

LXXV.—*The Synthesis of meso-Alkyl and meso-Aryl Anthracene Derivatives. Part III.*

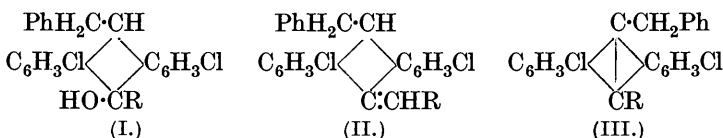
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A. THE action of Grignard solutions upon anthrones has been further studied (for references to previous work, see Part II, J., 1927, 1724) with the following results.

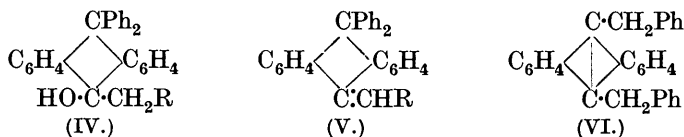
1. The dihydroanthranols (I) obtained from 1:5-dichloro-9-benzylanthrone could not be made to crystallise with the exception of the phenyl and benzyl compounds (I, R = Ph and CH₂Ph).

2. The methyl and benzyl compounds (I, R = Me and CH₂Ph,

respectively), on being heated with acetic acid containing a little hydrochloric or sulphuric acid, gave colourless and non-fluorescent methylene derivatives (II, R = H and Ph, respectively), but the phenyl compound, with which such a reaction is impossible, gave benzylphenyldichloroanthracene (III, R = Ph). From the remaining oily dihydroanthranols, only resinous products were formed, although from the *isopropyl* derivative *isopropylbenzyl*dichloroanthracene (III, R = Pr^β) was obtained in very small yield. 1 : 5-Dichloro-9-benzylanthrone therefore resembles 1 : 5-dichloroanthrone (Barnett, Cook, and Matthews, *Ber.*, 1926, 59, 2863), 1 : 5-dichloro-9-phenylanthrone (Barnett, Cook, and Wiltshire, *J.*, 1927, 1724), and 1 : 5-dichloro-9-methylanthrone (Barnett and Cook, *Ber.*, 1928, 61, 314) in its behaviour towards Grignard solutions.



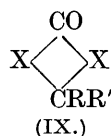
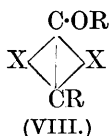
3. Since the methylene derivative (II) might be formed either by direct loss of water or by the preliminary formation of an alkylanthracene and subsequent transannular migration of a hydrogen atom (Barnett and Cook, *loc. cit.*), dihydroanthranols (IV) were prepared by the action of magnesium methyl iodide and magnesium benzyl chloride on 9 : 9-diphenylanthrone, and the behaviour of these dihydroanthranols towards acetic acid containing a little mineral acid was studied. In both cases, transannular loss of water is impossible, but methylene derivatives (V) were readily formed.



4. 9 : 9-Dibenzylanthrone gave well-crystallised dihydroanthranols on treatment with magnesium methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride. All of these became fluorescent on heating with acetic acid containing mineral acid. From the methyl and the phenyl compound no definite decomposition product could be isolated, but from tribenzylidihydroanthranol considerable quantities of 9 : 10-dibenzylanthracene (VI) were obtained, and although the yield is poor this is probably the best method at present known of preparing this hydrocarbon. The formation of dibenzylanthracene from tribenzylidihydroanthranol must be due to transannular loss of benzyl alcohol (the acetic acid

liquor smelt strongly of benzyl acetate), and the reaction, which is an interesting one, is being further investigated.

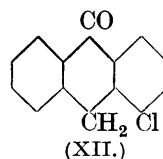
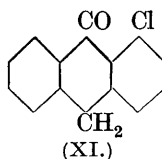
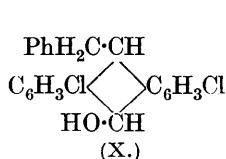
B. Previous work on the action of alkyl halides and caustic alkali on anthrones (Goldman, *Ber.*, 1888, **21**, 1178, 2505; Hallgarten, *ibid.*, 1888, **21**, 2508; K. H. Meyer and Schlösser, *Annalen*, 1920, **420**, 130; Barnett, Cook, and Matthews, J., 1923, **123**, 391, 2631; *Ber.*, 1928, **61**, 314) has shown that one or more of the following products may result: anthranyl alkyl ether (VII), alkylanthranyl alkyl ether (VIII), alkylanthrone (IX, R = H), dialkylanthrone (IX).



