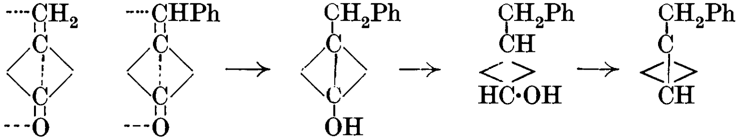
CCLXXXVI.—*The Reactivity of* meso-*Substituted Anthracenes. Part III.*

By JAMES WILFRED COOK.

IT has been shown that, when an unsaturated or negative substituent is attached to one of its *meso*-carbon atoms, the capacity of an anthracene derivative to enter into reactions of 9 : 10-addition is greatly lessened and in a former communication (this vol., p. 1282) it was foreshadowed that this limitation would be removed when the *meso*-substituent is saturated. This hypothesis has been fairly well substantiated by a comparison of 9-benzoylanthracene with 9-benzylanthracene, the reactions of which are now described.

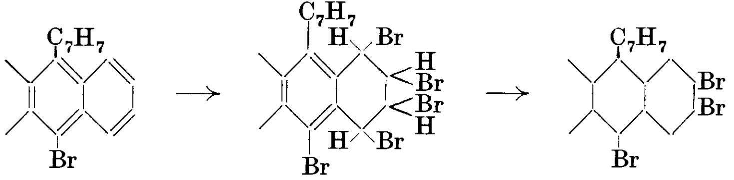
9-Benzylanthracene (V) was obtained in an impure state by Bach (*Ber.*, 1890, **23**, 1567) by the reduction of benzylhydroxyanthrone or of benzylideneanthrone (II) with hydriodic acid and red phosphorus. Barnett and Matthews (*Ber.*, 1926, **59**, 767) have shown that reduction of methyleneanthrone (I) leads to union of the methylene carbon atoms of two molecules, a reaction which suggests that the methylene carbon atom and the carbonyl oxygen atom are endowed with free residual affinity :



(I.) (II.) (III.) (IV.) (V.)

In the case of benzylideneanthrone (II) steric factors prevent union of two molecules, but there seems little doubt that the distribution of free residual affinity is similar, since reduction with zinc and acetic anhydride leads to the production of the acetate of benzylanthranol (III). Reduction of benzylideneanthrone proceeds a stage further when zinc dust and ammonia are used, so that the benzylanthranol first formed is converted into benzyldihydroanthranol (IV), which is considerably more stable than 9 : 10-dihydroanthranol but loses water across the ring under the influence of acetic acid and passes into benzylanthracene (V). Since benzylideneanthrone is readily obtained by condensing anthrone with benzaldehyde, benzylanthracene is conveniently obtained by the above series of reactions. If this mechanism of the reactions involved be accepted, the position of the hydroxyl group in benzyldihydroanthranol (IV) follows, in conformity with the orientation given by Bach (*Ber.*, 1890, **23**, 2527), although not in agreement with Tschilikin (*ibid.*, 1914, **47**, 1055), and the fact that the substance is more stable than dihydroanthranol can scarcely be attributed to steric influences. The reduction of methyleneanthrone and its derivatives is thus analogous to that of anthraquinone derivatives and in the former case the course taken by the reaction cannot be explained on the basis of a peroxide structure but must be due to conjugation (compare Barnett and Matthews, *loc. cit.*). The production of dianthranol and not dianthrone by the reduction of dianthraquinone (Matthews, this vol., p. 236) lends further support to this view of the mechanism.

9-Benzylanthracene resembles anthraphenone in yielding no stable additive compound with bromine, the product of the reaction with 1 mol. of bromine being 10-bromo-9-benzylanthracene (VI). Bromination probably proceeds through the intermediate formation of an additive compound, however, since if the reaction is carried out in the presence of excess of bromine the benzyl group is lost before re-establishment of the " bridge " occurs and 9 : 10-dibromoanthracene results. That this is not due to the action of bromine on bromobenzylanthracene is shown by the fact that the latter compound gives a tetrabromide (VII) when treated with bromine under the same experimental conditions, no dibromoanthracene being isolated :

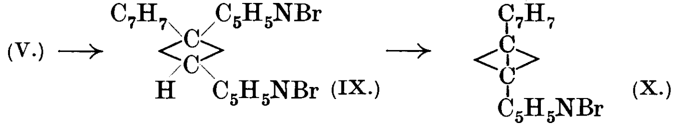


(VI.) (VII.) (VIII.)

