179. *The Direct Synthesis of 2′-Halogeno*meso*benzanthrones.*[*]

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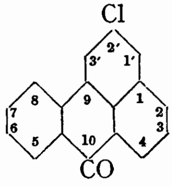
Numerous examples are to be found, especially in the patent literature, of the formation of *meso*benzanthrone and its derivatives by condensation of αβ-unsaturated aldehydes and ketones with anthraquinone and its reduction products. With the object of extending this reaction to the synthesis of 2′-chloro*meso*benzanthrone (I) it was decided to attempt the condensation of anthrone with chloromalondialdehyde, which reacts in its enol-form as an αβ-unsaturated aldehyde and is readily available from αβγγ-tetrachloro-Δ^{α}-propylene according to Prins's method (*J. pr. Chem.*, 1914, **89**, 414). In practice it has been found unnecessary to isolate the aldehyde, since 2′-chloro*meso*benzanthrone is readily produced by the direct interaction of anthrone and the chloro-olefin in warm concentrated sulphuric acid. It is probable that the liberation of hydrogen chloride which occurs during the reaction is due entirely to the hydrolysis of the tetrachloropropylene to chloromalondialdehyde, which immediately condenses with the anthrone, although the possibility that condensation may commence with the intermediate αβ-dichloroacraldehyde cannot be completely eliminated.



(I.)

The structure of the 2′-chloro*meso*benzanthrone (m. p. 191—192°), which appears to be identical with the *Bz*-2-chlorobenzanthrone (m. p. 190°) obtained by Kalle and Co. (Sw.P. 122,904; *Chem. Zentr.*, 1928, **99**, I, 1100) by a tedious synthesis from 1′-nitro*meso*benzanthrone, has been confirmed during the present investigation by its direct synthesis from 2′-amino*meso*benzanthrone.

αβγγ-Tetrachloro-Δ^{α}-propylene reacts equally well with substituted anthrones; *e.g.*, 1 : 4- and 1 : 5-dichloroanthrone give respectively 2′ : 5 : 8- and 2′ : 4 : 8-*trichloro*meso*benzanthrone*. From 4-chloroanthrone, two isomeric dichloro*meso*benzanthrones are theoretically obtainable, and these have been isolated in approximately equal amounts,

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[*] The compound hitherto known as "benzanthrone" will in future be named "*meso*benzanthrone."—Ed.

their separation depending upon their differing solubility in benzene. By oxidation to the corresponding chloroanthraquinone-1-carboxylic acid by the method of Perkin and Spencer (J., 1922, **121**, 478), the more soluble compound, m. p. 240°, was shown to be 2′ : 5-*dichloro*-meso*benzanthrone*, and the less soluble isomeride, m. p. 203—204°, the 2′ : 4-*dichloro*-derivative.

The chlorine atom in 2′-chloro*meso*benzanthrone is extremely unreactive and all attempts to replace it by a methoxy-, cyano-, or amino-group have given unsatisfactory results. On the other hand, alcoholic potash fusion under the normal conditions employed for the preparation of dibenzanthrones readily yields a purple vat dye, which, however, is almost devoid of chlorine. The behaviour of the di- and tri-chloro*meso*benzanthrones mentioned above on fusion with alcoholic potash has led to the interesting observation that, whereas both the 2′ : 5-dichloro- and the 2′ : 5 : 8-trichloro-compound readily undergo conversion into dibenzanthrones, the isomeric 2′ : 4-dichloro- and 2′ : 4 : 8-trichloro-*meso*benzanthrones fail to do so. From this it would appear that the introduction of the *op*-directive group into the 4-position in the *meso*benzanthrone molecule inhibits the reactivity of the hydrogen atom in position 2 sufficiently to prevent fusion to the di-molecule.

