Vat Dyes of Acenaphthene Series. V. Constitution of Dibromoanthanthrone (Indanthrene Brilliant Orange RK).[1]

By Toshio MAKI and Harukichi HASHIMOTO

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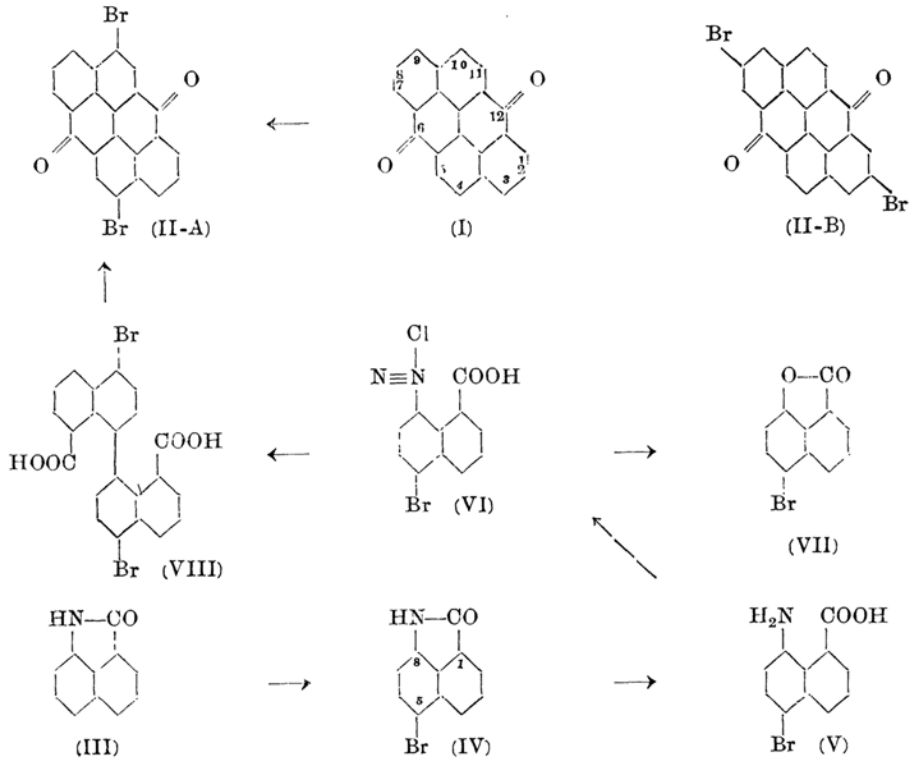
A brilliant reddish orange vat dye of excellent fastness (light 7～8), commercially known as Indanthrene Brilliant Orange RK, has been obtained by direct bromination of anthanthrone. Among various methods of bromination it has been acknowledged in our laboratory that only the bromination in oleum (about 8% SO_3) in the presence of a little iodine gives the best result by the application of the least amount of bromine.[2] The crude product, however, contains a small quantity of orange brown impurity and, according to our experiment, the purification can be most effectively carried out by using 92～94% sulfuric acid, in which the pure reddish orange dibromoanthanthrone is insoluble.

The constitution of the dibromoanthanthrone was hitherto not at all experimentally determined and only by assumption 4, 10-dibromo formula (II-A) has usually been suggested,[3] but sometimes the other 2, 8-dibromo structure

(1) Read before the 5th Annual Meeting of the Chemical Society of Japan on April 5, 1952.

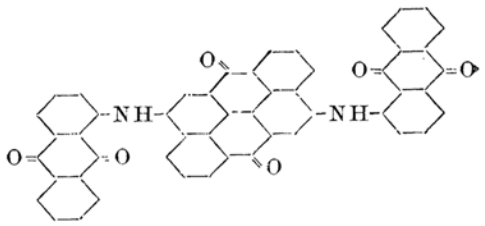
(2) G. P. 478738, *Frdl.* **16**, 1417; See also PB 84316-3471, *FIAT* **1313**, Vol. II, 90.

(3) Rowe, "The Development of the Chemistry of Commercial Synthetic Dyes (1856～1938), 87; PB 84316-3471.