The facile addition of bromine to the benzene ring suggests that introduction of the *meso*-bromine atom favours the ortho-quinonoid structure of the anthracene ring, and similar addition of bromine has been observed with other *meso*-disubstituted anthracenes in which at least one substituent is negative (Barnett and Matthews, *Ber.*, 1926, **59**, 1429). With other disubstituted anthracenes, no such addition occurs, 9 : 10-dibenzylanthracene, for example, being brominated in the benzyl groups (Lippmann and Pollak, *Monatsh.*, 1902, **23**, 672; Lippmann and Fritsch, *Annalen*, 1907, **351**, 52).

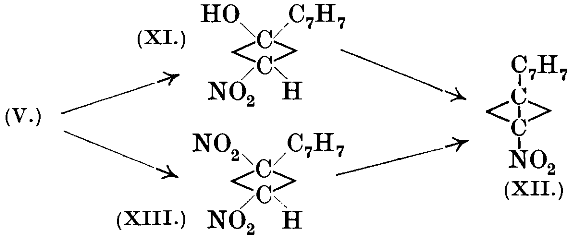
Bromobenzylanthracene tetrabromide (VII) is converted by treatment with an alcoholic solution of potassium hydroxide into 2 : 3 : 10-tribromo-9-benzylanthracene (VIII), the orientation of which is shown by its oxidation to 2 : 3-dibromoanthraquinone.

Further evidence that bromination of benzylanthracene is preceded by addition is afforded by the observation that a dipyridinium dibromide (IX) is formed when benzylanthracene is treated with pyridine perbromide in pyridine solution. In fact, the action of this reagent illustrates in a very striking manner the transition from 9 : 10-additive power to direct replacement at 10 as the substituent in the 9-position of the anthracene molecule becomes increasingly negative in character, for 9-benzoylanthracene (anthraphenone) is unattacked under the same conditions, whilst 9-phenylanthracene is readily converted into 10-bromo-9-phenylanthracene. Benzyldihydroanthraquinyldipyridinium dibromide (IX) loses pyridine hydrobromide under the influence of acid or alkaline reagents and passes into benzylanthranylpyridinium bromide (X) (compare Barnett and Cook, J., 1921, **119**, 901) :



The action of chlorine on benzylanthracene leads to the production of 10-chloro-9-benzylanthracene, and the same product is obtained when chlorination is effected by means of sulphuryl chloride, although in the latter case a considerable amount of 9 : 10-dichloroanthracene is also formed.

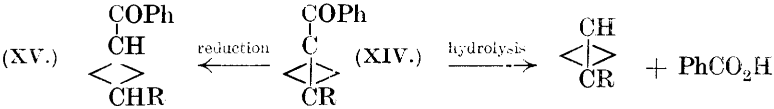
When treated with nitric acid in the presence of acetic acid, benzylanthracene yields a moderately stable additive compound (XI), which, however, loses water under the influence of mineral acids and passes into 10-nitro-9-benzylanthracene (XII) :



Anthracene itself under similar conditions gives only the acetate of the nitrodihydroanthranol (Meisenheimer and Connerade, *Annalen*, 1904, **330**, 133; Barnett, Cook, and Matthews, J., 1923, **123**, 1994) and the diminished reactivity of the free hydroxy-compound obtained from benzylanthracene is probably due to steric hindrance and has been observed with the corresponding additive compound of 9-ethylanthracene (Meisenheimer and Connerade, *loc. cit.*). The extreme sensitivity of benzylnitrodihydroanthranol (XI) to mineral acids in contrast to its stability towards other reagents is significant and suggests that the non-isolation of additive compounds in certain other cases should not be taken as proof of general instability.