Which type of compound is produced in any given case depends both on the particular anthrone used and on the alkyl halide. The following further results have now been obtained:

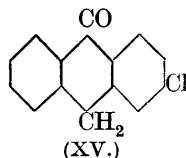
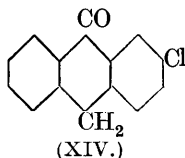
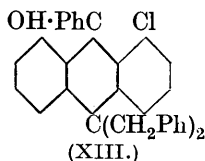
1. 1:5-Dichloroanthrone when boiled with benzyl chloride and caustic potash gave an almost quantitative yield of benzyl-dichloroanthrone (IX, X = C₆H₃Cl, R = H, R' = CH₂Ph). In this respect dichloroanthrone differs from anthrone itself, as the latter under similar conditions gives dibenzylanthrone (IX, X = C₆H₄, R and R' = CH₂Ph) in about 40% yield, together with much resinous matter. This benzyldichloroanthrone can be neither methylated by means of methyl *p*-toluenesulphonate nor acetylated by boiling with acetic anhydride in pyridine solution. It can be reduced to the dihydroanthranol (X) by zinc dust and alcoholic ammonia.

2. 1-Chloro-9-anthrone (XI) (Barnett and Matthews, J., 1923, **123**, 2549; compare Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839) gave a dibenzyl compound which must be the dibenzylanthrone (IX) and not the benzylanthranyl benzyl ether (VIII), since it gives a dihydroanthranol (XIII) on treatment with magnesium phenyl bromide. The isomeric 1-chloro-10-anthrone (XII) (Barnett and Matthews, *loc. cit.*) gave only resinous products.



3. 2-Chloro-9-anthrone (XIV) (future communication; compare F. Meyer and Fischbach, *Ber.*, 1925, **58**, 1251) gave only resinous

products, easily soluble in ether, when boiled with benzyl chloride and caustic alkali, and presumably the isomeric 2-chloro-10-anthrone (XV) gives the same result, since no crystalline substance could be



isolated from the resinous product obtained by benzylating the crude mixture of isomerides prepared by reducing 2-chloroanthraquinone (Barnett and Matthews, *loc. cit.*).

4. Attempts to prepare unsymmetrical dialkylanthrones by benzylating 9-methylanthrone and 9-phenylanthrone yielded only resinous products.

5. 1 : 5-Dichloroanthrone and benzal chloride also gave only resinous substances.

It is possible that the failure to introduce more than one alkyl group into 1 : 5-dichloroanthrone is due to the hindering effect of one of the α -chlorine atoms, and this hindering effect may also account for the failure of 1 : 5-dichloroanthrone to give a benzylidene derivative with benzaldehyde in the presence of piperidine, and for the failure of 1 : 5-dichloroanthracene to give a ketone on treatment with benzoic anhydride and aluminium chloride (compare Cook, J., 1926, 1282, 2160). The data at present available, however, are insufficient to permit useful speculation on the causes influencing these reactions.

E X P E R I M E N T A L.

Action of Grignard Solutions on 1 : 5-Dichloro-9-benzylanthrone.—The finely powdered anthrone was slowly added to an ethereal solution of the Grignard reagent (3 mols.), cooled in a freezing mixture. After being kept in the freezing mixture for an hour and at the ordinary temperature for 4 hours, the whole was poured on a mixture of ice and solid ammonium chloride, and the washed ethereal solution evaporated to dryness on the water-bath. As a rule a viscous oil was left, but when magnesium benzyl chloride was used 1 : 5-dichloro-9 : 10-dibenzyl-9 : 10-dihydroanthranol (I, R = CH₂Ph) was obtained in the solid state; after recrystallisation from acetone, it formed snow-white needles, m. p. 197° (Found : Cl, 15.8. C₂₈H₂₂OCl₂ requires Cl, 15.7%).

The oil obtained when magnesium phenyl bromide was employed became solid on the addition of alcohol, and after recrystallisation from mixtures of acetone-aqueous alcohol and benzene-light petroleum 1 : 5-dichloro-10-phenyl-9-benzyl-9 : 10-dihydroanthranol-10

(I, R = Ph) formed colourless, glistening crystals, m. p. 167° (Found : Cl, 16.5. $C_{27}H_{20}OCl_2$ requires Cl, 16.5%).

