CLXXIV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part VII.*

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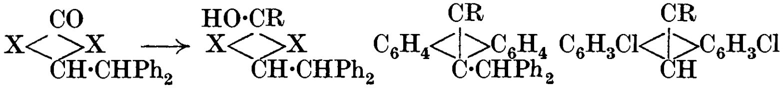
THE isolation of 3-chloro-9-anthrone (Barnett and Matthews, J., 1923, 2549) from the mixture of 2- and 3-chloro-9-anthrone obtained by the reduction of 2-chloroanthraquinone with tin and hydrochloric acid or with aluminium powder and concentrated sulphuric acid can be readily effected by the method used by Barnett and Goodway (J., 1929, 1754) for the isolation of 3-methyl-9-anthrone, *viz.*, acetylation and fractional crystallisation of the mixed anthranyl acetates.

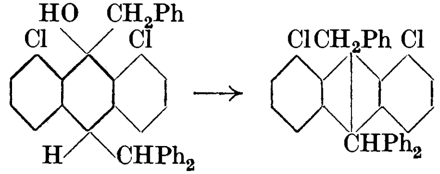
2- and 3-Chloro-9-anthrone condense readily with benzyl chloride in the presence of potassium hydroxide and yield, as would be expected, the *chlorodibenzylanthrones.*

By interaction with magnesium alkyl halides (Barnett and Goodway, J., 1929, 20, 1745), 10-benzhydrylanthrone (I, X = C_6H_4) gives dihydroanthranols (II, X = C_6H_4) which undergo transannular loss of water to form the alkylbenzhydrylanthracenes (III), whereas 1 : 5-dichloro-10-benzhydrylanthrone (I, X = C_6H_3Cl) gives dihydroanthranols (II, X = C_6H_3Cl) which undergo transannular loss of benzhydrol to give the alkylanthracene (IV).


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

$$X\overset{\text{CO}}{\underset{\text{CH·CHPh}_2}{<>}}X \longrightarrow X\overset{\text{HO·CR}}{\underset{\text{CH·CHPh}_2}{<>}}X \qquad C_6H_4\overset{\text{CR}}{\underset{\text{C·CHPh}_2}{<|>}}C_6H_4 \qquad C_6H_3Cl\overset{\text{CR}}{\underset{\text{CH}}{<|>}}C_6H_3Cl$$

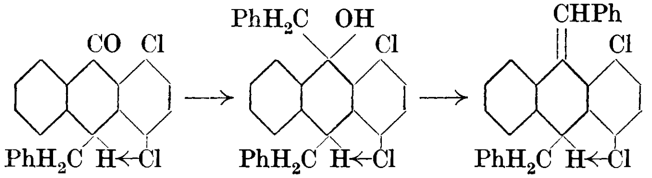
As it seemed possible that this difference in behaviour was due to the co-ordination of the hydrogen atom at 10 with the chlorine atom at 5 (compare Barnett and Wiltshire, *Ber.*, 1929, **62**, 3063; Barnett, Goodway, and Wiltshire, *ibid.*, 1930, **63**, 472), the behaviour of the dihydroanthranols obtained by the action of magnesium benzyl chloride on some other *Bz.*-chloro-10-benzhydrylanthrones has been examined. The results obtained, which are summarised below, show that co-ordination of the *meso*-hydrogen atom cannot possibly be the factor determining the type of transannular loss suffered under the influence of hydrogen ions: for instance, 1-*chloro*-, 2-*chloro*-, 4-*chloro*-, 1 : 4-*dichloro*-, and 4 : 5-*dichloro*-9-*benzyl*-10-*benzhydryl*-9 : 10-*dihydro*-9-*anthranol* all underwent loss of benzhydrol and yielded the corresponding chlorinated 9-benzylanthracene; 1 : 8-*dichloro*-9-*benzyl*-10-*benzhydryl*-9 : 10-*dihydro*-9-*anthranol* (V), on the other hand, lost water and passed into 1 : 8-*dichloro*-9-*benzyl*-10-*benzhydrylanthracene* (VI).



(V.) (VI.)