Addition of nitrogen dioxide to benzylanthracene is readily effected and although the resulting compound (XIII) could not be obtained pure its identity was established by its conversion into nitrobenzylanthracene (XII) under the influence of cold pyridine.

In former parts of this series (this vol., pp. 1282, 1677), it was shown that anthraphenone and 10-benzoylanthraphenone are readily reduced to the corresponding dihydroanthracene derivatives and that benzoylanthraphenone, unlike anthraphenone, does not easily lose a benzoyl group by hydrolysis. The suggestion was made that the greater stability of benzoylanthraphenone is due to the suppression of *meso*-additive power by the attachment of the unsaturated benzoyl group to the carbon atom in position 10, and in order to test this hypothesis 10-benzylanthraphenone and 10-phenylanthraphenone have now been examined.



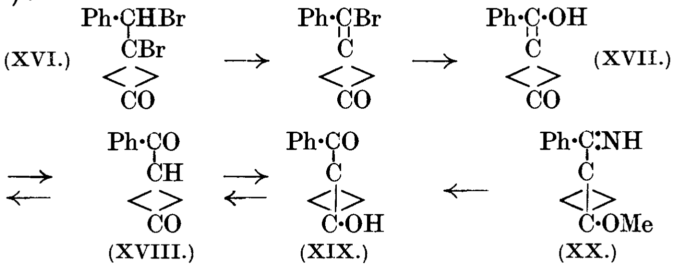
$$\text{(XV.)}\ \begin{matrix}\text{COPh}\\ |\\ \text{CH}\\ <>\\ \text{CHR}\end{matrix} \xleftarrow{\text{reduction}} \begin{matrix}\text{COPh}\\ |\\ \text{C}\\ <|>\\ \text{CR}\end{matrix}\ \text{(XIV.)} \xrightarrow{\text{hydrolysis}} \begin{matrix}\text{CH}\\ <|>\\ \text{CR}\end{matrix} + \text{PhCO}_2\text{H}$$

(R = C_7H_7, $C_6H_5{\cdot}CO$, C_6H_5, or H.)

Both compounds are reduced to the dihydroanthracene derivatives only with difficulty and the retarding influence of the substituent in position 10 is readily explicable on the theory of steric hindrance and is further evidence of primary addition to the carbonyl oxygen atoms in the case of benzoylanthraphenone. As was foreseen, the more saturated nature of the benzyl group resulted in benzylanthraphenone being hydrolysed under conditions in which benzoylanthraphenone was not affected, but with phenylanthraphenone the result was unexpected, this compound undergoing hydrolysis also. At present, no satisfactory explanation can be given of this anomaly.

Benzyldihydroanthracene is conveniently obtained by reducing benzylanthracene with sodium and amyl alcohol and is more stable than dihydroanthracene, being recovered unchanged after treatment with bromine or with nitric acid under conditions which lead to reaction in the case of dihydroanthracene. The benzyl group has a greater influence than an ethyl group in stabilising the dihydroanthracene derivative, since Meisenheimer and Connerade (*loc. cit.*) have shown that ethyldihydroanthracene is readily attacked by nitric acid in acetic acid even at 0°.

It was shown in Part II of this series that 9 : 10-dihydroanthraphenone is a tautomeric compound and it seemed of interest to study the cyclol-keto-enol tautomerism which benzoylanthrone (XVIII) might feasibly exhibit. This substance was obtained by Krollpfeiffer (*Ber.*, 1923, **56**, 2360) by hydrolysis of 10-methoxy-9-anthranylphenylketimide (XX). Krollpfeiffer gave no experimental details and it seemed probable that benzoylanthrone would be obtained more conveniently from benzylideneanthrone dibromide (XVI) :



(XVI.) (XVII.)

(XVIII.) (XIX.) (XX.)

