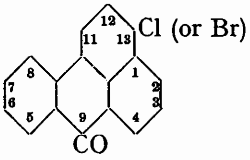
272. *Nitration of the* 13-*Halogenobenzanthrones.*

By Frank H. Day.

The nitro-compounds which separate readily when nitrobenzene solutions of 13-chloro- and 13-bromo-benzanthrones are treated with nitric acid are mononitro-compounds and are shown to be 13-halogeno-6-nitrobenzanthrones. There is no evidence that nitration occurs in the *Bz*-nucleus.

The formation of nitro-compounds from 13-chloro- and 13-bromo-benzanthrones has been described in B.P. 254,742 (I.G.F.A.), 326,140 (I.G.F.A.), 256,281 (R. Fraser Thomson, Thomas and Scottish Dyes, Ltd.), and G.P. 516,535 (Scottish Dyes, Ltd.). The orientation of the compounds is not stated, but the claim is made that they give nitroanthraquinonecarboxylic acids on oxidation, and B.P. 254,742 suggests position 6 as the probable one for the nitro-group. On the other hand Nakanishi [*Sci. Papers Inst. Phys. Chem. Res.*, **16**, Nr. 328, 9; *Bull. Inst. Phys. Chem. Res.* (abstracts), *Tokyo*, **10**, 79—81 (*British Chem. Abs.*, 1931, *A*, 1419)] describes a monobromomononitrobenzanthrone which it is claimed cannot be oxidised but is reducible to an amine, oxidation of which leads to anthraquinone-1-carboxylic acid and anthraquinone, and on this unsatisfactory evidence it is claimed that nitration has occurred in the *Bz*-nucleus.



The author has confirmed the preparations and obtained from 13-chloro- and 13-bromo-benzanthrones by nitration in nitrobenzene solution well-characterised nitro-compounds, the melting points of which agree well with those given in the patent literature, *viz.*, 289—290° and 297—298° respectively. Both of these substances when oxidised by Perkin's method give the same nitroanthraquinone-1-carboxylic acid, m. p. 277—278°, the properties of which are not those of an α-nitroanthraquinone; the orientation of the two 13-halogenonitrobenzanthrones is therefore the same and it suffices to determine the position of the nitro-group in one of them.

Reduction of the 13-chloronitrobenzanthrone (compare G.P. 516,535) readily gave the amine, which after diazotisation was converted by the usual Sandmeyer method into a dichlorobenzanthrone, m. p. 267—268°, agreeing with that of 6 : 13-dichlorobenzanthrone (Cahn, Jones, and Simonsen, J., 1933, 445). Oxidation of this dichlorobenzanthrone gave a chloroanthraquinone-1-carboxylic acid, m. p. 305—306°, not depressed by authentic 6-chloroanthraquinone-1-carboxylic acid.

Experimental.

13-*Chloro*-6-*nitrobenzanthrone.*—Into 53 g. of 13-chlorobenzanthrone (m. p. 184°; obtained by twice crystallising the technical product from nitrobenzene) in 300 g. of nitrobenzene at 90—100°, 19 g. of nitric acid (98%) were stirred in during 1 hour. The mixture was heated on the water-bath for an hour and cooled and the crystals were collected, washed with benzene and ethanol, dried, and recrystallised from nitrobenzene, giving 37 g. of 13-chloro-6-nitrobenzanthrone in bright yellow needles, m. p. 286°.

13-Chlorobenzanthrone was recovered unchanged after attempted nitration in acetic acid.

13-*Bromo*-6-*nitrobenzanthrone.*—13-Bromobenzanthrone (30 g.) was added to 150 g. of nitrobenzene and dissolved by warming and then treated with 98% nitric acid (25 g.) with stirring, the whole operation being carried out at 50° during 1 hour and the temperature then maintained for a further hour. The nitro-compound, which separated readily, was washed with benzene and ethanol, dried (yield 22 g., m. p. 292°), and recrystallised from nitrobenzene, forming bright yellow needles, m. p. 298°.

Oxidation of the Halogenonitrobenzanthrones.—The substance was boiled with acetic acid (20 parts), and chromium trioxide (2½ parts) in acetic acid and water run in. Bromine was evolved from the bromo-compound. The solution was boiled for 1 hour, sulphuric acid added, and most of the acetic acid removed by distillation; on cooling, 6-nitroanthraquinone-1-carboxylic acid crystallised. This was reprecipitated from sodium carbonate solution with hydrochloric acid and recrystallised from acetic acid (yield, *ca.* 40%), forming pale yellow needles, m. p. 277—278° (Found: C, 60·85; H, 2·2; N, 4·55. Calc. for $C_{15}H_7O_6N$: C, 60·6; H, 2·35; N, 4·7%). The acid was reduced by alkaline hyposulphite, giving a reddish-brown aminocarboxylic acid, m. p. 246—248° (Pritchard and Simonsen, J., 1938, 2049, give m. p. 247—249° for 6-aminoanthraquinone-1-carboxylic acid).

13-*Chloro*-6-*aminobenzanthrone.*—13-Chloro-6-nitrobenzanthrone (25 g.) was added to aniline (200 g.) at 100°, aniline hydrochloride (75 g.) introduced, the temperature raised to 120°, and zinc dust (15 g.) added during ½ hour with rapid stirring; the dark red solution was finally heated at 140° for ¼ hour. The amine which separated on cooling was washed with dilute hydrochloric acid, dried, and recrystallised from nitrobenzene, giving 13-chloro-6-aminobenzanthrone (15 g.) in fine, dark red needles with a marked yellowish-brown reflex, m. p. 280—281°. Its solution in concentrated sulphuric acid was red with a brownish fluorescence; dilution precipitated a fairly stable, olive-green sulphate, which required dilute alkali to reconvert it into the base. Concentrated hydrochloric acid gave a yellowish-white hydrochloride, which after diazotisation coupled with naphthols to give rose-pink azo-dyes.

6 : 13-*Dichlorobenzanthrone.*—13-Chloro-6-aminobenzanthrone (5 g.) in 120 c.c. of concentrated hydrochloric acid was stirred and diazotised with sodium nitrite (1 g.) at room temperature. After 15 minutes, the mixture was treated with cuprous chloride (12 g.) in hydrochloric acid (50 c.c.), gradually heated to 100°, diluted with water (200 c.c.), and heated on the water-bath for ½ hour. The precipitated dichlorobenzanthrone was boiled with dilute sodium hydroxide solution, dried, and crystallised from nitrobenzene, forming yellow plates (4·7 g.), m. p. 267—268° (Found: C, 67·75; H, 2·65; Cl, 23·1. Calc. for $C_{17}H_8OCl_2$: C, 68·2; H, 2·7; Cl, 23·7%).

6-*Chloroanthraquinone*-1-*carboxylic Acid.*—6 : 13-Dichlorobenzanthrone (4 g.) was oxidised by Perkin's method with chromium trioxide (20 g.). The product crystallised from acetic acid in pale yellow needles (2 g.), m. p. 305—306°, not depressed by authentic 6-chloroanthraquinone-1-carboxylic acid (Found: C, 62·7; H, 2·3; Cl, 12·1. Calc. for $C_{15}H_7O_4Cl$: C, 62·8; H, 2·45; Cl, 12·4%).

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