An attempt has also been made to apply the new *meso*benzanthrone synthesis described above to the preparation of 2′-bromo*meso*benzanthrone. By analogy this would involve the preparation of αβγγ-tetrabromo-Δ^{α}-propylene from the corresponding *s*.-pentabromopropane. According to Prins (*loc. cit.*) the latter is formed by the condensation of *s*.-dibromoethylene with bromoform in presence of anhydrous aluminium bromide. The comparative inaccessibility of the last two reagents led us to explore alternative routes and the following was adopted: dibromoethylene was condensed with chloroform in the presence of anhydrous aluminium chloride and the product, presumably αγγ-trichloro-αβ-dibromopropane, was converted by alcoholic potash into a substance which, judged from analytical data, was a mixture of the three theoretically possible compounds $CHCl{:}CBr{\cdot}CHBrCl$, $CHBr{:}CBr{\cdot}CHCl_2$, and $CHCl{:}CBr{\cdot}CHCl_2$. When this was hydrolysed with concentrated sulphuric acid, bromomalondialdehyde was obtained in high yield, the presence of a bromine atom in the β-position in all the propylene derivatives present thus being established.

Condensation of the mixture of halogenated propylenes with anthrone under the conditions described in the case of αβγγ-tetrachloro-Δ^{α}-propylene proved abortive owing to the liberation of bromine and extensive oxidation of the anthrone to anthraquinone. Eventually a method was evolved whereby the propylene was first hydrolysed to bromomalondialdehyde, which, without isolation, was condensed with anthrone in the sulphuric acid solution in presence of sulphur dioxide, giving a bromo*meso*benzanthrone (A), m. p. 174—175°, at first thought to be the anticipated 2′-bromo-derivative. Its general properties, however, *e.g.*, its deep red-violet solution in concentrated sulphuric acid, in contrast with the orange-red colour of all the 2′-chloro*meso*benzanthrones, and its extremely facile conversion into a cyano*meso*benzanthrone having the same melting point as that recorded in G.P. 476,118 for 1′-cyano*meso*benzanthrone, led us to consider the possibility of its being actually 1′-bromo-*meso*benzanthrone. That this view was correct was shown by the preparation of 1′-bromo-*meso*benzanthrone by direct bromination of *meso*benzanthrone (compare G.P. 193,959), the product having the same m. p. whether heated alone or mixed with (A). The identity of (A) as 1′-bromo*meso*benzanthrone was further confirmed by the direct synthesis of both 2′-*bromo*meso*benzanthrone*, m. p. 194—195°, and 2′-*cyano*meso*benzanthrone*, m. p. 285—286°, from 2′-amino*meso*benzanthrone.

The unexpected formation of 1′-bromo*meso*benzanthrone may be due to migration of the bromine atom or to the complete elimination of bromine at an intermediate stage of the condensation with the formation of *meso*benzanthrone itself, which is then attacked by the displaced bromine in the normal 1′-position.

EXPERIMENTAL.

s.-*Pentachloropropane*.—Prins (*loc. cit.*) gives no details of the preparation. The following procedure was found satisfactory: A mixture of dry chloroform (150 g.) and *s*.-dichloroethylene

(60 g.) was slowly added with cooling and stirring to an intimate suspension of powdered aluminium chloride (15 g.) and fine white sand (60 g.) in chloroform (20 g.). After 20 hours' stirring at 30°, the product was decomposed with water, and the chloroform layer separated. After removal of solvent from the washed and dried solution, the residual oil was fractionated under reduced pressure, *s.*-pentachloropropane being collected as a heavy colourless liquid, b. p. 98—100°/20 mm. (yield, 63% calc. on the dichloroethylene).

$\alpha\beta\gamma\gamma$-Tetrachloro-Δ^{α}-propylene was conveniently prepared by treatment of *s.*-pentachloropropane with the requisite amount of alcoholic potassium hydroxide. After several hours the solution was filtered, the alcohol removed, and the residual oil fractionally distilled, the tetrachloropropylene being obtained as a colourless heavy oil, b. p. 165—167° (yield, 70%).