Up to the present, a satisfactory method for bringing about the first stage of the reaction has not been devised, treatment of the dibromide with pyridine, diethylamine, aqueous acetone, alcohol or dry silver oxide leading to loss of bromine and the formation of benzylideneanthrone as the main product of the reaction. With moist silver oxide, however, the reaction appeared to take the desired course and a product was obtained which gave analytical figures agreeing with those required for hydroxybenzylideneanthrone (XVII) or benzoylanthrone (XVIII), yielded a monoacetyl derivative when treated with acetic anhydride in the presence of pyridine, and dissolved in aqueous sodium hydroxide to give a deep red solution, presumably of the sodium salt of benzoylanthranol (XIX). Since these experiments were carried out, it has been found that the tautomerism of benzoylanthrone has been investigated by Thorn (Dissertation,* Marburg, May 1924) and the study of this subject has therefore been postponed. It seemed desirable, however, to place on record the above results, since the properties of the compound obtained by the action of silver hydroxide on benzylideneanthrone dibromide indicate that it is certainly not the benzoylanthrone obtained by Krollpfeiffer (*loc. cit.*) and Thorn.

EXPERIMENTAL.

Benzylideneanthrone (II) was obtained by Levi (*Ber.*, 1885, **18**, 2152), Bach (*ibid.*, 1890, **23**, 1567), Padova (*Compt. rend.*, 1905, **141**, 857; *Ann. Chim.*, 1910, **19**, 353), and Tschilikin (*Ber.*, 1914, **47**,

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* I am indebted to Dr. E. de Barry Barnett for placing at my disposal a copy of this dissertation, which was kindly lent to him by Prof. F. Krollpfeiffer.

1055) by dehydration of benzylhydroxyanthrone, and by Padova (*loc. cit.*) in 38% yield by condensing benzaldehyde with anthrone. The latter method is more convenient and by using the following simplification of Padova's method a 65% yield of pure benzylideneanthrone was obtained.

Anthrone (200 g.), benzaldehyde (125 c.c.), pyridine (500 c.c.), and piperidine (5 c.c.) were boiled together for 4 hours; 375 c.c. of the solvent were removed by distillation and alcohol (300 c.c.) was added to the residue. After cooling, the resulting solid was collected and recrystallised from alcohol; it then melted at 127° in agreement with Levi, Bach, and Padova, although Tschilikin gives the m. p. as 117°.

Reduction of Benzylideneanthrone.—(*a*) Benzylideneanthrone (10 g.) was heated at 150—155° for 5 hours with zinc dust (20 g.) and acetic anhydride (100 c.c.). The excess of zinc dust was filtered off and the crystals which separated from the filtrate on cooling were collected and recrystallised from glacial acetic acid, then from alcohol and finally from benzene and light petroleum (Found: C, 84·6; H, 5·7. $C_{23}H_{18}O_2$ requires C, 84·7; H, 5·5%). 9-*Benzylanthranyl* 10-*acetate* forms colourless, glistening needles, m. p. 210—211°. It is readily soluble in acetic acid and in benzene and its solutions have an intense violet fluorescence. It is hydrolysed by alcoholic potassium hydroxide, giving the deep orange colour characteristic of an anthranol.

(*b*) An intimate mixture of benzylideneanthrone (50 g.) and zinc dust (150 g.) was heated on the water-bath with 500 c.c. of concentrated ammonia diluted with 250 c.c. of water. The zinc dust was activated by the addition of a little copper sulphate solution. At first, the solution assumed a deep orange colour, but became colourless after 1½ hours. Heating was continued for a further ½ hour, and the solid collected, dried between filter-paper, and extracted with 500 c.c. of boiling benzene. After filtering off the zinc dust, the benzene solution was concentrated and light petroleum added. On cooling, 45 g. of pure 10-hydroxy-9-benzyl-9 : 10-dihydroanthracene (IV) separated. It formed colourless needles, m. p. 122—125° (compare Bach, *Ber.*, 1890, **23**, 2527; Tschilikin, *loc. cit.*). Benzyldihydroanthranol is readily soluble in alcohol and its solutions are devoid of fluorescence. It is completely converted into benzylanthracene by boiling with acetic acid, but differs from 9 : 10-dihydroanthranol in being only partly dehydrated by heating with aqueous sodium hydroxide or hydrochloric acid.

