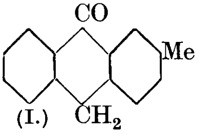
CCXXXI.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part VI.*

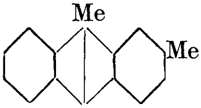
By EDWARD DE BARRY BARNETT and NORMAN FREDERICK GOODWAY.

IN Part V (this vol., p. 20) it was shown that the dihydroanthranol obtained by the action of magnesium phenyl bromide on 1 : 5-dichloro-9-benzhydrylanthrone was isomerised by heat. An examination of the corresponding unchlorinated compound has failed to reveal any tendency to undergo a similar change. Like the corresponding 1 : 5-dichloro-compound, however, 9-benzhydrylanthrone gives erratic results on treatment with Grignard solutions. In most cases, resinous products only were obtained, although the preparation of 9-*methyl*(or *benzyl*)-10-*benzhydryl*-9 : 10-*dihydroanthranol*-9 takes place smoothly. These, however, differ from the corresponding 1 : 5-dichloro-compounds by undergoing transannular loss of water and not of benzhydrol and thereby passing into the 9-alkyl-10-benzhydrylanthracene. The phenylbenzhydryldihydroanthranol mentioned above, on treatment with an acid, gave a fluorescent product which was probably 9-phenyl-10-benzhydrylanthracene; its poor power of crystallisation, however, rendered its purification impossible.

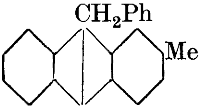
2-Methyl-9-anthrone (I) (prepared by loss of water from 4′-methyldiphenylmethane-2-carboxylic acid; Limpricht, *Annalen*, 1901, **314**, 241) gave as a rule only resinous products on treatment with Grignard solutions, but 2 : 9-*dimethylanthracene* (II) (in poor yield) and 9-*benzyl*-2-*methylanthracene* (III) (in excellent yield) were obtained from it. This is in harmony with the general rule that magnesium benzyl chloride reacts most smoothly with an anthrone.



(I.)

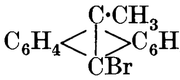


(II.)



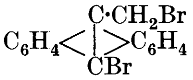
(III.)

2 : 9-Dimethylanthracene differs materially from 9-methylanthracene in its behaviour towards bromine. For instance, Barnett and Matthews (*Ber.*, 1926, **59**, 1429) showed that the latter is first brominated to 10-bromo-9-methylanthracene (IV) and that further bromination leads to lateral substitution (V) and finally to the formation of ω : 10-dibromo-9-methylanthracene tetrabromide (VI) :



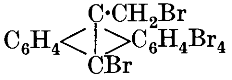
$C_6H_4<\overset{C\cdot CH_3}{\underset{CBr}{|}}>C_6H_4$

(IV.)



$C_6H_4<\overset{C\cdot CH_2Br}{\underset{CBr}{|}}>C_6H_4$

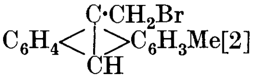
(V.)



$C_6H_4<\overset{C\cdot CH_2Br}{\underset{CBr}{|}}>C_6H_4Br_4$

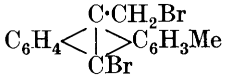
(VI.)

2 : 9-Dimethylanthracene on the other hand yields first a monobromo-compound containing a reactive bromine atom (formation of *piperidino-* and *anilino*-derivatives) which, in view of its deep yellow colour, is undoubtedly 9-*bromomethyl*-2-*methylanthracene* (VII). The further action of bromine on this leads to the facile formation of a *dibromo*-compound in which the new bromine atom is non-reactive and to which formula (VIII) is assigned.



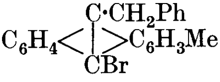
$C_6H_4<\overset{C\cdot CH_2Br}{\underset{CH}{|}}>C_6H_3Me[2]$

(VII.)



$C_6H_4<\overset{C\cdot CH_2Br}{\underset{CBr}{|}}>C_6H_3Me$

(VIII.)



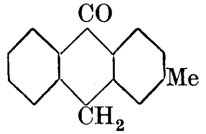
$C_6H_4<\overset{C\cdot CH_2Ph}{\underset{CBr}{|}}>C_6H_3Me$

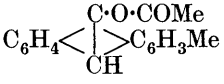
(IX.)