*Preparation of the 2′-Chloro*meso*benzanthrones.*—The following general procedure was employed: A solution of the anthrone (1 part) in concentrated sulphuric acid (8 parts) was treated with a slight excess of $\alpha\beta\gamma\gamma$-tetrachloro-Δ^{α}-propylene, added during 15 minutes, the temperature being maintained first at 40° for 16 hours and then at 50° for 6 hours, with continuous stirring. A vigorous evolution of hydrogen chloride occurred and the solution gradually became orange or red. The cold product was poured on ice and the crude *meso*benzanthrone was collected, washed with water, and extracted with boiling dilute sodium hydroxide solution (2%) to remove unchanged anthrone and sulphonation products.

*2′-Chloro*meso*benzanthrone.* (1) The dark green reaction product obtained as described above was washed by decantation with boiling alcohol, whereby easily soluble impurities were removed, and then exhaustively extracted with benzene, the insoluble black residue being rejected. The crude 2′-chloro*meso*benzanthrone (yield, 30%) obtained on concentration of the benzene solution was repeatedly crystallised from the same solvent, from which it separated in yellowish-green plates, m. p. 191—192°. Its solution in concentrated sulphuric acid was deep orange-red with a brown fluorescence (Found: C, 77·0; H, 3·6; Cl, 13·7. Calc. for $C_{17}H_9OCl$: C, 77·1; H, 3·4; Cl, 13·4%). Potash fusion at 220° for 15 minutes yielded a dibenzanthrone almost free of chlorine, dyeing cotton a deep purple shade from a red-violet vat (Found: Cl, 2·7. Calc. for $C_{34}H_{14}O_2Cl_2$: Cl, 13·5%).

(2) 2′-Amino*meso*benzanthrone (24·5 g.), prepared from 2′-nitro*meso*benzanthrone by reduction with sodium sulphide, was dissolved in concentrated sulphuric acid (250 g.), and sodium nitrite (10·5 g.) added during 2 hours with stirring, the temperature being maintained at 5—10°. After a further 2 hours, the solution was diluted with ice-water (250 c.c.) and kept over-night in an ice-chest. The partly separated diazonium sulphate was completely precipitated by further dilution with ice-water (200 c.c.), collected, and made into a fine paste with concentrated hydrochloric acid (100 c.c.). This was added with rapid stirring at 30—35° during 1 hour to a solution of freshly prepared cuprous chloride (20 g.) in hydrochloric acid (600 c.c. of 17%) and after a further 3 hours the temperature was raised to 70—80°. The crude product was collected and extracted successively with hot dilute nitric acid to remove copper salts, with boiling aqueous sodium hydroxide to remove traces of 2′-hydroxy*meso*benzanthrone, and with water. It was crystallised first from benzene and finally from glacial acetic acid, from which it separated in yellowish-green needles, m. p. 192—193°, giving no depression on admixture with the benzanthrone described above.

*2′ : 5 : 8-Trichloro*meso*benzanthrone.* The required 1 : 4-dichloroanthrone was prepared as described by Barnett and Wiltshire (*Ber.*, 1929, **62**, 1971). The crude reaction product, after removal of soluble impurities with hot alcohol, was repeatedly crystallised from benzene, pure 2′ : 5 : 8-*trichloro*meso*benzanthrone* being obtained in golden-yellow needles, m. p. 180—181° (yield, 75%) (Found: C, 61·0; H, 2·2; Cl, 31·7. $C_{17}H_7OCl_3$ requires C, 61·2; H, 2·1; Cl, 31·9%). On fusion with alcoholic potash it yields a dibenzanthrone which dyes cotton a red-violet shade from a clear blue vat.

*2′ : 4 : 8-Trichloro*meso*benzanthrone*, prepared from 1 : 5-dichloroanthrone (Barnett and Matthews, J., 1923, **123**, 2553), separated from benzene or xylene in yellow nodules, m. p. 190—191° (yield, 60%) (Found: C, 61·1; H, 2·4; Cl, 31·2%). Its solution in concentrated sulphuric acid was deep red with a brown fluorescence.