When treated with acetic anhydride in pyridine at the ordinary temperature, benzyldihydroanthranol gave a product which melted at 80° after recrystallisation from alcohol, but further attempts at purification led to conversion into benzylanthracene. The substance was undoubtedly an acetate of the dihydroanthranol, since it gave a strong smell of ethyl acetate when heated with sulphuric acid and alcohol. Dihydroanthranol itself is merely converted into anthracene by this treatment. Benzyldihydroanthranol gave only benzylanthracene and carbanilide when treated with phenylcarbimide in boiling benzene solution.

(*c*) When benzylideneanthrone was reduced with zinc dust and acetic acid, with zinc and hydrochloric acid, or with tin and hydrochloric acid in glacial acetic acid solution, only resinous products were obtained.

9-*Benzylanthracene.*

A solution of benzyldihydroanthranol (90 g.) in acetic acid (600 c.c.) was boiled for $\frac{3}{4}$ hour. On cooling, pure benzylanthracene (65 g.) separated. For analysis, a sample was recrystallised from alcohol and formed colourless needles, m. p. 133° (Bach, *loc. cit.*, gives the m. p. as 119°). Benzylanthracene is but sparingly soluble in alcohol and its solutions have a violet fluorescence. As stated by Bach, it dissolves in sulphuric acid, giving a dark green solution with a red fluorescence (Found : C, 93·8; H, 6·1. Calc. : C, 94·0; H, 6·0%).

Action of Bromine.—(*a*) A solution of benzylanthracene in carbon disulphide readily absorbed bromine (1 mol.), hydrogen bromide being liberated. After evaporation of the solvent the residual 10-*bromo*-9-*benzylanthracene* (VI) was recrystallised from acetic acid and obtained as lemon-yellow needles, m. p. 144° (Found : Br, 22·8. $C_{21}H_{15}Br$ requires Br, 23·0%). The compound obtained in this way by Bach (*loc. cit.*) decomposed at 113—114°, which suggests that anthracene was present in his benzylanthracene and that his bromo-compound was contaminated with the unstable anthracene dibromide.

(*b*) When 2 or 3 mols. of bromine were used in the above preparation, bromine was still present after the solution had been kept at the ordinary temperature for several hours. The solvent was evaporated and the resinous product triturated with cold alcohol. By the addition of alcohol to a solution of the residue in pyridine, lemon-yellow needles were obtained which, after recrystallisation from benzene, melted at 220° alone or when mixed with 9 : 10-dibromoanthracene (Found : Br, 47·5. Calc. : Br, 47·6%).

(*c*) Bromine (2 c.c.; 2 mols.) was added to a solution of 10-bromo-9-benzylanthracene (6·5 g.) in carbon disulphide (50 c.c.), and the solution kept over-night at the ordinary temperature. The solution was washed with dilute aqueous sodium hydroxide and with water, and the solvent allowed to evaporate. The resinous product was triturated with ether; the 2·5 g. of a colourless solid remaining were recrystallised from chloroform and ether (Found: Br, 60·1. $C_{21}H_{15}Br_5$ requires Br, 60·0%).

10-*Bromo*-9-*benzylanthracene tetrabromide* (VII) forms a colourless, crystalline powder, m. p. 192° (decomp.).

On one occasion, the ethereal solution, after the above tetrabromide had been filtered off, slowly deposited crystals; these, on recrystallisation from benzene and light petroleum, formed colourless needles of constant m. p. 127° (decomp.). The substance was evidently one of the stereoisomeric tetrabromides, but could not be investigated, as it was never isolated again (Found: Br, 60·0%).

The tetrabromide melting at 192° (1 g.) was heated for 2 hours on the water-bath with alcohol (25 c.c.) to which had been added a concentrated aqueous solution of potassium hydroxide (2 g.). The resulting yellow solid was recrystallised from pyridine and alcohol and then from methyl ethyl ketone (Found: Br, 47·4. $C_{21}H_{13}Br_3$ requires Br, 47·5%).