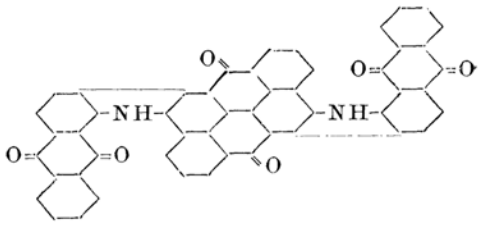


(II-B) is also adopted.[4]

We have now brominated naphthostyril (III) in acetic acid solution and found that the product is 5-bromonaphthostyril (IV) (m.p. 257°), which had been obtained by Eckstrand[5] from 5-bromo-8-nitro-1-naphthoic acid by reduction. The constitution of the bromonaphthostyril was further confirmed by converting it, after hydrolyzing the styril ring, into 5-bromo-8-hydroxy-1-naphthoic acid lactone (VII) (m. p. 193°) by diazotization and heating with dilute sulfuric acid. From this 5-bromonaphthostyril (IV) we have synthesized 4, 10-dibromoanthanthrone (II-A) via dibromodinaphthyl-dicarboxylic acid (VIII) by application of the diazo reaction and ring formation in conc. sulfuric acid analogous to the synthesis of anthanthrone from naphthostyril.[6] Our method of applying an ammoniacal solution of reduced copper sulfate and precipitated metallic copper was also useful for this diazo reaction.



(IX)



(X)

4, 10-Dibromoanthanthrone (II-A) thus synthesized is completely identical with the brilliant reddish orange dibromoanthanthrone (Indanthrene Brilliant Orange RK), which had been obtained by the direct bromination of anthanthrone. They are identical not only in their dyeings and color reactions, but in all other chemical reactivity and condensation products, for example in the formation of gravish violet di-α-anthraquinonyl-diimide

(4) *FIAT* **1313**, Vol. II, 89.
(5) Eckstrand, *J. prakt. Chem.* [2] **38**, 173, 281 (1888); *Ber.* **19**, 1136, 1139 (1886).
(6) T. Maki, H. Hashimoto and K. Kamada, *J. Chem. Soc. Japan, Ind. Chem. Section*, **55**, 483 (1952); See also PB 84316-3480; *FIAT* **1313**, Vol. II, 90.

(IX) and olive gray biscarbazole derivative (X).

Thus, as in the case of benzanthrone[7] the diphenyl residue in the molecule of anthanthrone is also found to be reactive to halogenation and in the present case p-and p'-position to the centre union are brominated. Indanthrene Brilliant Orange GK must similarly has 4, 10-dichloro structure. The formula (II-B) given in FIAT[4] is improbable as the constitution of Indanthrene Brilliant Orange RK, but may be rather that of the orange brown isomeric dibromoanthanthrone, which has been found by us as an impurity of the bromination and soluble in 90% sulfuric acid.

Experimental Part

Direct Bromination of Anthanthrone.—Anthanthrone (1.50 g., 1 mol. ratio)[6] was dissolved in 45 g. of oleum (8% SO_3) with 0.075 g. of iodine and 1.10 g. (2.8 atomic ratio, 70% of the apparent theory) of bromine was dropped down with stirring in about 30 min. at room temperature. It was then heated to 60° and kept at this temperature for 5 hours. The product was poured into ice water, the precipitate was collected, treated with 500 cc. of 1% aqueous sodium bisulfite, 500 cc. of 1% aqueous sodium carbonate and after acidification with dilute hydrochloric acid washed thoroughly with cold water. The yield of the crude product, a dark red orange powder, was 2.20 g. (96.8% of the theory). Found. Br, 38.40; calcd. for $C_{22}H_8O_2Br_2$ (II-A): Br, 34.44%. The crude dibromoanthanthrone (1 part), as a fine powder, was heated with 30 parts of 92% sulfuric acid on a water bath for 30 min. and allowed to stand over-night at room temperature. The black brown insoluble part was collected on a glass filter and when this was carried into water a brilliant red orange precipitate resulted, which was filtered and washed neutral. The yield was 72% of the crude product, corresponding to 69.7% of the theory from anthanthrone. Found: Br, 33.95; calcd. for $C_{22}H_8O_2Br_2$ (II-A): Br, 34.44%. Clear red orange powder, soluble in conc. sulfuric acid with clear green color. Hydrosulfite vat (IK) is violet red, from which brilliant reddish orange cotton dyeing is obtained. The shade of the dyeing is quite identical with that of the commercial Indanthrene Brilliant Orange RK[8].

In the above purification the concentration of sulfuric acid has unusually sensitive effect both on the yield of dye and on the shade of dyeing. Thus, the similar treatment with 94% sulfuric acid gives dibromoanthanthrone of the highest purity as the insoluble part, whose cotton dyeing is more clear and brilliant than that of the commercial dye, but the yield of the purification was 62% of the crude product. A dye almost identical with the commercial product, but of rather slightly yellowish shade, is obtained using 90% sulfuric acid in 84% yield of the crude product.

