61. *The Orientation of the α-Chloroanthrones.*

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The orientation at present in use of 1- and 2-chloro- and of 1 : 8- and 4 : 5-dichloro-anthrone depends on experiments by Eckert and Tomaschek (*Monatsh.*, 1918, **39**, 839) and requires confirmation, especially in the case of 1 : 8-dichloroanthrone, as it has been shown (Barnett and Matthews, J., 1923, **123**, 2549) that these investigators were dealing with a very impure material.

Chloroanthraquinones can be converted into nitriles by heating with cuprous cyanide in phenylacetonitrile solution (E.P. 261,422) and although the patent specification states that the reaction is general for halogenoanthraquinones it was deemed probable that the replacement would only take place when a chlorine atom was in the *o*-position to a carbonyl group. This opinion was confirmed by the recovery unchanged of 2-chloroanthraquinone after 12 g. had been heated at 235—240° (bath temperature) for 45 minutes with 6 g. of cuprous cyanide.* If the reaction is limited to chlorine atoms in the *o*-position to a carbonyl group, it should take place with 1-chloro- and with 1 : 8-dichloro-anthrone but not with 4-chloro- or with 4 : 5-dichloro-anthrone. All these anthrones, however, are easily enolised and, as was anticipated, heating with cuprous cyanide resulted only in resinous products. 1-Chloroanthrone, however, gives the dibenzylanthrone when heated with benzyl chloride and caustic potash (Barnett and Cook, J., 1927, 572), and since in this there is no mobile hydrogen atom enolisation is impossible and it was found to pass smoothly into the nitrile, thus providing evidence that the orientation in use is correct. The behaviour of the isomeric 4-chloro-10 : 10-dibenzylanthrone could not be examined, as 4-chloroanthrone gives only resinous products when heated with benzyl chloride and alkali.

4 : 5-Dichloroanthrone when heated with benzyl chloride and caustic potash gives a monobenzylanthrone (Barnett and Wiltshire, *Ber.*, 1929, **62**, 3063). This is not enolised and was recovered unchanged after being heated with cuprous cyanide (1 part) and phenylacetonitrile (5 parts) at 235° for 30 minutes, the orientation thus being confirmed. The isomeric 1 : 8-dichloro-10-benzylanthrone (Barnett and Wiltshire, *loc. cit.*), on the other hand, is

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* Dr. J. W. Cook (private communication) has found that neither 6-chloro-1 : 2-benzanthraquinone (Schwenk and Waldmann, *J. pr. Chem.*, 1930, **128**, 323) nor the chloro-1 : 2-benzanthraquinone obtained from 2-chloronaphthalene and phthalic anhydride (Heller, *Ber.*, 1912, **45**, 671 ; Scholl, Seer, and Zinke, *Monatsh.*, 1920, **41**, 583) reacts with cuprous cyanide in phenylacetonitrile solution.

easily enolised and when heated with cuprous cyanide heavy resinification took place, and although a small amount of a nitrogenous product was isolated it could not be purified for analysis. Although 1 : 8-dichloroanthrone gives only a monobenzyl derivative with benzyl chloride, it gives a di-*o*-chlorobenzyl derivative with *o*-chlorobenzyl chloride under the same conditions (Barnett and Wiltshire, *Ber.*, 1930, **63**, 1114). This, of course, is incapable of enolisation and yields a dicyano-compound with cuprous cyanide, clear evidence that the chlorine atoms are in *o*-positions to carbonyl groups. 1 : 8-Dichloro-10-methoxy-10-phenylanthrone also yielded what was almost certainly a dinitrile, but the reaction was accompanied by much resinification and the product was not obtained pure.

Both 1 : 4- and 1 : 5-dichloro-10-benzylanthrone (Barnett and Goodway, J., 1930, 1348; Barnett and Cook, J., 1928, 566) are only enolised with great difficulty and in each case one chlorine atom is replaced by the nitrilo-group on heating with cuprous cyanide, the products being regarded as 4- and 5-chloro-1-cyano-10-benzylanthrone. It is remarkable that both these are readily enolised by cold alkali and in this way differ sharply from the dichlorobenzylanthrones from which they are derived, as neither of these gives a red colour even on boiling.

Attempts to hydrolyse the cyanoanthrones mentioned above were not successful, as boiling with sulphuric acid of various strengths gave no product soluble in alkali and there was a strong tendency for resinification to take place.

EXPERIMENTAL.

1-*Cyano*-10 : 10-*dibenzylanthrone.*—4 G. of 1-chlorodibenzylanthrone, 1·5 g. of cuprous cyanide, and 20 c.c. of phenylacetonitrile were heated for 20 minutes at 230—235° (bath temperature). After cooling and dilution with methyl alcohol the solid was extracted with hot concentrated potassium cyanide solution and recrystallised from glacial acetic acid (charcoal) and from xylene. It was then colourless and melted to a dark liquid at 276° after slight previous sintering (Found: C, 87·1; H, 5·2. $C_{29}H_{21}ON$ requires C, 87·2; H, 5·3%).