2 : 3 : 10-*Tribromo*-9-*benzylanthracene* (VIII) forms silky, yellow needles, m. p. 206—207°. Its solutions have a violet fluorescence. By oxidation with chromic acid in acetic acid, this tribromo-compound yielded a product which contained bromine and melted at 279—280° alone or when mixed with authentic 2 : 3-dibromoanthraquinone (Barnett and Cook, J., 1925, **127**, 1489).

Action of Pyridine Perbromide.—To a suspension of benzylanthracene (2·7 g.) in pyridine (6 c.c.) was added a solution of bromine (0·5 c.c.; 1 mol.) in pyridine (4 c.c.). After 2 hours, the solid in suspension was collected and washed with pyridine and with ether. It was recrystallised from 10 c.c. of warm (not boiling) water, dried in a vacuum desiccator, and finally recrystallised from anhydrous alcohol with the addition of anhydrous ether (Found: Br, 25·3. $C_{31}H_{26}N_2Br_2,C_2H_6O$ requires Br, 25·3%). 9-*Benzyl*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide* (IX) forms a snow-white, crystalline powder which melts to a yellow liquid at 138—140°. The presence of alcohol of crystallisation was shown by the ethyl acetate reaction.

This dibromide was decomposed by boiling water with the production of a resinous substance which dissolved in aqueous sodium hydroxide with the orange-red colour of an anthranol (compare Barnett and Cook, J., 1921, **119**, 901). By the action of boiling aniline or of warm dilute mineral acids the dibromide lost pyridine hydrobromide and passed into 9-*benzylanthranyl*-10-*pyridinium bromide* (X). This substance was precipitated by the addition of dilute ammonium hydroxide solution to an aqueous solution of the dibromide and was recrystallised from water (from which it separated as a heavily hydrated curd) and afterwards from alcohol (Found: Br, 18·6. $C_{26}H_{20}NBr$ requires Br, 18·8%). This bromide forms fluffy, yellow needles, m. p. 226°. It is sparingly soluble in water and is stable towards boiling water, but gives coloured products with sodium hydroxide.

Anthraphenone was treated with pyridine perbromide under the conditions described above and was recovered unchanged. If 2 mols. of bromine were employed and the solution was kept at the ordinary temperature for several days, 10-bromoanthraphenone (this vol., p. 1282) was obtained.

9-Phenylanthracene, treated for 2 hours with a solution of bromine (1 mol.) in pyridine under the conditions described for benzylanthracene, was converted into 10-*bromo*-9-*phenylanthracene*, which, after recrystallisation from acetic acid and from methyl ethyl ketone and alcohol, formed glistening, yellow leaflets, m. p. 154—155° (Found: Br, 24·0. $C_{20}H_{13}Br$ requires Br, 24·0%). The same product was obtained when a solution of phenylanthracene in carbon disulphide or chloroform was treated with bromine at the ordinary temperature, and the position of the bromine atom was shown by the production of phenylhydroxyanthrone (compare Barnett and Cook, J., 1923, **123**, 2638) by oxidation with chromic acid in acetic acid solution.

Action of Chlorine.—9-Benzylanthracene, suspended in carbon tetrachloride, was treated with a solution of chlorine (1 mol.) in carbon tetrachloride. Reaction took place rapidly with the liberation of hydrogen chloride and the formation of 10-*chloro*-9-*benzylanthracene*, which crystallised from amyl alcohol in yellow needles, m. p. 127—128° (Found: Cl, 11·7. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

The same product was formed, mixed with 9 : 10-dichloroanthracene, when a solution of benzylanthracene (2·7 g.) in chloroform (10 c.c.) was heated on the water-bath for an hour with sulphuryl chloride (2 c.c.). The dichloroanthracene separated on cooling and was identified by direct comparison with an authentic sample. The chlorobenzylanthracene remained in solution and was only obtained pure after repeated recrystallisation.