9-Benzyl-2-methylanthracene, on the other hand, on bromination resembles 9-benzylanthracene (Cook, J., 1926, 2160) and gives 10-*bromo*-9-*benzyl*-2-*methylanthracene* (IX), the further action of bromine being very sluggish and consisting in addition and not substitution. The additive compound was not obtained in the pure state but was almost certainly a dibromide. In the latter respect 10-bromo-9-benzyl-2-methylanthracene differs from 10-bromo-9-benzylanthracene, as this gives a tetrabromide (Cook, *loc. cit.*), but resembles 2-chloro-10-bromo-9-benzylanthracene (Barnett and Wiltshire, J., 1928, 1822).

3-Methyl-9-anthrone (X) has been described by Liebermann and Mamlock (*Ber.*, 1905, **38**, 1792) and by Padova (*Ann. Chim.*, 1910, **19**, 395) as being obtained by the reduction of 2-methylanthraquinone with tin and hydrochloric acid in acetic acid solution. The former investigators give the melting point as 80—84° (the analysis recorded indicates an impure product), and the latter 86—88°. Experience renders it improbable that 3-methyl-9-anthrone would differ materially in melting point from the isomeric 2-methyl-9-anthrone (m. p. 103°), and an investigation of the reduction product of 2-methylanthraquinone obtained both by the tin–hydrochloric acid method and by the aluminium powder–concentrated sulphuric acid method (D.R.-P. 201,542) has shown that the product is undoubtedly a mixture of isomerides (compare Barnett and Matthews, J., 1923, **123**, 2549, on the similar mixture of isomerides obtained by the reduction of 2-chloroanthraquinone). From this mixture it is possible by fractional crystallisation from methyl alcohol to obtain 3-*methyl*-9-*anthrone*, which melts when pure at 101° (depressed by addition of 2-methyl-9-anthrone). The very similar solubility of the two anthrones and the exceedingly poor power of crystallisation exhibited by the mixture render the preparation of 3-methyl-9-anthrone very laborious and the yield of pure product obtained does not exceed 5% of the weight of the crude mixture. However, by acetylating the crude mixture, repeatedly crystallising the resulting *anthranyl acetates* (XI), and hydrolysing the product, the pure anthrone is obtained in yields amounting to 10% of the weight of 2-methylanthraquinone reduced.

(X.)



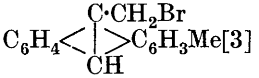


$$C_6H_4\Big<\overset{C\cdot O\cdot COMe}{\underset{CH}{|}}\Big>C_6H_3Me$$

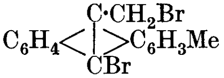
(XI.)

On treatment with magnesium methyl iodide, 3-methyl-9-anthrone gives 3 : 9-*dimethylanthracene* in poor yield, and this reacts with bromine in exactly the same way as the isomeric 2 : 9-dimethylanthracene, giving first the ω-*bromo*-compound (XII) and then the *dibromo*-compound (XIII).

(XII.)



$$C_6H_4\Big<\overset{C\cdot CH_2Br}{\underset{CH}{|}}\Big>C_6H_3Me[3]$$



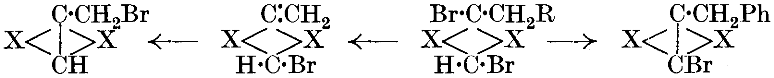
$$C_6H_4\Big<\overset{C\cdot CH_2Br}{\underset{CBr}{|}}\Big>C_6H_3Me$$

(XIII.)

The monobromo-compound reacted at once with piperidine with evolution of heat, the product being completely soluble in dilute hydrochloric acid to give a fluorescent solution.

9-*Benzyl*-3-*methylanthracene* was obtained in good yield from 3-methyl-9-anthrone and magnesium benzyl chloride. It behaved towards bromine in the same way as the isomeric 9-benzyl-2-methylanthracene.

The results obtained by the bromination of the above β-methyl-*ms*-methyl(and benzyl)anthracenes are difficult to explain. In every case bromination obviously takes place by the preliminary formation of an unstable dibromide (XIV), which can then lose hydrogen bromide in two directions :



$$X\Big<\overset{C\cdot CH_2Br}{\underset{CH}{|}}\Big>X \longleftarrow X\Big<\overset{C\colon CH_2}{\underset{H\cdot C\cdot Br}{}}\Big>X \longleftarrow X\Big<\overset{Br\cdot C\cdot CH_2R}{\underset{H\cdot C\cdot Br}{}}\Big>X \longrightarrow X\Big<\overset{C\cdot CH_2Ph}{\underset{CBr}{|}}\Big>X$$

(XVII.) (XVI.) (XIV.) (XV.)