1 : 8-*Dicyano*-10 : 10-*di*-o-*chlorobenzylanthrone.*—2·5 G. of 1 : 8 : 2′ : 2″-tetrachloro-10 : 10-dibenzylanthrone, 1·5 g. of cuprous cyanide, and 15 c.c. of phenylacetonitrile were heated for 10 minutes at 225—230° (bath temperature). The black tar was washed with alcohol and purified as described above; the product then formed colourless crystals, m. p. 264° (Found: C, 73·0; H, 3·9. $C_{30}H_{18}ON_2Cl_2$ requires C, 73·0; H, 3·7%).

4-*Chloro*-1-*cyano*-10-*benzylanthrone*.—6 G. of 1 : 4-dichloro-10-benzylanthrone, 4 g. of cuprous cyanide, and 15 c.c. of phenylacetonitrile were heated for 5 minutes at 235° (bath temperature). On cooling and dilution with methyl alcohol a black tar was obtained, which was digested with hot concentrated potassium cyanide solution and then boiled with glacial acetic acid. After cooling, the almost black solid thus obtained was washed successively with glacial acetic acid, methyl alcohol, and acetone until the washings were only slightly coloured. It was then recrystallised from glacial acetic acid (charcoal), ethyl acetate, and toluene. The resulting colourless crystals, m. p. 208°, gave a crimson colour with alcoholic alkali, slowly in the cold, rapidly on heating (Found : C, 76·9; H, 4·2. $C_{22}H_{14}ONCl$ requires C, 76·9; H, 4·1%).

5-*Chloro*-1-*cyano*-10-*benzylanthrone*.—7 G. of 1 : 5-dichloro-10-benzylanthrone, 4 g. of cuprous cyanide, and 25 c.c. of phenylacetonitrile were heated at 230—240° for 15 minutes, the solution was then cooled and diluted with methyl alcohol, and the solid washed with methyl alcohol to remove resinous products. After digestion with hot concentrated potassium cyanide solution the solid was again washed with methyl alcohol, more resinous substances being removed and an almost colourless substance left. After recrystallisation from glacial acetic acid (charcoal) and from toluene this was completely colourless and melted at 234° (Found : C, 76·9; H, 4·3. $C_{22}H_{14}ONCl$ requires C, 76·9, H, 4·1%). This product gave a wine-red solution with alcoholic alkali, slowly in the cold, rapidly on warming, but was not completely acetylated even after boiling for 3 hours under reflux with acetic anhydride in pyridine solution.

1 : 8-*Dichloro*-10-*bromo*-10-*phenylanthrone*.—When 1·6 g. (1 mol.) of bromine were added to 3·4 g. of 1 : 8-dichloro-10-phenylanthrone suspended in carbon disulphide at the ordinary temperature, no reaction took place at first but after a few minutes bromination proceeded vigorously. When the reaction had subsided, the whole was warmed for a few minutes and then cooled in a freezing mixture. The solid was washed with light petroleum and recrystallised from benzene, forming almost colourless crystals which melted to a red liquid at about 224° after slight previous sintering (Found : C, 57·4; H, 2·7. $C_{20}H_{11}OCl_2Br$ requires C, 57·4; H, 2·6%).

1 : 8-*Dichloro*-10-*methoxy*-10-*phenylanthrone*.—10 G. of the above bromoanthrone, 4 g. of calcium carbonate, and 250 c.c. of methyl alcohol were boiled under reflux for 6 hours and the solid was washed with cold, very dilute hydrochloric acid. On recrystallisation from benzene–*cyclo*hexane it formed colourless crystals, m. p. 237° (Found : C, 68·2; H, 3·9. $C_{21}H_{14}O_2Cl_2$ requires C, 68·3; H, 3·8%).

1 : 8-*Dichloro*-10 : 10-*diphenylanthrone*.—3·7 G. of finely powdered

aluminium chloride were added fairly rapidly to 5 g. of the above bromoanthrone suspended in 50 c.c. of benzene at the ordinary temperature. The solution, which became deep green and then deep red, was kept over-night at the ordinary temperature and poured into dilute hydrochloric acid. After removal of benzene in steam, the red solid was washed with acetone and recrystallised from pyridine and from xylene, forming colourless crystals which did not melt below 310° (Found: C, 74·9; H, 3·8. $C_{26}H_{16}OCl_2$ requires C, 75·2; H, 3·8%).

1 : 8-*Dichloro*-4′-*dimethylamino*-10 : 10-*diphenylanthrone*.—3 G. of the above anthrone and 6 c.c. of dimethylaniline were warmed gently for 15 minutes on the water-bath and the whole was then cooled and diluted with methyl alcohol. After being washed with methyl alcohol, the solid separated from xylene in slightly yellow crystals, m. p. 308° (Found: C, 73·7; H, 4·7. $C_{28}H_{21}ONCl_2$ requires C, 73·4; H, 4·6%).

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