CCXXXIV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part IV.*

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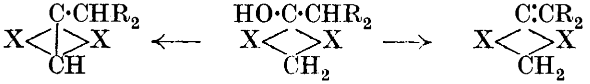
THE normal product of the action of a Grignard solution on an anthrone is the alkyl or aryl dihydroanthranol (I), from which the alkyl or aryl anthracene (II) or the alkylidene dihydroanthracene (III) is obtained by loss of water (for references, see Part II, J., 1927, 1725) :



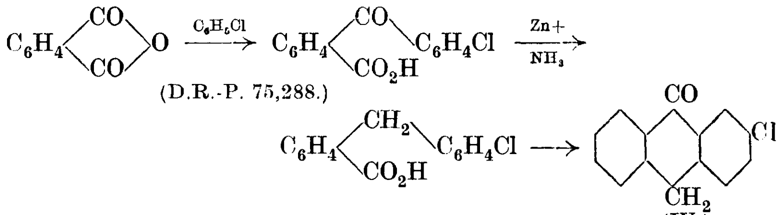
$$X\overset{\text{C·CHR}_2}{\underset{\text{CH}}{<\!|\!>}}X \longleftarrow X\overset{\text{HO·C·CHR}_2}{\underset{\text{CH}_2}{<\;>}}X \longrightarrow X\overset{\text{C:CR}_2}{\underset{\text{CH}_2}{<\;>}}X$$

(II.) (I.) (III.)

(X = C_6H_4 or substituted C_6H_4; R = alkyl, aryl or hydrogen.) The reaction, however, is profoundly affected by the presence of chlorine atoms in α-positions, and when these are present the synthesis either completely breaks down or gives only exceedingly poor yields except in the cases of magnesium methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride.

It has now been found that a somewhat similar influence is exerted by a chlorine atom in a β-position, since with 2-chloro-9-anthrone (IV) satisfactory yields of the alkyl anthracene were obtained only with magnesium ethyl bromide and magnesium benzyl chloride, the other magnesium alkyl halides giving extremely poor results. The excellent yield obtained with magnesium ethyl bromide as compared with the very poor yield obtained with magnesium methyl iodide or bromide is interesting, as it is the reverse of what is the case with 1 : 5-dichloroanthrone (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 2863).

The 2-chloro-9-anthrone employed in the above experiments was prepared according to the scheme :



(IV.)

It differed from the β-chloroanthrone previously isolated from the reduction of 2-chloroanthraquinone (Barnett and Matthews, J., 1923, **123**, 2554), so the latter must be 3-chloro-9-anthrone.

2-Chloro-9-anthrone (apparently in an impure state) has been described by Meyer and Fischbach (*Ber.*, 1925, **58**, 1251), who obtained it by condensing ω-bromo-*o*-toluoyl bromide with benzene, and oriented it by converting it into a benzanthrone derivative.

EXPERIMENTAL.

4-*Chlorodiphenylmethane-2′-carboxylic Acid.*—4-Chloro-*o*-benzoylbenzoic acid (50 g.) was dissolved in 300 c.c. of ammonia (*d* 0·880) and 150 c.c. of water, 150 g. of zinc dust were added slowly, and finally a few c.c. of copper sulphate solution. Reduction was effected on the water-bath and was complete in about 20 hours. The product was isolated in the usual way and after recrystallisation from alcohol melted at 132° (Found : Cl, 14·1. $C_{14}H_{11}O_2Cl$ requires Cl, 14·4%).

2-*Chloro*-9-*anthrone* (IV).—The above carboxylic acid was added slowly with cooling to concentrated sulphuric acid (3 c.c. per g.) and after it had dissolved the solution was kept at the ordinary temperature for an hour and then poured on ice. The resulting anthrone after recrystallisation from alcohol melted constantly at 155° and depressed the melting point of the β-chloroanthrone previously described (Barnett and Matthews, *loc. cit.*).

2-*Chloro*-9-*anthranyl acetate* was obtained from the above anthrone by the usual acetic anhydride–pyridine method (Barnett and Matthews, J., 1923, **123**, 389). After recrystallisation from alcohol it melted at 143° (Found : Cl, 13·2. $C_{16}H_{11}O_2Cl$ requires Cl, 13·1%).

3-*Chloro*-9-*anthranyl acetate* was similarly prepared from 3-chloro-9-anthrone. After recrystallisation from alcohol it melted at 146° and depressed the melting point of the above 2-chloro-9-anthranyl acetate (Found : Cl, 13·3%).

Action of Grignard Solutions on 2-*Chloro*-9-*anthrone.*—In all cases 7 g. of the finely powdered anthrone were added slowly to the Grignard solution prepared from 2·2 g. of magnesium (3 mols.) and the requisite amount of the halogen compound. After being kept in a freezing mixture for 3 hours, the solution was poured on a mixture of ice and solid ammonium chloride, the washed ethereal layer evaporated to dryness, and the residual oil heated on the water-bath for a short time with acetic acid containing hydrochloric acid. The following compounds were obtained, all of which, unless otherwise stated, were recrystallised from methyl or ethyl alcohol and formed pale yellow needles.

2-*Chloro*-9-*methylanthracene*, m. p. 84°. Yield, very small (Found : Cl, 15·8. $C_{15}H_{11}Cl$ requires Cl, 15·7%).

2-*Chloro*-9-*ethylanthracene*, m. p. 79°. Yield, excellent (Found : Cl, 15·0. $C_{16}H_{13}Cl$ requires Cl, 14·8%).

2-*Chloro*-10-*bromo*-9-*ethylanthracene*. By the action of bromine (1 mol.) on the above chloroethylanthracene in carbon disulphide solution. Yellow crystals from benzene–light petroleum; m. p. 128° (Found: Cl + Br, 36·1. $C_{16}H_{12}ClBr$ requires Cl + Br, 35·9%).

2-*Chloro*-9-n-*propylanthracene*, m. p. 82° (Found : Cl, 14·3. $C_{17}H_{15}Cl$ requires Cl, 13·9%).

2-*Chloro*-9-*benzylanthracene*, m. p. 132°. Yield, excellent (Found : Cl, 11·9. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

2-*Chloro*-10-*bromo*-9-*benzylanthracene*. By the action of bromine (1 mol.) on the above chlorobenzylanthracene in carbon disulphide solution. Yellow needles from acetic acid or ethyl acetate; m. p. 167° (Found: Cl + Br, 30·4. $C_{21}H_{14}ClBr$ requires Cl + Br, 30·3%).

When the above chlorobenzylanthracene was kept over-night with excess (3 to 4 mols.) of bromine in carbon disulphide solution a substance was obtained (isolated by the addition of light petroleum) which after recrystallisation from benzene–light petroleum formed a cream-coloured powder; this melted and decomposed violently at about 150°, was difficult to obtain pure, and appeared to be a *dibromide* of 2-chloro-10-bromo-9-benzylanthracene (Found: Cl + Br, 51·4. $C_{21}H_{14}ClBr_3$ requires Cl + Br, 50·9%).

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