Transannular loss of hydrogen bromide by the benzyl compound leads to (XV), but in the case of the methyl compounds loss of hydrogen bromide must first lead to the formation of the methylene derivative (XVI), subsequent migration of the bromine atom resulting in the production of (XVII) (compare Cook, *Ber.*, 1927, **60**, 2366; J., 1928, 2798; Barnett and Goodway, *Ber.*, 1929, **62**, 423). Since in the benzyl compound the phenyl group should lead to increased reactivity of the methylene hydrogen atoms, the mode of loss of hydrogen bromide by the two dibromides is the reverse of what would be expected. The course of the reaction is obviously profoundly influenced by the methyl group in the side ring, but theoretical speculations on the nature of this influence cannot be indulged in profitably at present.

EXPERIMENTAL.

The reaction between 9-benzhydrylanthrone and a Grignard reagent was carried out by adding the finely powdered anthrone (5·4 g.) to the reagent (3 mols.) in a freezing mixture, keeping the whole for 2 hours at the ordinary temperature, and pouring it on a mixture of ice and solid ammonium chloride. In some cases the whole of the dihydroanthranol was brought into solution by the addition of ether; in others, where the dihydroanthranol was only sparingly soluble, part of it remained undissolved.

10-*Benzhydryl*-9-*methyl*-9 : 10-*dihydroanthranol*-9, obtained from 9-benzhydrylanthrone and magnesium methyl iodide and recrystallised from aqueous acetone and from benzene–light petroleum, formed colourless crystals, m. p. 216° (Found : C, 89·3; H, 6·5. $C_{28}H_{24}O$ requires C, 89·3; H, 6·4%).

10-*Benzhydryl*-9-*methylanthracene*, prepared from the above dihydroanthranol by heating for an hour on the water-bath with glacial acetic acid containing hydrochloric acid, separated from benzene–light petroleum in colourless crystals with a strong violet fluorescence (Found : C, 93·8; H, 6·3. $C_{28}H_{22}$ requires C, 93·85; H, 6·15%).

10-*Benzhydryl*-9-*benzyl*-9 : 10-*dihydroanthranol*-9, obtained from 9-benzhydrylanthrone and magnesium benzyl chloride, formed colourless crystals, m. p. 181°, from aqueous acetone (Found : C, 89·9; H, 6·1. $C_{34}H_{28}O$ requires C, 90·2; H, 6·1%).

10-*Benzhydryl*-9-*benzylanthracene*, prepared from the above dihydroanthranol by heating for an hour on the water-bath with acetic acid containing hydrochloric acid, separated from aqueous pyridine and from benzene–light petroleum in colourless crystals, m. p. 236° (Found : C, 94·1; H, 6·1. $C_{34}H_{26}$ requires C, 94·0; H, 6·0%).

9-*Phenyl*-10-*benzhydryl*-9 : 10-*dihydroanthranol*-9, obtained from 9-benzhydrylanthrone and magnesium phenyl bromide, formed colourless crystals, m. p. 222°, from aqueous acetone and from benzene–light petroleum (Found : C, 90·3; H, 6·0. $C_{33}H_{26}O$ requires C, 90·4; H, 5·9%).

2-*Methyl*-9-*anthrone* (I).—This was obtained by reducing toluoylbenzoic acid with zinc dust and ammonia in the same way as benzoylbenzoic acid (Barnett, Cook, and Nixon, J., 1927, 504) and subsequently closing the ring by treatment with cold concentrated sulphuric acid (Limpricht, *loc. cit.*). The latter process is accompanied by considerable loss by sulphonation and the yield does not exceed 50%. The pure anthrone (recrystallised from methyl alcohol) melts at 103° and not at 100° as stated by Limpricht.

2-*Methyl*-9-*anthranyl acetate* (XI), obtained from the above anthrone by the pyridine–acetic anhydride method (Barnett, Cook, and Matthews, J., 1923, **123**, 389, 2640) and recrystallised from acetic acid and from benzene–light petroleum, was slightly yellow and melted at 143° (Found : C, 81·3; H, 5·8. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

2-*Methyl*-9-*anthranyl methyl ether*, obtained by methylating the anthrone in boiling alcoholic alkaline solution with methyl *p*-toluenesulphonate (Barnett, Cook, and Matthews, J., 1923, **123**, 2001), formed colourless crystals, m. p. 77°, from methyl alcohol (Found : C, 86·2; H, 6·3. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