*2′ : 4- and 2′ : 5-Dichloro*meso*benzanthrones.* The required 4-chloroanthrone was prepared according to Barnett and Matthews's method (*loc. cit.*). The dark green reaction product (yield, 85%) was exhaustively extracted with boiling benzene, leaving a black residue (5%) which was not further examined. The combined extracts were concentrated; 2′ : 4-*dichloro*meso*benzanthrone* then separated and after recrystallisation from the same solvent was obtained in yellow-green needles, m. p. 203—204°. It dissolved in concentrated sulphuric acid to an intense orange-red solution with a yellow fluorescence (Found: C, 68·1; H, 2·5; Cl, 24·1. $C_{17}H_8OCl_2$

requires C, 68·2; H, 2·7; Cl, 23·7%). On oxidation with chromic acid in glacial acetic acid solution (Perkin and Spencer, *loc. cit.*) it yielded a chloroanthraquinonecarboxylic acid (pale yellow crystals, m. p. 231—232°), the methyl ester of which (yellow needles, m. p. 185—186°) showed no depression in m. p. when mixed with authentic methyl 4-chloroanthraquinone-1-carboxylate kindly supplied by Professor Simonsen.

Further concentration of the benzene mother-liquor from which the above benzanthrone had separated gave 2' : 5-*dichloro*meso*benzanthrone* in hard green nodules, m. p. 240°. Its solution in concentrated sulphuric acid was indistinguishable from that of the 2' : 4-isomeride (Found : C, 68·3; H, 2·8%). Chromic acid oxidation gave a chloroanthraquinonecarboxylic acid, separating from glacial acetic acid in yellow needles, m. p. 312—313°. The methyl ester (pale yellow needles, m. p. 183°) showed no depression when melted with authentic methyl 5-chloroanthraquinone-1-carboxylate (compare Cahn, Jones, and Simonsen, J., 1933, 444).

Bromomalondialdehyde from s.-*Dibromoethylene.*—*s*.-Dibromoethylene was condensed with chloroform in presence of aluminium chloride as described in the preparation of *s*.-pentachloropropane. The αγγ-trichloro-αβ-dibromopropane, obtained as a heavy colourless liquid, b. p. 130—133°/30 mm. (yield, 70% calc. on the dibromoethylene), was treated with alcoholic potassium hydroxide, giving the mixed chlorobromopropylenes, b. p. 195—202°. These (15 g.) were stirred for 16 hours at 30—40° with concentrated sulphuric acid (50 c.c.) and the mixture was diluted with water (200 c.c.) and cooled to 5°. The separated bromomaldondialdehyde was recrystallised from benzene, giving long needles (4·7 g.), m. p. 139—140°. Dieckmann and Platz (*Ber.*, 1904, **37**, 4638) give m. p. 140° (Found : C, 23·9; H, 2·0; Br, 52·9. Calc. for $C_3H_3O_2Br$: C, 24·1; H, 2·1; Br, 53·0%).

Owing to its appreciable solubility in water, only a partial isolation of the aldehyde is effected by the above method. The following modification was adopted for its complete isolation : The acid reaction mixture was diluted with ice-water (100 c.c.) and treated with a solution of aniline hydrochloride (9 g.) in water (200 c.c.); α-bromo-β-anilinoacraldehyde (10·5 g.) separated on standing. It crystallised from alcohol in long colourless needles, m. p. 162°, giving no depression on admixture with the compound, m. p. 164°, described by Beattie, Heilbron, and Irving (J., 1932, 260).