The part soluble in 90% sulfuric acid was obtained as a dark brown powder when the acid filtrate was poured into water. Its amount was ca. 14% of the crude dibromoanthanthrone. It dyes cotton in orange brown from a violet red hydrosulfite vat (IK); The solution in conc. sulfuric acid is dark green. This substance is a hitherto unknown impurity and our analysis indicates that it is an isomer of dibromoanthanthrone. We suggest the formula (II-B) as its probable constitution taking into consideration the reactivity of the remaining diphenyl residues in the molecule. Found: Br, 31.74; calcd. for $C_{22}H_8O_2Br_2$ (II-B): Br, 34.44%.

5-Bromonaphthostyril (IV).—To the solution of 5.08 g. (1 mol. ratio) of naphthostyril[6] in 51 g. of glacial acetic acid 4.55 g. (1.9 atomic ratio, 95% of the theory) of bromine, dissolved in 23 g. of glacial acetic acid, was added dropwise at 25° in 3 hours and agitated further 4 hours at the same temperature. After standing over-night the crystalline precipitate was collected and washed with water. Its yield was 6.19 g. (83.2% of the theory), m. p. 250.5~257.5° (corr.). By recrystallization from 10 parts of glacial acetic acid greenish yellow needles melting at 256.5~260.5° (corr.) were obtained. The yield was 76% of the crude product. Found: Br, 31.99; calcd. for $C_{11}H_6ONBr$ (IV): Br, 32.22%. This is identical with the 5-bromonaphthostyril (m. p. 257°) obtained by Eckstrand[5] from 5-bromo-8-nitro-1-naphthoic acid by reduction.

Conversion of Bromonaphthostyril into 5-Bromo-8-hydroxy-1-naphthoic Acid Lactone (VII).—The bromonaphthostyril (2,48 g. 1 mol. ratio), which had been obtained by the bromination of naphthostyril, was dissolved in 15 g. of 10% aqueous sodium hydroxide by heating on a water bath and diluted with 20 cc. of water. After ice cooling 0.69 g. of sodium nitrite (1 mol. ratio), dissolved in 4 cc. of water, was added to the solution and diazotized at 0° by giving 17 cc. of ice cooled 4 N hydrochloric acid and stirring further 20 min. The diazo solution was slowly poured into 100 g. of hot 20% sulfuric acid on a boiling water bath. The evolution of nitrogen gas ceased in ca. 20 min. and the color of the precipitate changed into yellow from brown. The heating was continued for further 30 min., then it was allowed to cool and the precipitate collected. Light brown powder of m.p. 182~187° (corr.), the yield was 2.24 g. or 89.9% of the theory. After crystallizing from 10 parts of glacial acetic acid 1.72 g. (76.8% of the crude product) of light brown needles melting at 191° (corr.) were obtained. By further recrystallization a sample of constant m. p. 193° (corr.) was obtained. Found: Br, 31.82; calcd. for $C_{11}H_5O_2Br$ (VII): Br 32.09%.

(7) T. Maki and Y. Nagai, *J. Soc. Chem. Ind. Japan, Suppl.* **38**, 491 B (1935); T. Maki, and T. Aoyama, *J. Soc. Chem. Ind. Japan, Suppl.* **38**, 636 B (1935); T. Maki and Y. Nagai, *Ber.* **70**, 1837 (1937); T. Maki and A. Kikuchi, *Ber.* **71**, 2031, 2036 (1938); T. Maki and A. Kikuchi, *J. Soc. Chem. Ind. Japan*, **50**, 141 (1947).

(8) The dyestuff content of the commercial Indanthrene Brilliant Orange RK (I. G.) was 75.6% and actual bromine content of this dyestuff was found to be 32.25%.

This substance was identical with 5-bromo-8-hydroxy-1-naphthoic acid lactone of Eckstrand[5] (m. p. 192°).

Synthesis of 4, 10-Dibromoanthanthrone (II-A) from 5-Bromonaphthostyril. — Two mol. ratio (5.0 g.) of copper sulfate ($CuSO_4 \cdot 5H_2O$) was dissolved in 20 cc. of water, 24 g. of 25% aqueous ammonia added and the solution was completely (rather to a faintly red color) decolorized by introduction of sulfur dioxide under ice cooling. To this solution of cuprous oxide complex, 10 g. of 25% aqueous ammonia and freshly precipitated metallic copper paste (1 mol. ratio)[9] were added.

