0·16 g. of material, m. p. 230—320°. Several repetitions of the experiment gave additional amounts of similar products. These were combined and extracted with boiling glacial acetic acid. A portion remained undissolved; this was insoluble in the common solvents with the exception of pyridine, from which it crystallised as the free *acid* (IV), m. p. above 360° (Found : C, 81·7; H, 3·9. Found, after washing with dilute hydrochloric acid, then water, and drying: C, 82·3; H, 4·7. $C_{34}H_{22}O_4$ requires C, 82·6; H, 4·5%). The acetic acid-soluble portion of the product was recrystallised several times from 50% acetic acid giving a *substance*, m. p. 258—260° (Found: C, 80·9; H, 4·3. $C_{34}H_{22}O_5$ requires C, 80·0; H, 4·4%). Increasing the time of fusion did not lead to an increase in the yield of acids. In one experiment the character of the non-acidic portion of the product was examined; it consisted of crude violanthrone (0·11 g.) and of a substance insoluble in alkali or a mixture of sodium hydroxide and sodium hyposulphite (dithionite) (0·55 g.). Weakly alkaline solutions of both acids give first a brownish-red coloration and then a reddish-brown precipitate on addition of a solution of diazotised *p*-nitroaniline. Similarly, the yellow, flocculent, freshly precipitated acids are rendered reddish-brown when diazotised *p*-nitroaniline is added to their weakly acid suspensions.

The acid of higher m. p. was recovered unchanged when its solution in cold, concentrated sulphuric acid was kept for several days and then added to water. No re-formation of 4 : 4′-di*meso*benzanthronyl occurred when the lower-melting acid was treated similarly, or when the acid of higher m. p. was warmed with 80% sulphuric acid for 3 hours at 60—70°, or when the same acid was heated at 140° in nitrobenzene solution with a molecular proportion of phosphorus pentachloride for 2 hours and then at 40° for an hour with the addition of 4 molecular proportions of anhydrous aluminium chloride. The higher-melting acid was sulphonated by cold, 20—25% oleum.

Fusion of 6 : 6′-*Di*meso*benzanthronyl with Potassium Hydroxide at* 260—270°.—The quantities and procedure employed in the experiment at 240—250° were adopted, the heating being maintained for 2·5 hours. The cooled melt, added to water, gave a colourless and non-fluorescent alkaline solution (absence of 2-hydroxy*meso*benzanthrone) from which only a negligible amount of acidic material separated when it was acidified by adding hydrochloric acid.

The alkali-insoluble portion of the product was blue. It was extracted first with water and then with benzene, and the benzene solution was evaporated and the absence of 6-hydroxy*meso*benzanthrone confirmed by applying the boroacetate test (*J.*, 1937, 1791). The benzene-insoluble material was further extracted with acetone, giving a solution which contained only a trace of violanthrone. The acetone-insoluble residue was dried and then digested at 70—80° with 10% sodium hydroxide solution containing sodium hyposulphite (dithionite). A blue-violet and then a deep violet-red solution formed quickly; it exhibited an intense brownish-red fluorescence. The solution was separated and the residue again treated with alkaline hyposulphite (dithionite) until nothing more dissolved; a dark blue residue (0·35 g.) remained. The combined extracts were filtered and then aerated, giving 0·4 g. of crude violanthrone.

Another experiment in which the period of fusion was 3 hours gave alkali-soluble products (0·04 g.), crude violanthrone (0·46 g.), and non-vattable residue (0·26 g.).

The crude violanthrone was purified by crystallisation from quinoline, giving an almost black powder, m. p. above 360° (Found : C, 87·1; H, 3·8. Calc. for $C_{34}H_{16}O_2$: C, 89·5; H, 3·5%), the properties of which were identical with those of a sample of violanthrone provided by Messrs. I.C.I. (Dyestuffs) Ltd., which had been purified similarly. In particular, it was almost completely insoluble in hot xylene, the faintly violet solution was bluish-violet, becoming violet-red as the concentration was increased, and all solutions exhibited a fluorescence. It dissolved readily in cold, concentrated sulphuric acid, forming a violet solution. Its reduced form obtained by treatment with alkaline sodium hyposulphite (dithionite) was easily soluble in dilute sodium hydroxide and showed very high affinity for cotton. In almost all of these respects it differed from *iso*violanthrone, which is more sparingly soluble in xylene and pyridine and forms a green solution in cold, concentrated sulphuric acid, and whose reduced form is much less soluble in sodium hydroxide solutions.

The residue insoluble in alkaline sodium dithionite was a dark blue powder almost completely insoluble in boiling pyridine, and only slowly dissolved by cold, concentrated sulphuric acid, forming a violet solution. When it was boiled with a mixture of pyridine, 20% sodium hydroxide, and sodium dithionite the pyridine acquired a green colour and a yellow fluorescence. A solid separated on cooling, leaving the pyridine solution pink; the green colour was restored on heating. In the same circumstances *iso*violanthrone forms first a violet and then a green solution, whilst violanthrone and the vattable product of the present experiments behave identically, giving first a violet and then a blue colour to the pyridine.