The dehydration of the dihydroanthranols was effected by heating on the water-bath for 1—3 hours in glacial acetic acid solution to which a little hydrochloric or sulphuric acid had been added. The following compounds were obtained :

1 : 5-*Dichloro-9-benzyl-10-methylene-9 : 10-dihydroanthracene* (II, R = H). From the crude dihydroanthranol obtained by means of magnesium methyl iodide. Snow-white crystals, m. p. 123°, from alcohol (Found : Cl, 20.2. $C_{22}H_{16}Cl_2$ requires Cl, 20.2%).

1 : 5-*Dichloro-9-benzyl-10-benzylidene-9 : 10-dihydroanthracene* (II, R = Ph). From the crystalline dihydroanthranol described above. Snow-white crystals, m. p. 158°, from glacial acetic acid (Found : Cl, 16.5. $C_{28}H_{20}Cl_2$ requires Cl, 16.6%).

1 : 5-*Dichloro-9-benzyl-10-isopropylantracene* (III, R = Pr^β). A glacial acetic acid solution of the crude dihydroanthranol obtained by the action of magnesium isopropyl bromide was kept over-night at the ordinary temperature after a little hydrochloric acid had been added. The yellow crystals which separated were freed from red resinous matter by recrystallisation from ethyl acetate-alcohol and finally from alcohol. The substance then formed yellow plates, m. p. 138°, and exhibited a green fluorescence when in solution (Found : C, 76.2; H, 5.4. $C_{24}H_{20}Cl_2$ requires C, 75.9; H, 5.3%).

1 : 5-*Dichloro-10-phenyl-9-benzylantracene* (III, R = Ph). Obtained in 90% yield from the crystalline dihydroanthranol by heating on the water-bath with glacial acetic acid containing hydrochloric acid. After recrystallisation from toluene, it formed glistening, yellow crystals which melted at 213° either alone or when mixed with an authentic sample (Barnett, Cook, and Wiltshire, J., 1927, 1732).

Action of Grignard Solutions on 9 : 9-Diphenyl- and 9 : 9-Dibenzyl-anthrone.—In each case the finely powdered anthrone was slowly added to the well-cooled Grignard solution ($1\frac{1}{2}$ —2 mols.). After being kept for 10—30 minutes in the freezing mixture and for 3—4 hours at the ordinary temperature (or over-night in the ice chest), the whole was poured on a mixture of ice and solid ammonium chloride, and sufficient ether added to dissolve the dihydroanthranol. The washed and filtered ethereal solution was then evaporated to dryness on the water-bath. The following compounds were obtained :

9 : 9-*Diphenyl-10-methylene-9 : 10-dihydroanthracene* (V, R = H). The dihydroanthranol formed by the action of magnesium methyl iodide on diphenylantrone could not be obtained pure owing to the ease with which loss of water took place. The crude product

was therefore heated on the water-bath for 30 minutes with 8 parts of glacial acetic acid containing a little hydrochloric or sulphuric acid; the solid which separated on cooling crystallised from ethyl acetate in colourless prisms, m. p. 192° (Found: C, 93.9; H, 5.9. $C_{27}H_{20}$ requires C, 94.2; H, 5.8%).

9 : 9-*Diphenyl-10-benzyl-9 : 10-dihydroanthranol-10* (IV, R = Ph), recrystallised from mixtures of benzene-alcohol and benzene-light petroleum, formed colourless needles, m. p. $228-230^{\circ}$ (Found: C, 90.2; H, 6.1. $C_{33}H_{26}O$ requires C, 90.4; H, 5.9%).

9 : 9-*Diphenyl-10-benzylidene-9 : 10-dihydroanthracene* (V, R = Ph). From the above dihydroanthranol by heating on the water-bath with acetic acid containing hydrochloric or sulphuric acid. Colourless, glistening crystals, m. p. $254-255^{\circ}$, from toluene (Found: C, 94.1; H, 5.8. $C_{33}H_{24}$ requires C, 94.3; H, 5.7%).

9 : 9-*Dibenzyl-10-methyl-9 : 10-dihydroanthranol-10*. Snow-white crystals, m. p. 175° , from aqueous acetone (Found: C, 88.8; H, 6.6. $C_{29}H_{26}O$ requires C, 89.2; H, 6.7%).

10-*Phenyl-9 : 9-dibenzyl-9 : 10-dihydroanthranol-10*. Snow-white crystals, m. p. 189° , from acetone; gave a positive iodoform test (Found: C, 87.1; H, 6.7. $C_{34}H_{28}O, C_3H_6O$ requires C, 87.1; H, 6.7%).