1 : 8- and 4 : 5-Dichloro-9-anthrone differ markedly from anthrone itself in their behaviour towards benzophenone chloride, for whereas anthrone yields diphenylmethyleneanthrone (anthrafuchsone) (Padova, *Compt. rend.*, 1906, **143**, 121; *Ann. Chim.*, 1910, **19**, 388), the two dichloroanthrones are merely oxidised to the dianthrones. Also, after boiling for 3 hours with phthaloyl chloride in xylene solution, they were largely recovered unchanged and, although some resinous matter was formed in each case, no compound corresponding to the phthalylidene derivative obtained by Padova (*Compt. rend.*, 1909, **418**, 290) from anthrone itself could be detected.

As was foreseen, 1 : 4-dichloroanthrone condenses with benzyl chloride in the presence of sodium hydroxide to give 1 : 4-*dichloro*-10-*benzylanthrone* (VII), and the *dihydroanthranol* (VIII) obtained from this by the action of magnesium benzyl chloride undergoes loss of water to form the *benzylidene* derivative (IX). This behaviour is in harmony with the suggestion (Barnett, Goodway, and Wiltshire, *loc. cit.*) that a *meso*-hydrogen atom forms a chelate ring with the chlorine atom in the *peri*-position, as indicated in the formulæ below.



(VII.) (VIII.) (IX.)

The failure of 1 : 4-dichloro-10-benzylanthrone to undergo enolisation when boiled with alcoholic sodium hydroxide furnishes further evidence of the immobilisation of the *meso*-hydrogen atom.

EXPERIMENTAL.

3-*Chloro*-9-*anthrone*.—The mixture of anthrones obtained by the reduction of 2-chloroanthraquinone by the tin–hydrochloric acid method was acetylated on the water-bath with pyridine and acetic anhydride and the resulting anthranyl acetates were recrystallised from benzene–light petroleum or toluene–light petroleum. 3-Chloro-9-anthranyl acetate (m. p. 146°; Barnett and Wiltshire, J., 1928, 1822) was thus easily obtained in the pure state; it yielded the corresponding anthrone on hydrolysis with alcoholic alkali in an inert atmosphere (compare Barnett and Goodway, J., 1929, 1754).

2-*Chloro*-10 : 10-*dibenzylanthrone*.—2-Chloro-9-anthrone (10 g.) and benzyl chloride (10 c.c.) were boiled under reflux with a solution of potassium hydroxide (7 g.) in water (25 c.c.) for an hour. After being washed with water and with ice-cold ether, the *product* was recrystallised from glacial acetic acid and from benzene–light petroleum. It was then colourless and melted at 185° (Found : C, 82·0; H, 5·3. $C_{28}H_{21}OCl$ requires C, 82·2; H, 5·1%).

3-*Chloro*-10 : 10-*dibenzylanthrone*, prepared in exactly the same way as the above compound, formed colourless crystals, m. p. 174° (Found : C, 82·3; H, 5·4%).

Bz.-*Chloro*-10-*benzhydrylanthrones*.—In all cases the anthrone (5—10 g.) was boiled with an excess of crude benzhydryl chloride (10—20 c.c.) and aqueous sodium hydroxide (75—100 c.c.; about 12% strength) until the black tar at first formed vanished (10—30 minutes). After cooling, the viscous product was washed with water, triturated with ice-cold ether to remove resinous by-products, and crystallised from acetic acid or acetone and then from benzene–light petroleum. The products were all colourless and, when boiled with alcoholic alkali, gave a distinct colour only when there was no chlorine atom in position 4 or 5.

In the following table the figures under " Analysis " refer to carbon and hydrogen, the calculated figures being given in parentheses.

Cl at	M. p.	Analysis.	Cl at	M. p.	Analysis.
1	204°	82·3; 5·0 (82·1; 4·8)	1 : 4	191°	75·4; 4·4 (75·5; 4·2)
2	171	82·1; 5·0 ,, ,,	1 : 8	242	75·4; 4·4 ,, ,,
4	175	82·0; 4·8 ,, ,,	4 : 5	224	75·4; 4·3 ,, ,,

A crystalline product could not be isolated from the resin obtained when 3-chloro-9-anthrone was boiled with benzhydryl chloride and alkali.

Bz.-*Chloro*-9-*benzyl*-10-*benzhydryl*-9 : 10-*dihydro*-9-*anthranols*.—In all cases the benzhydrylanthrone was added slowly to an ethereal solution of magnesium benzyl chloride (3 mols.) cooled in a freezing mixture, and after being kept over-night at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium chloride. Sparingly soluble dihydroanthranols were isolated by filtration, and the more soluble dihydroanthranols by evaporation of the washed and dried (Na_2SO_4) ethereal solution. In the latter case the dihydroanthranol was sometimes left as an oil which became solid on treatment with aqueous acetone or light petroleum, but the dihydroanthranol obtained from 1-chloro-10-benzhydrylanthrone refused to crystallise. Purification was effected by recrystallisation from aqueous acetone and then from benzene–light petroleum. The products were all colourless.