8-*Chloro*meso*benzanthrone*.—Glycerol (8 g.) and 1-chloroanthr-9-one (10 g.) were added to a solution of concentrated sulphuric acid (10 c.c.) in water (20 c.c.) and the mixture was heated at 140—150° for 3 hours. A violet colour developed; later, sulphur dioxide was evolved and a dark solid separated. Water was added to the cooled product and the solid was collected, washed with water, and dried. A tacky product was obtained when the solid was extracted by means of chloroform and the solvent was evaporated from the filtered extract. This became granular when it was washed with light petroleum, and a residue, m. p. 173—175°, remained when it was repeatedly extracted by means of boiling dilute alcohol (75%). Crystallisation of the residue from alcohol gave yellow needles of (XV), m. p. 178—179° (Found: C, 76·9; H, 3·5; Cl, 13·3. Calc. for $C_{17}H_9OCl$: C, 77·1; H, 3·4; Cl, 13·4%). Evaporation of the dilute alcohol extracts gave a solid, m. p. 85—110°, which was raised only very slowly by repeated crystallisation from alcohol. Ultimately a substance, m. p. 120—121°, was obtained, evidently a eutectic of (XIV) and (XV) (Found : C, 77·4; H, 3·4; Cl, 12·5%).

5-*Chloroanthraquinone*-1-*carboxylic Acid*.—A solution of chromium trioxide (1 g.) in 50% acetic acid (5 c.c.) was added to a suspension of the above chloro*meso*benzanthrone, m. p. 178—179° (0·5 g.), in glacial acetic acid (10 c.c.) and the mixture was boiled for four hours. Water was added to the product, and the precipitated solid was collected, washed, extracted with warm dilute ammonia solution, and the extract filtered and acidified. A precipitate formed which crystallised from glacial acetic acid in almost colourless needles, m. p. 312—313° (Found : C, 62·7; H, 2·7; Cl, 12·4. Calc. for $C_{15}H_7O_4Cl$: C, 62·8; H, 2·5; Cl, 12·4%).

Action of Sodium Methoxide and of Amines on 8- *and* 6-*Chloro*meso*benzanthrone*.—8-Chloro*meso*benzanthrone was recovered almost completely unchanged when 0·5 g. was boiled for 3 hours with either aniline (2 g.) or monomethylaniline (1·5 g.), or when 0·2 g. was boiled for 7 hours with a solution of sodium methoxide prepared from sodium (1 g.) and methanol (10 c.c.).

6-*Methylamino*meso*benzanthrone*. A suspension of 6-chloro*meso*benzanthrone (0·5 g.) in 10 c.c. of 33% aqueous methylamine was heated at 180—190° for 7 hours. The *product* was cooled and then mixed with water. The solid was collected, washed, and recrystallised from alcohol. It formed orange-yellow needles, m. p. 160—161° (Found: C, 83·7; H, 5·0; N, 5·8. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·1; N, 5·4%), which dissolved in pyridine with a yellow colour unaltered by the addition of a few drops of 20% ethyl-alcoholic potassium hydroxide.

6-*Anilino*meso*benzanthrone*. A solution of 6-chloro*meso*benzanthrone (0·5 g.) in 2·5 g. of freshly distilled aniline was boiled for 4 hours. A red solution resulted from which a yellow solid separated on cooling. The product was warmed with excess of dilute hydrochloric acid, and the undissolved solid was collected, washed, and then crystallised from alcohol. It formed yellow needles, m. p. 156—157° (Found : C, 86·1; H, 4·7; N, 4·4. $C_{23}H_{15}ON$ requires C, 86·0; H, 4·7; N, 4·4%). A yellow solution of this *compound* in pyridine is rendered yellowish-orange when a drop of ethyl-alcoholic potassium hydroxide is added.

The following analogues of 6-anilino*meso*benzanthrone were prepared by similar means. (The statements enclosed within parentheses refer to the colour changes which occur when a drop of ethyl-alcoholic potassium hydroxide is added to pyridine solutions of the several amines).

6-p-*Toluidino*meso*benzanthrone*, orange-yellow needles from alcohol, m. p. 131—132° (Found : C, 85·6; H, 5·0; N, 4·5. $C_{24}H_{17}ON$ requires C, 86·0; H, 5·1; N, 4·2%) (yellow to yellowish-orange). 6-p-*Chloranilino*meso*benzanthrone*, orange-yellow needles from nitrobenzene, m. p. 217—218° (Found : C, 77·5; H, 3·9; N, 4·1; Cl, 9·8. $C_{23}H_{14}ONCl$ requires C, 77·6; H, 4·0; N, 4·0; Cl, 10·0%) (yellow to pale orange-red, pink in thin layers). 6-p-*Nitroanilino*meso*benzanthrone*, orange needles from nitrobenzene, m. p. 293—294° (Found : C, 75·6; H, 3·9; N, 7·8. $C_{23}H_{14}O_3N_2$ requires C, 75·4; H, 3·9; N, 7·6%) (yellow to intense blue). 6-α-*Naphthylamino*meso*benzanthrone*, yellow needles from nitrobenzene, m. p. 243—244° (Found : C, 87·7; H, 4·7; N, 4·0. $C_{27}H_{17}ON$ requires C, 87·3; H, 4·6; N, 3·8%) (golden-yellow to deep reddish-orange). 6-β-*Naphthylamino*meso*benzanthrone*, red needles from nitrobenzene, m. p. 189—190° (Found : C, 87·2; H, 4·7; N, 3·7. $C_{27}H_{17}ON$ requires C, 87·3; H, 4·6; N, 3·8%) (golden-yellow to deep orange-red).

Hydrolysis of 6-*Chloro*meso*benzanthrone*.—6-Chloro*meso*benzanthrone (0·5 g.) was boiled with a solution prepared from sodium (2 g.) and methanol (20 c.c.) for 4 hours. Water and then dilute hydrochloric acid were added to the cooled product. The yellow precipitate was collected, washed, and then crystallised from glacial acetic acid. It gave yellow needles, m. p. 177—178°, alone or mixed with 6-hydroxy*meso*benzanthrone. Admixture with 6-chloro*meso*benzanthrone depressed the m. p. below 136°.

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