5-Bromonaphthostyril (2.48 g., 1 mol. ratio), dissolved in 15 g. of 10% aqueous sodium hydroxide, was diazotized using 0.69 g. of sodium nitrite and 17 cc. of 4 N hydrochloric acid at 0° for 20 min., as in the case of the lactone (VII), and cooled to −5°. The diazo solution was poured into the copper solution at −5°, stirred at this temperature for 1 hour, allowed to rise in 2 hours to 20° and then stirred further 2 hours at 20°. After standing over-night the solution was filtered and dibromodinaphthyldicarboxylic acid (VIII) was precipitated from the filtrate with hydrochloric acid. Yield of a light brown powder was 1.69 g. This was dissolved without purification in 17 g. of conc. sulfuric acid, kept in a boiling water bath for 1 hour and after cooling poured into ice water. The precipitate was collected, washed neutral and heated with 300 cc. of 5% aqueous sodium carbonate in order to remove carbonate soluble impurities. The yield of dibromoanthanthrone, a dark red orange powder, was 1.41 g. or 60.8% of the theory. Further purification was carried out by heating 1 part of the finely powdered crude product with 30 parts of 92% sulfuric acid 30 min. in a boiling water bath and allowing to cool, when pure 4, 10-dibromoanthanthrone (II-A) was obtained as an insoluble precipitate. The Yield was 1.24 g. or 87.9% of the crude product. Found: Br, 33.94; calcd. for $C_{22}H_8O_2Br_2$ (II-A): Br, 34.44%.

It is a clear reddish orange powder, soluble in conc. sulfuric acid with clear green color and brilliant reddish orange cotton dyeing is obtained from a violet red hydrosulfite vat (IK). This synthetic 4, 10-dibromo compound is completely identical with the direct brominated dibromoanthanthrone in dyeings and all color reactions.

Condensation of Dibromoanthanthrone with 1-Aminoanthraquinone.[10]—One mol. ratio (1.00 g.) of the synthetic dibromoanthanthrone (Br, 33.94%), 2 mol. ratio (0.962 g.) of 1-aminoanthraquinone, 0.4 mol. ratio (0.069 g.) of precipitated cupric oxide and 2 mol. ratio (0.457 g.) of anhydrous sodium carbonate were boiled with 29.4 g. of nitrobenzene under reflux and stirring for 3 hours. Alcohol (15 g.) was added at 70° and after agitated for 30 min. the product was allowed to stand over-night. The precipitate was collected, washed with alcohol, heated with 200 cc. of dilute hydrochloric acid (1: 50) for 30 min. in a water bath, filtered and thoroughly washed with hot water. Yield was 1.534 g (94.1% of the theory). Violet gray powder, hardly soluble in organic solvents, soluble in conc. sulfuric acid with blue green color, from which violet precipitate separated by adding water. It dyes cotton grayish violet from a violet red vat (IK). The substance is completely free from bromine. Found: N, 3.49; calcd. for $C_{50}H_{24}O_6N_2$ (IX): N, 3.74%.

Dibromoanthanthrone (Br, 33.65%) obtained by the direct bromination of anthanthrone gave also quite the same di-α-anthraquinonyl-diimide (IX) both in yield and properties. Found: N, 3.57; calcd. for $C_{50}H_{24}O_6N_2$ (IX): N, 3.74%.

The carbazolation to the substance (X) was carried out by heating 1.00 g. of the diimide (IX) with 8.0 g. of anhydrous aluminium chloride and 2.0 g. of dry sodium chloride at 180° (oil bath temperature) for 6 hours and treating as usual with water and hydrochloric acid. The yield of the crude product was 1.00 g. It was then, as a dry fine powder, agitated with 10 cc. of 3.7% sodium hypochlorite solution and 5 cc. of water 1 hour at room temperature and 3 hours under reflux on a boiling water bath. The precipitate was collected, acidified with hydrochloric acid and then washed neutral. Yield was 0.94 g. Black powder, hardly soluble in organic solvents, soluble in conc. sulfuric acid with yellowish green black color, from which yellowish green black precipitate separated by the addition of water. Hydrosulfite vat (IK) is dark violet red and cotton is dyed in olive gray shade. Found: N, 3.71; calcd. for $C_{50}H_{26}O_6N_2$ (X): N, 3.76%.

The direct brominated dibromoanthanthrone gave also via the above diimide quite the same biscarbazole derivative (X) both in yield and properties. Found: N, 3.82; calcd. for $C_{50}H_{26}O_6N_2$ (X): N, 3.76%.

Dyestuffs Research Laboratory, Department of Applied Chemistry, Tokyo University, Tokyo

(9) Prepared from 2.5 g. of copper sulfate in 16 cc. of water by the addition of 0.03 cc. of turkey red oil and then 0.78 g. of zinc dust followed by decantation and washing.

(10) Compare with G. P. 485961, 487023, *Frdl.* **16**, 1422, 1424.