Action of Nitric Acid.—Nitric acid (*d* 1·4; 0·4 c.c.) was added to a suspension of benzylanthracene (1·35 g.) in acetic acid (5 c.c.). The benzylanthracene rapidly dissolved and after keeping at the ordinary temperature for 2 hours the colourless solid which had separated was washed with a little acetic acid and crystallised from benzene and light petroleum (Found: C, 76·0; H, 5·3. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%). 9-*Hydroxy*-10-*nitro*-9-*benzyl*-9 : 10-*dihydroanthracene* (XI) forms colourless needles, m. p. 160° (with evolution of gas). It was not attacked by brief boiling with sodium hydroxide in aqueous or alcoholic solution and was but slightly decomposed by pyridine at 100°. With mineral acids in acetic acid solution, however, the substance lost water and passed into 10-nitro-9-benzylanthracene (XII) (see later). When hydriodic acid was used, this dehydration occurred rapidly at the ordinary temperature and was accompanied by very little reduction.

Action of Nitrogen Dioxide.—The gas, prepared by heating lead nitrate, was led into a suspension of benzylanthracene (5 g.) in chloroform (10 c.c.) cooled in a freezing mixture. After 2·4 g. of nitrogen dioxide had been taken up, the clear solution was kept in the freezing mixture for an hour and light petroleum was then added. An oil separated which refused to solidify. It was therefore dissolved in a mixture of pyridine (5 c.c.) and alcohol (10 c.c.) and kept over-night at the ordinary temperature. The orange crystals which separated were recrystallised from acetic acid, then from pyridine and alcohol, and finally from amyl alcohol (Found : N, 4·6. $C_{21}H_{15}O_2N$ requires N, 4·5%). 10-*Nitro*-9-*benzylanthracene* (XII) forms slender, golden-yellow needles, m. p. 178—180°.

Reduction of Benzylanthracene.—Sodium (1 g.) was added to a boiling solution of benzylanthracene (2·5 g.) in amyl alcohol (10 c.c.). After the sodium had dissolved, the hot solution was poured into water, and the solid collected and recrystallised from alcohol. It melted at 119—120°, alone or mixed with the 9-benzyl-9 : 10-dihydroanthracene obtained by the reduction of dihydroanthraphenone (this vol., p. 1677).

Benzyldihydroanthracene was recovered unchanged after its solution in carbon disulphide containing an excess of bromine had been kept for 2 hours at the ordinary temperature. 9 : 10-Dihydroanthracene yields 9 : 10-dibromoanthracene under these conditions.

A suspension of benzyldihydroanthracene in acetic acid was treated with nitric acid (*d* 1·4; 2 mols.) and kept over-night at the ordinary temperature. No reaction took place.

Derivatives of Anthraphenone.

Benzylanthraphenone (XIV).—A solution of benzylanthracene (15 g.) in carbon disulphide (100 c.c.) was treated with anhydrous aluminium chloride (15 g.) followed by benzoic anhydride (15 g.). After heating on the water-bath for 6 hours, the aluminium compound was decomposed with cold dilute hydrochloric acid, and the carbon disulphide removed with steam. The residue was extracted with sodium hydroxide solution and recrystallised from benzene and afterwards from benzene and light petroleum (Found : C, 90·1; H, 5·5. $C_{28}H_{20}O$ requires C, 90·3; H, 5·4%).

10-*Benzylanthraphenone* forms a cream-coloured, crystalline powder, m. p. 237°. In common with other anthraphenone derivatives, its solutions are not fluorescent. It dissolved in sulphuric acid with a cornflower-blue colour which soon changed to dark green, and at the same time the characteristic dark red fluorescence of benzylanthracene was developed. That fission had occurred was shown by the fact that benzoic acid was isolated from the diluted solution. Benzylanthraphenone was decomposed with the production of tarry matter by ½ hour's boiling with sulphuric acid in acetic acid, and benzylanthracene gave similar products under these conditions.

Benzylanthraphenone was not reduced by boiling for 6 hours with zinc dust and acetic acid or by heating with zinc dust and ammonia, although some slight reduction was effected with zinc dust and hydrochloric acid in acetic acid. Partial reduction was also brought about by boiling a solution of the ketone (2·5 g.) in acetic acid (25 c.c.) with 50% hydriodic acid (2·5 c.c.) and red phosphorus (0·65 g.) for 5 hours. After cooling, the excess of phosphorus and the unchanged material were filtered off and the filtrate was diluted with water. The resinous product was obtained pure after two recrystallisations from alcohol and then gave no colour with sulphuric acid (Found: C, 89·5; H, 5·9. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%). 10-*Benzyl*-9 : 10-*dihydroanthraphenone* (XV) forms yellow needles, m. p. 171—172°.