Condensation of the Chlorobromopropylenes with Anthrone.—The chlorobromopropylenes (6 g.) were hydrolysed as described above with concentrated sulphuric acid (36 g.), sulphur dioxide was then rapidly passed through the red-brown solution for 15 minutes, the temperature being simultaneously raised to 60°, and a solution of anthrone (5 g.) in concentrated sulphuric acid (20 g.) was added in four equal portions during 2 hours. After being maintained at 60° for a further 10 hours, the red solution was poured on ice and the precipitated dark green solid was collected and washed, first with hot dilute sodium hydroxide solution to remove sulphonation impurities, and then with water. The dried product was exhaustively extracted with boiling glacial acetic acid; when the combined extracts were concentrated, crude 1'-bromo*meso*benzanthrone separated. The pure compound crystallised from glacial acetic acid in golden-yellow plates, m. p. 174—175° (G.P. 193,959 gives the m. p. as 170°) (Found : C, 66·1; H, 3·1; Br, 25·7. Calc. for $C_{17}H_9OBr$: C, 66·0; H, 2·9; Br, 25·9%).

1'-*Cyano*meso*benzanthrone*.—The above bromobenzanthrone (2 g.) was refluxed in phenylacetonitrile solution (30 c.c.) with freshly prepared cuprous cyanide (1 g.) for 12 hours. After cooling, the separated solid was collected, washed with alcohol, repeatedly boiled with dilute nitric acid to remove copper salts, and dried. On recrystallisation, first from glacial acetic acid and finally from nitrobenzene, 1'-cyano*meso*benzanthrone was obtained in pale yellow needles, m. p. 242—243°, which dissolved in concentrated sulphuric acid to an intense orange solution with a characteristic yellow-green fluorescence.

2'-*Bromo*meso*benzanthrone*, prepared by the addition of *meso*benzanthrone-2'-diazonium sulphate to a solution of cuprous bromide in 15% hydrobromic acid solution according to the method given for 2'-chloro*meso*benzanthrone, separated from glacial acetic acid in bright yellow needles, m. p. 194—195°. Its solution in concentrated sulphuric acid was orange-red, like that of 2'-chloro*meso*benzanthrone (Found : C, 66·0; H, 3·0; Br, 26·1. $C_{17}H_9OBr$ requires C, 66·0; H, 2·9; Br, 25·9%). On alcoholic potash fusion a dibenzanthrone was produced, which dyed cotton a bluish-purple shade from a red-violet vat.

2'-*Cyano*meso*benzanthrone*.—A suspension of *meso*benzanthrone-2'-diazonium sulphate (prepared from 2'-amino*meso*benzanthrone, 24·5 g.) in water (150 c.c.) was added during one hour with rapid stirring to a solution of potassium cyanide (62·5 g.) and copper sulphate (57·5 g.) in water (400 c.c.), the temperature being maintained at 30—35°. After a further 3 hours, the temperature was slowly raised to 80° and the crude reaction product was collected and washed first with boiling dilute nitric acid and then with water. After repeated crystallisation from nitrobenzene, 2′-*cyano*meso*benzanthrone* was obtained in pale yellow needles, m. p. 285—286°; its solution in concentrated sulphuric acid was orange-yellow with an intense yellow fluorescence (Found: C, 84·2; H, 3·4. $C_{18}H_9ON$ requires C, 84·6; H, 3·5%).

meso*Benzanthrone-2′-carboxylic Acid.*—A solution of 2′-cyano*meso*benzanthrone (3 g.) in glacial acetic acid (60 c.c.) was refluxed for 16 hours with 50% sulphuric acid (48 c.c.). The reaction mixture, after cooling to 60°, was treated with sodium nitrite (1·5 g.) during one hour with rapid stirring, to decompose any amide. The carboxylic acid, precipitated with water and dried, crystallised from nitrobenzene in pale lemon-yellow needles, m. p. 341—342° (Schaarschmidt, *Ber.*, 1917, **50**, 294, gives m. p. 347°) (Found: C, 78·8; H, 3·8. Calc. for $C_{18}H_{10}O_3$: C, 78·8; H, 3·6%). The *ethyl* ester prepared by passing dry hydrogen chloride into a boiling suspension of the acid in absolute alcohol for 12 hours, separated from the same solvent in long yellow needles, m. p. 172—173° (Found: C, 79·2; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·6%).

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