3-*Methyl*-9-*anthrone* (X) *and* 3-*Methyl*-9-*anthranyl Acetate* (XI).—2-Methylanthraquinone was reduced by the aluminium powder–concentrated sulphuric acid method, and the dried crude product acetylated by heating on the water-bath with pyridine (2 c.c. per g.) and acetic anhydride (1 c.c. per g.). After an hour the solution was heated to boiling, cooled, the excess of acetic anhydride destroyed by the cautious addition of water, and the whole diluted with a large volume of water. The dark solid obtained, after repeated crystallisation from alcohol (animal charcoal), became colourless; it then melted at 139° (constant) and depressed the m. p. of the 2-methyl-9-anthranyl acetate described above. For analysis a sample was recrystallised from benzene–light petroleum (Found : C, 81·5; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

Potassium hydroxide (1 part) in 50% aqueous solution was slowly added to 3-*methyl*-9-*anthranyl acetate* (3 parts) in boiling alcoholic solution, nitrogen being passed through the flask in order to prevent oxidation. After boiling for 10 minutes, the solution was cooled, acidified with hydrochloric acid, and diluted with water. The resulting solid was recrystallised from methyl alcohol and was then slightly yellow and melted at 101°; it was identified as 3-*methyl*-9-*anthrone*. For analysis a sample was recrystallised from benzene–light petroleum (Found : C, 86·4; H, 5·8. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%).

2 : 9-*Dimethylanthracene* (II).—The anthrone (11 g.) was added to magnesium methyl iodide (3 mols.) in a freezing mixture and, after remaining over-night at the ordinary temperature, the whole was decomposed with ice and solid ammonium chloride in the

usual way. The oil left on evaporation of the washed ethereal solution was heated on the water-bath for a few minutes with acetic acid containing hydrochloric acid, and the solid obtained on cooling and dilution was crystallised several times from methyl alcohol and finally from light petroleum. It was then yellow and melted at 85° (yield, 3 g.) (Found: C, 93·0; H, 6·8. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The poor yield is largely due to the enolising action of the Grignard solution, but the use of 2 or 5 mols. of magnesium methyl iodide failed to improve it. Part of the unchanged anthrone can be removed by washing the ethereal solution several times with very dilute sodium hydroxide solution, but the solubility of the sodium salt of the anthranol in ether renders impracticable the removal of the whole of it by this method.

3 : 9-*Dimethylanthracene*, obtained from 3-methyl-9-anthrone and magnesium methyl iodide exactly as described above, formed slightly yellow crystals from methyl alcohol and from light petroleum. It melted at 85° and depressed the m. p. of 2 : 9-dimethylanthracene (Found: C, 93·1; H, 6·9%).

9-*Bromomethyl*-2-*methylanthracene* (VII).—Bromine (2·4 g.; 1 mol.) in 5 c.c. of carbon disulphide was slowly added to 3 g. of 2 : 9-dimethylanthracene in 10 c.c. of carbon disulphide cooled in a freezing mixture. The bromine was taken up instantly, but very little hydrogen bromide was evolved until the solution was allowed to reach the ordinary temperature. When the evolution had ceased, most of the carbon disulphide was evaporated in a current of air, and light petroleum added. The resulting solid, after recrystallisation from benzene–light petroleum and from benzene, formed deep yellow crystals, m. p. 150° (with violent decomp. to a red liquid) (Found: C, 67·2; H, 4·6. $C_{16}H_{13}Br$ requires C, 67·4; H, 4·6%).

When 3 : 9-dimethylanthracene was treated with bromine under the above conditions, a yellow product was isolated which melted with violent decomposition to a red liquid at 145°. Analysis, however, suggested that this *monobromo*-compound (XII) was not quite free from dibromo-compound and insufficient material was available to enable thorough purification to be effected (Found: C, 66·4; H, 4·7%).

10-*Bromo*-9-*bromomethyl*-2-*methylanthracene* (VIII) was obtained by adding bromine (1 mol.) to a suspension of the above monobromo-compound (VII) in carbon disulphide at the ordinary temperature. It was also obtained, together with unchanged material, on one occasion when the bromination of 2 : 9-dimethylanthracene was carried out by the addition of 1 mol. of bromine at the ordinary temperature. After recrystallisation from benzene it formed yellow crystals, m. p. 190° to a red liquid (Found : C, 52·8; H, 3·45. $C_{16}H_{12}Br_2$ requires C, 52·75; H, 3·3%).