Phenylanthraphenone (XIV).—The phenylanthracene used in this preparation was obtained by the action of magnesium phenyl bromide on anthrone, the excess of anthrone being removed by extraction with boiling aqueous sodium hydroxide. The method is simpler than that previously described (Barnett and Cook, J., 1923, **123**, 2638), but the yields are poor.

Phenylanthracene (12·5 g.) suspended in carbon disulphide (80 c.c.) was treated with aluminium chloride (15 g.) and benzoic anhydride (16 g.) in the manner described for the benzyl compound. The crude product, after extraction with alkali, was recrystallised from acetic acid and yielded 14 g. of pure phenylanthraphenone. For analysis, a sample was recrystallised twice from benzene and light petroleum and then formed a cream-coloured, crystalline powder, m. p. 218—219° (Found: C, 90·7; H, 5·2. $C_{27}H_{18}O$ requires C, 90·5; H, 5·0%).

10-*Phenylanthraphenone* gives a transient cornflower-blue colour when dissolved in sulphuric acid and undergoes fission when boiled for ¾ hour with sulphuric acid (1 part) in acetic acid (10 parts), pure phenylanthracene separating from the solution on cooling.

A suspension of phenylanthraphenone (2 g.) in acetic acid (25 c.c.) was boiled for 4 hours with zinc dust (4 g.). After cooling, the unchanged material and the excess of zinc dust were removed, water was added to the filtrate, and the resulting precipitate recrystallised from alcohol and then from benzene and light petroleum (Found : C, 89·7; H, 5·7. $C_{27}H_{20}O$ requires C, 90·0; H, 5·6%).

10-*Phenyl*-9 : 10-*dihydroanthraphenone* (XV) forms colourless, silky needles, m. p. 165°, and gives no colour with sulphuric acid.

Very little reduction took place when phenylanthraphenone was boiled with hydriodic acid and phosphorus in acetic acid.

Benzylideneanthrone Dibromide (XVI).

Attempts to prepare bromobenzylideneanthrone by boiling this dibromide with alcohol or with alcohol and water were fruitless, the only products isolated being benzylideneanthrone and anthraquinone (compare Bach, *Ber.*, 1890, **23**, 1567). Loss of bromine also took place when a solution of the dibromide in benzene was boiled with diethylamine or with dry silver oxide, and a similar result was obtained with aqueous acetone in the presence of calcium carbonate and with pyridine in the presence of acetic anhydride (coloured resinous products were obtained with pyridine alone).

Action of Silver Oxide.—Water (20 c.c.) was added to a solution of benzylideneanthrone dibromide (10 g.) in acetone (100 c.c.), followed by the silver oxide prepared from 10 g. of silver nitrate. After keeping at the ordinary temperature for 3 hours, the whole was heated to boiling, filtered, and the filtrate diluted with water. The resulting solid (2·6 g.) was twice recrystallised from alcohol and obtained as colourless needles, m. p. 133—134° (Found : C, 84·5; H, 4·75. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). This *compound* gave a magenta solution in sulphuric acid and a blood-red colour with aqueous or alcoholic sodium hydroxide. It was not decomposed by alcoholic sodium hydroxide under conditions which sufficed for the hydrolysis of 9 : 10-dihydroanthraphenone, or by sulphuric acid in acetic acid under conditions which led to hydrolysis of anthraphenone (compare Cook, *loc. cit.*).

By heating the above compound (1 g.) on the water-bath for an hour with acetic anhydride (1 c.c.) and pyridine (2 c.c.), an *acetate* was obtained which, after recrystallisation from alcohol and then from benzene and light petroleum, formed colourless nodules, m. p. 140—141° (Found : C, 81·0; H, 4·8. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%).

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