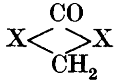
IV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part V.*

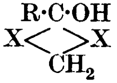
By EDWARD DE BARRY BARNETT and NORMAN FREDERICK GOODWAY.

THE formation of an alkyl or aryl dihydroanthranol (II) and the formation from it of the *meso*-alkyl or *meso*-aryl anthracene (III) by transannular loss of water by the action of a Grignard solution on an anthrone (I) (for references to earlier work see Part II, J., 1927, 1725; also Cook, J., 1928, 2798) are profoundly influenced by substituents both in the *meso*-positions and also in the side rings.

(I.)



$$\mathrm{X}\Big<\begin{matrix}\mathrm{CO}\\ \\ \mathrm{CH_2}\end{matrix}\Big>\mathrm{X}$$



$$\mathrm{X}\Big<\begin{matrix}\mathrm{R{\cdot}C{\cdot}OH}\\ \\ \mathrm{CH_2}\end{matrix}\Big>\mathrm{X}$$

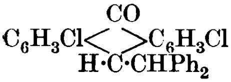
(II.)

$$\mathrm{X}\Big<\begin{matrix}\mathrm{R{\cdot}C}\\ |\\ \mathrm{CH}\end{matrix}\Big>\mathrm{X}$$

(III.)

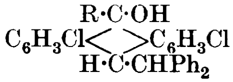
In the case of 1 : 5-dichloroanthrone the method leads to satisfactory yields of the *meso*-methyl-, -ethyl-, and -benzyl-anthracene, but breaks down with the other magnesium alkyl halides (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 2863; 1927, **60**, 2353). 1 : 5-Dichloro-9-methylanthrone (Barnett and Cook, *Ber.*, 1928, **61**, 314), 1 : 5-dichloro-9-benzylanthrone (Barnett and Cook, J., 1928, 566), and 1 : 5-dichloro-9-phenylanthrone (Barnett, Cook, and Wiltshire, J., 1927, 1724) behave in much the same way, but it seemed possible that better results might be obtained with 1 : *5-dichloro-9-benzhydrylanthrone* (IV) (readily obtained by boiling 1 : 5-dichloroanthrone with benzhydryl chloride and caustic alkali), as this shows hardly any tendency to enolise to the anthranol; and as the resulting dihydroanthranol (V) might be expected to lose the benzhydryl group easily (compare the conversion of tribenzyldihydroanthranol into 9 : 10-dibenzylanthracene; Barnett and Cook, J., 1928, 566 : and the facile reduction of dianthrone to anthrone; Barnett and Matthews, J., 1923, **123**, 380), this would permit of an indirect method of preparing the higher alkyl dichloroanthracenes.

These expectations have been only partly fulfilled, as, although 1 : 5-dichloro-9-benzhydrylanthrone does give crystalline dihydroanthranols when treated with a Grignard solution, the yields obtained are very poor (about 5%) except in the cases of the methyl, benzyl, and phenyl compounds.



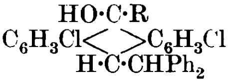
$$\mathrm{C_6H_3Cl}\Big<\begin{matrix}\mathrm{CO}\\ \\ \mathrm{H{\cdot}C{\cdot}CHPh_2}\end{matrix}\Big>\mathrm{C_6H_3Cl}$$

(IV.)



$$\mathrm{C_6H_3Cl}\Big<\begin{matrix}\mathrm{R{\cdot}C{\cdot}OH}\\ \\ \mathrm{H{\cdot}C{\cdot}CHPh_2}\end{matrix}\Big>\mathrm{C_6H_3Cl}$$

(V.)



$$\mathrm{C_6H_3Cl}\Big<\begin{matrix}\mathrm{HO{\cdot}C{\cdot}R}\\ \\ \mathrm{H{\cdot}C{\cdot}CHPh_2}\end{matrix}\Big>\mathrm{C_6H_3Cl}$$

(VI.)

The loss of benzhydrol takes place even more easily than would be expected, as brief heating on the water-bath with acetic acid containing a little hydrochloric acid resulted in the production of methyl-, ethyl-, benzyl-, and phenyl-dichloroanthracene. That transannular loss of benzhydrol takes place in preference to transannular loss of water suggests configuration (V) rather than configuration (VI) for the dihydroanthranol, and benzhydryldichloroanthrone itself, on reduction both in acid and in alkaline solution, loses its benzhydryl group and passes into dichloroanthracene, possibly owing to transannular loss of benzhydrol from the dihydroanthranol which is probably first formed during the reduction.

Phenylbenzhydryldichlorodihydroanthranol (V, R = Ph) undergoes change on thermal treatment in boiling xylene and passes into an isomeric *substance*. This may be the geometrical isomeride represented by (VI), or the isomerism may be due to the non-coplanar arrangement of the anthracene ring system, of which evidence has recently been obtained by Schlenk (*Annalen*, 1928, **463**, 1). As both isomerides undergo facile transannular loss of benzhydrol with formation of 1 : 5-dichloro-9-phenylanthracene, the balance of evidence is rather in favour of the latter type of isomerism; at present, however, methods of obtaining definite proof are not available.