Dehydration was brought about by means of acetic acid containing a little concentrated hydrochloric acid, either by keeping over-night at the ordinary temperature or by brief heating on the water-bath. The resulting *Bz*.-chloro-9-benzylanthracenes were identified by direct comparison with authentic specimens.

Cl at	M. p.	Analysis.	Cl at	M. p.	Analysis.
2	166°	83·8; 5·7 (83·9; 5·6)	1 : 4	199°	78·2; 5·2 (78·3; 5·0)
4	208	83·6; 5·8 ,, ,,	1 : 8	190	78·4; 5·3 ,, ,,
			4 : 5	186	78·5; 5·1 ,, ,,

1 : 8-*Dichloro*-9-*benzyl*-10-*benzhydrylanthracene* (VI) formed pale yellow crystals, m. p. 139°, from acetone (Found : C, 81·1; H, 4·8. $C_{34}H_{24}Cl_2$ requires C, 81·1; H, 4·8%).

Action of Benzophenone Chloride on 1 : 8- *and* 4 : 5-*Dichloroanthrones*.—The anthrone (5·4 g.) was boiled for 3 hours with benzophenone chloride (5·5 g.) and xylene (50 c.c. in the case of 1 : 8-dichloroanthrone; 15 c.c. in the case of 4 : 5-dichloroanthrone). 1 : 8 : 1′ : 8′-Tetrachloro-10 : 10′-dianthrone separated from the boiling solution, and after being washed with xylene was recrystallised from nitrobenzene (Found : C, 64·0; H, 2·7. Calc. : C, 64·1; H, 2·7%). 4 : 5 : 4′ : 5′ - Tetrachloro - 10 : 10′- dianthrone was isolated by the addition of light petroleum and subsequent recrystallisation from benzene–ethyl acetate. On heating, it darkened but did not melt below 315° (compare Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1926, **45**, 75).

Neither of the above dianthrones gave any colour on boiling with alcoholic alkali. The latter, however, was enolised by pyridine and after boiling for 3 minutes with this solvent gave an immediate red colour on the addition of a drop of sodium hydroxide. The former gave no colour after similar treatment, presumably owing to the immobilisation of the *meso*-hydrogen atoms by co-ordination with the chlorine atoms.

1 : 4-*Dichloro*-10-*benzyl*-9-*anthrone* (VII).—1 : 4-Dichloroanthrone (10 g.) was boiled with benzyl chloride (10 c.c.) and a solution of potassium hydroxide (7 g.) in water (30 c.c.) for an hour. The product having been washed with water and freed from volatile

material by distillation with steam, the resinous residue was triturated with cold ether and crystallised from benzene–light petroleum. The resulting colourless crystals melted at 123° (Found : C, 71·3; H, 4·1. $C_{21}H_{14}OCl_2$ requires C, 71·4; H, 4·0%).

1 : 4-*Dichloro*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthranol* (VIII).—1 : 4-Dichloro-10-benzylanthrone (6 g.) was added slowly to an ethereal solution of magnesium benzyl chloride (3 mols.) cooled in a freezing mixture, and the whole kept over-night at the ordinary temperature and then poured on a mixture of ice and solid ammonium chloride. The oil obtained by evaporation of the washed ethereal solution became solid on cooling and was then recrystallised from aqueous acetone and from benzene–light petroleum. The resulting colourless crystals melted at 165° (Found : C, 75·5; H, 5·1. $C_{28}H_{22}OCl_2$ requires C, 75·5; H, 4·9%).

1 : 4-*Dichloro*-10-*benzylidene*-9 : 10-*dihydroanthracene* (IX).—The above dihydroanthranol was kept over-night at the ordinary temperature in glacial acetic acid solution to which a little concentrated hydrochloric acid had been added. The resulting solid separated from benzene–light petroleum in colourless non-fluorescent crystals, m. p. 186° (Found : C, 78·7; H, 4·9. $C_{28}H_{20}Cl_2$ requires C, 78·7; H, 4·7%).

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