10-*Bromo*-9-*bromomethyl*-3-*methylanthracene* (XIII), prepared in the same way from (XII), formed yellow needles, m. p. 186° to a red liquid (Found : C, 52·7; H, 3·4%).

9-*Piperidinomethyl*-2-*methylanthracene*.—When 1 g. of 9-bromomethyl-2-methylanthracene, suspended in 5 c.c. of chloroform, was treated with 1 c.c. of piperidine in 5 c.c. of chloroform, a clear solution was formed at once with evolution of heat. After an hour the chloroform was evaporated; the residue, having been washed with methyl alcohol, separated from aqueous alcohol in almost colourless crystals, m. p. 128° (Found : C, 87·0; H, 8·2. $C_{21}H_{23}N$ requires C, 87·2; H, 7·95%).

9-*Anilinomethyl*-2-*methylanthracene*.—A mixture of 1 g. of 9-bromomethyl-2-methylanthracene and 5 c.c. of aniline, which reacted at the ordinary temperature, was heated for a few minutes on the water-bath. The solid obtained on cooling and dilution with methyl alcohol, after recrystallisation from aqueous alcohol, was very pale yellow and melted at 159° (164° after solidifying and re-heating) (Found : C, 88·7; H, 6·7. $C_{22}H_{19}N$ requires C, 88·9; H, 6·4%).

10-*Bromo*-9-*piperidinomethyl*-2-*methylanthracene* was prepared from 10-bromo-9-bromomethyl-2-methylanthracene (1·5 g.) and 1·5 c.c. of piperidine in 30 c.c. of chloroform. The solid obtained by concentrating and cooling the solution, after being washed with methyl alcohol and recrystallised from alcohol, was pale yellow and melted at 167° (Found : C, 68·6; H, 6·4. $C_{21}H_{22}NBr$ requires C, 68·5; H, 6·0%).

10-*Bromo*-9-*piperidinomethyl*-3-*methylanthracene*, similarly prepared, formed long, silky, yellow needles, m. p. 140° from alcohol (Found : C, 68·5; H, 6·3. $C_{21}H_{22}NBr$ requires C, 68·5; H, 6·0%).

10-*Bromo*-9-*anilinomethyl*-2-*methylanthracene*, prepared from 1 g. of 10-bromo-9-bromomethyl-2-methylanthracene and 5 c.c. of aniline and isolated in the same way as the preceding anilino-compound, separated from alcohol in pale yellow crystals, m. p. 144° (Found : C, 70·1; H, 5·1. $C_{22}H_{14}NBr$ requires C, 70·2; H, 4·8%).

9-*Benzyl*-2-*methylanthracene* (III).—This was prepared in the usual way from 2-methyl-9-anthrone and magnesium benzyl chloride, the dihydroanthranol not being purified but at once converted into the anthracene by heating on the water-bath with acetic acid containing hydrochloric acid. The yield was 9 g. from 11 g. of the anthrone, and the *substance* separated from methyl alcohol in almost colourless crystals, m. p. 139° (Found : C, 93·5; H, 6·5. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%).

9-*Benzyl*-3-*methylanthracene*, prepared from 3-methyl-9-anthrone in exactly the same way as the above, formed almost colourless crystals, m. p. 101°, from methyl alcohol and from light petroleum (Found : C, 93·5; H, 6·6%).

10-*Bromo*-9-*benzyl*-2-*methylanthracene* (IX).—This was prepared in the same way as 9-bromomethyl-2-methylanthracene (bromine, 3·2 g., in carbon disulphide, 5 c.c.; 9-benzyl-2-methylanthracene, 5·6 g., suspended in 20 c.c. of carbon disulphide). The solid precipitated by the light petroleum separated from benzene as a bright yellow, crystalline powder, m. p. 164° (Found : C, 73·3; H, 4·8. $C_{22}H_{17}Br$ requires C, 73·1; H, 4·7%).

10-*Bromo*-9-*benzyl*-3-*methylanthracene*, similarly obtained from 9-benzyl-3-methylanthracene, formed pale yellow crystals, m. p. 139°, from benzene–light petroleum. It is much paler in colour and much more soluble than the isomeride described above (Found : C, 73·2; H, 4·9%).

Both the above bromo-compounds were recovered unchanged after boiling for an hour with piperidine in chloroform solution and after heating for an hour on the water-bath with aniline.

One of the authors (E. de B. B.) desires to express his thanks to Imperial Chemical Industries, Ltd., for a grant from which some of the expenses of this research have been met.

SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C. 3.

[*Received, June 20th*, 1929.]