EXPERIMENTAL.

1 : 5-*Dichloro*-9-*benzhydrylanthrone* (IV).—1 : 5-Dichloroanthrone (20 g.), potassium hydroxide (200 c.c. of 20% solution), and crude benzhydryl chloride (40 c.c.) were boiled under reflux until the liquid, which at first was almost black, became pale in colour (about 30 minutes). The cooled product was washed with water and then triturated with a little cold ether in order to remove resinous by-products. After recrystallisation from methyl ethyl ketone or ethyl acetate it formed colourless, glistening crystals, m. p. 191°. It gave scarcely any colour with boiling alcoholic alkali and all attempts to obtain an acetate of the corresponding anthranol failed (Found : C, 75·3; H, 4·3. $C_{27}H_{18}OCl_2$ requires C, 75·5; H, 4·2%).

The yield of the above compound does not exceed 50% owing to the simultaneous formation of a yellow, resinous substance. This was recovered from the ethereal washings but could not be made to crystallise.

Reduction of 1 : 5-*Dichloro*-9-*benzhydrylanthrone*.—Reduction was carried out (*a*) with zinc dust and caustic potash in alcoholic solution, (*b*) with zinc dust and hydrochloric acid in acetic acid solution. In each case 1 : 5-dichloroanthracene resulted and was identified by direct comparison with an authentic sample, and in each case the liquor smelt strongly of diphenylmethane.

Action of Grignard Reagents on 1 : 5-*Dichloro*-9-*benzhydrylanthrone*.—In each case the finely powdered anthrone (4·3 g.; 0·01 mol.) was added to an ethereal Grignard solution prepared from 0·72 g. (0·03 mol.) of magnesium, and after being kept for 30 minutes in the freezing mixture and for 4—5 hours at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium chloride. In the cases of the methyl, benzyl, and phenyl compounds the greater part of the resulting dihydroanthranol (V) was obtained directly in the solid state, and further amounts were obtained by evaporation of the washed ethereal solution. In all other cases the product was completely and easily soluble in ether and evaporation of the washed solution resulted in a viscous oil from which small quantities of the crystalline dihydroanthranol were obtained by cautious treatment with aqueous acetone, keeping over-night in contact with the solvent frequently being necessary. In these cases the yield did not exceed 5%. Purification of the crude dihydroanthranol was effected by recrystallisation from aqueous acetone, and the resulting colourless crystals were dried in the steam-oven before analysis.

No dihydroanthranol could be isolated when benzhydryldichloroanthrone was treated with magnesium *p*-anisyl bromide, magnesium *o*-tolyl bromide, or magnesium α-naphthyl bromide, the only solid product being the unchanged anthrone even when the preparation was kept over-night before being poured on ice and ammonium chloride.

In the following table the melting points and analytical data of the dihydroanthranols are recorded, the calculated figures being given in parentheses.

Alkyl or aryl group.	M. p.	Cl, %.
Me …………	160°	16·3 (16·0)
Et …………	140	15·7 (15·5)
Pr^{α} …………	185	15·0 (15·0)
Pr^{β} …………	170	15·0 (15·0)
n-C_4H_9………	182	14·5 (14·6)
iso-C_4H_9 ……………	212°	14·6 (14·6)
iso-C_5H_{11} …………	193	14·3 (14·2)
CH_2Ph………………	206	13·8 (13·6)
Ph (recrystallised from methyl ethyl ketone and rapidly from toluene) ……	259	13·9 (14·0)

The methyl, ethyl, benzyl, and phenyl compounds mentioned above, when heated on the water-bath with acetic acid containing a little hydrochloric acid, passed very easily into the corresponding alkyl (or phenyl) anthracene (identified by direct comparison with authentic samples). The amounts of the other dihydroanthranols were too small to allow their behaviour to be examined.

iso-1 : 5-*Dichloro*-9-*phenyl*-10-*benzhydryl*-9 : 10-*dihydroanthranol* (V or VI, R = Ph).—The phenyldihydroanthranol included in the foregoing table maintained a constant melting point so long as recrystallisation was effected from a solvent with a low boiling point (methyl ethyl ketone or toluene). Recrystallisation from xylene, however, led to a progressive rise in melting point, and when 1·5 g. of the substance were boiled under reflux with 20 c.c. of xylene for 4 hours the product obtained melted at 271° and showed no change in melting point on further thermal treatment (Found: Cl, 14·2. $C_{33}H_{24}OCl_2$ requires Cl, 14·0%). This product, on treatment on the water-bath with acetic acid containing hydrochloric acid, passed easily into 1 : 5-dichloro-9-phenylanthracene.

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

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