9 : 9 : 10-*Tribenzyl-9 : 10-dihydroanthranol*. Colourless, hygroscopic crystals, m. p. 140° , from benzene-light petroleum (Found: C, 90.1; H, 6.6. $C_{36}H_{30}O$ requires C, 89.8; H, 6.8%).

9 : 10-*Dibenzylanthracene* (VI). Tribenzyl-dihydroanthranol was dissolved in hot glacial acetic acid, a little concentrated hydrochloric acid added, and the whole heated for 4 hours on the water-bath. Colourless crystals separated from the hot solution and after cooling were collected and recrystallised from toluene. They then melted at 245° alone or mixed with an authentic sample of dibenzylanthracene prepared by a different method (future communication).

Action of Alkyl Halides and Caustic Alkali on Anthrones.—1 : 5-*Dichloro-9-benzylanthrone* (IX, X = C_6H_3Cl , R = H, R' = CH_2Ph). Fifty g. of 1 : 5-dichloroanthrone and 100 c.c. of benzyl chloride were boiled under reflux with 75 g. of potassium hydroxide in 300 c.c. of water until the black tar at first formed had completely vanished (about 2 hours). After cooling, the pasty product was washed with water by decantation and then agitated with ether. The almost colourless crystals thus formed were snow-white after recrystallisation from toluene or from ethyl acetate and then melted at 169° (Found: Cl, 20.3. $C_{21}H_{14}OCl_2$ requires Cl, 20.1%).

This anthrone gives a red solution in alcoholic alkali, but cannot be methylated even by prolonged treatment with methyl *p*-toluenesulphonate and potassium hydroxide in alcoholic solution, and in

this way resembles 1 : 5-dichloro-9-phenylanthrone (Barnett and Matthews, *Ber.*, 1926, 59, 670). On the other hand, whereas phenyldichloroanthrone is easily acetylated by pyridine and acetic anhydride (Barnett and Matthews, *loc. cit.*), benzyldichloroanthrone cannot be acetylated by this method, and was recovered unchanged even after boiling for 12 hours with acetic anhydride and picoline bases (b. p. 140—145°).

1 : 5-Dichloro-9-benzyl-9 : 10-dihydroanthranol-10 (X). Dichloro-benzylanthrone was recovered unchanged after boiling with hydriodic acid and red phosphorus in glacial acetic acid solution and was not reduced by zinc dust and aqueous ammonia. The reduction to the dihydroanthranol was effected by heating 5 g. with 15 g. of zinc dust and 150 c.c. of alcoholic ammonia (7.5% NH_3) on the water-bath for 4 hours. The crystals which separated from the filtrate on cooling became colourless on recrystallisation from alcohol and then melted at 179°. They contained no nitrogen (Found : C, 70.7; H, 4.7. $\text{C}_{21}\text{H}_{16}\text{OCl}_2$ requires C, 71.0; H, 4.5%). Facile trans-annular loss of water with formation of 1 : 5-dichloro-9-benzylanthracene (identified by direct comparison with an authentic sample) was brought about by heating on the water-bath with acetic acid containing a little hydrochloric acid.

1-Chloro-10 : 10-dibenzylanthrone. Five g. of 1-chloro-9-anthrone were boiled under reflux for 2 hours with 10 c.c. of benzyl chloride and 7 g. of potassium hydroxide in 30 c.c. of water. The cooled pasty product was washed with water and agitated with ether and the resulting almost colourless solid was recrystallised from glacial acetic acid. It was then snow-white, melted at 223°, and gave no colour with a boiling alcoholic solution of potassium hydroxide (Found : C, 82.1; H, 5.3. $\text{C}_{28}\text{H}_{21}\text{OCl}$ requires C, 82.2; H, 5.3%).

1-Chloro-9-phenyl-10 : 10-dibenzyl-9 : 10-dihydroanthranol-9 (XIII). Five g. of the above dibenzylchloroanthrone were added to an ethereal solution of magnesium phenyl bromide prepared from 0.7 g. of magnesium. During the addition the solution was cooled in a freezing mixture, and after being kept for 5 hours at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium chloride. The solid which separated was collected, and a small amount of rather less pure material was obtained by evaporating the ethereal layer of the filtrate. After recrystallisation from acetone it was snow-white and melted at 260° (Found : Cl, 17.1. $\text{C}_{34}\text{H}_{27}\text{OCl}$ requires Cl, 7.3%).

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