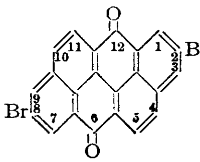
773. *Chemistry of Anthanthrone. Part II.* Rearrangement and Elimination Reactions in the Action of Potassium Hydroxide on Two Dibromoanthanthrones.*

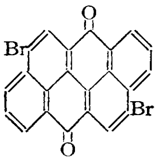
By William Bradley and Jeffrey Waller.

Direct bromination of anthanthrone affords the 4 : 10-derivative identical with the compound derived by ring synthesis. Though stable towards aniline the substituents of 2 : 8- and 4 : 10-dibromoanthanthrone are replaceable by morpholine. Potassium hydroxide converts both dibromo-compounds into 3 : 9-dihydroxyanthanthrone; the formation of anthanthrone and 4 : 10-dihydroxyanthanthrone has also been observed. The mechanism of the replacement, elimination, and rearrangement reactions is discussed.

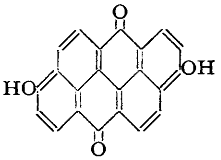
According to F.I.A.T. Final Report, 1313, Vol. II, pp. 89, 90, the bromination of anthanthrone in oleum containing iodine yields the 2 : 8-dibromo-derivative (I). Beilstein's " Handbuch," Vol. VII, 2nd Ergänzungsband, p. 784, and Corbellini and Atti (*Chim. e Ind.*, 1936, **18**, 295), however, represent the product of direct bromination as the 4 : 10-derivative (II), although apparently without proof. In the present experiments the procedure of F.I.A.T. 1313 was repeated and the product was purified through the oxonium sulphate and regenerated by addition to water. It showed the same absorption spectrum in sulphuric acid as authentic 4 : 10-dibromoanthanthrone prepared by cyclisation of 4 : 4'-dibromo-1 : 1'-dinaphthyl-8 : 8'-dicarboxylic acid (Rule and Smith, *J.*, 1937, 1096). 2 : 8-Dibromoanthanthrone, prepared by cyclisation of 6 : 6'-dibromo-1 : 1'-dinaphthyl-2 : 2'-dicarboxylic acid (Rule and Smith, *loc. cit.*), exhibited a closely related, yet different, spectrum. Both 2 : 8- and 4 : 10-dibromoanthanthrone dissolve in pyridine with a yellow colour changed to green on the addition of methanolic potassium hydroxide. The colour change is probably the result of combination of alkali hydroxide with the carbonyl groups, as with benzil (Scheuing, *Ber.*, 1923, **56**, 252), since addition to water reverses the change. Anthanthrone, 3 : 9-dimethoxyanthanthrone (III; OMe for OH), and the tetrachloroanthanthrone obtained by the action of phosphorus pentachloride on 3 : 9-dihydroxyanthanthrone (III), also show a colour change with alkali. On the other hand 4 : 10-dimorpholinoanthanthrone (II; $\cdot\mathrm{NC_4H_8O}$ for Br) does not, probably because basic substituents diminish the unsaturation of carbonyl groups in a conjugated system. 3 : 9-Dihydroxyanthanthrone, which is strongly acidic, affords a red-violet solution in pyridine unchanged by the addition of alkali. 3 : 9-Diacetoxyanthanthrone (III; OAc for OH) is hydrolysed by the alkaline reagent; the change in colour from yellow to red-violet is not reversed on the addition of water.



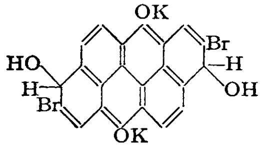
(I)



(II)



(III)



(IV)

2 : 8-Dibromoanthanthrone was unaffected when heated with aniline, but morpholine caused replacement, a violet product resulting. 4 : 10-Dibromoanthanthrone behaved similarly; morpholine afforded the violet 4 : 10-dimorpholinoanthanthrone (II; $\cdot\mathrm{NC_4H_8O}$ for Br).

2 : 8-Dibromoanthanthrone reacted easily with potassium hydroxide at 170—200°. The main product was 3 : 9-dihydroxyanthanthrone (III), identified by methylation to 3 : 9-dimethoxyanthanthrone and comparison with an authentic sample prepared by cyclising 5 : 5'-dimethoxy-1 : 1'-dinaphthyl-8 : 8'-dicarboxylic acid.

4 : 10-Dibromoanthanthrone was stable towards sodium methoxide in refluxing

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* Part I, preceding paper.

methanol and sodium ethoxide in ethanol. Heating with potassium hydroxide at 170—200° caused elimination of the halogen: the main product was 3 : 9-dihydroxyanthanthrone, identified by methylation to the dimethyl derivative and comparison with an authentic sample; in addition, anthanthrone was formed, and a phenol which showed the reactions of 4 : 10-dihydroxyanthanthrone.

The conversion of both 2 : 8- and 4 : 10-dibromoanthanthrone into 3 : 9-dihydroxyanthanthrone by hot alkali recalls the well-known conversion of benzene-*p*-disulphonic acid and *p*-chloro- and *p*-bromo-phenol into resorcinol in similar circumstances, and the change of *o*- and *p*-chlorotoluene into *m*-cresol reported by Meharg and Allen (*J. Amer. Chem. Soc.*, 1932, **54**, 5920) and Shreve and Marsel (*Ind. Eng. Chem.*, 1946, **38**, 354). With the dibromoanthanthrones the change probably originates in the attack of hydroxyl ions at the 3 : 9-positions which are *para* to carbonyl groups. With the 2 : 8-compound the intermediate (IV) would be expected, and finally (III) by loss of potassium bromide and rearrangement.

The suggested mechanism of elimination of the 2-bromo-substituent harmonizes with that advanced for the elimination of 2-aminoanthraquinone from reduced 2-amino-1 : 2'-dianthraquinonylamine (Bradley, Leete, and Stephens, *J.*, 1951, 2158), of the chloro-substituents from reduced 3 : 3'-dichloroindanthrone (Bradley and Nursten, *J.*, 1952, 3027), and of a 2-sulpho-substituent from reduced 1 : 5-diamino-4 : 8-dihydroxyanthraquinone-2 : 6-disulphonic acid (G.P. 108,578, 110,880).

With amyl-alcoholic potassium hydroxide 4 : 10-dibromoanthanthrone gave anthanthrone in addition to a hydroxy-compound which differed from 3 : 9-dihydroxyanthanthrone and had the recorded properties of 4 : 10-dihydroxyanthanthrone, the normal product of hydrolysis. The formation of anthanthrone can be explained as occurring by reduction of the dibromo-compound to the dihydro-form by the alcoholic alkali, followed by elimination of hydrogen bromide and repetition of the reduction and elimination reactions. Anthanthrone was formed in small amount, however, when the alcohol was absent. It is probable that in this instance the same reduction and elimination processes occurred but that the reduction was effected by transfer of hydrogen from an intermediate analogous to (IV) but derived from 4 : 10-dibromoanthanthrone. Mention should be made in this connection of Goldstein and Gardner's observation (*J. Amer. Chem. Soc.*, 1934, **56**, 2131) that the reduced forms of halogenoanthraquinones undergo dehalogenation on exposure to light.

During this work the relative rates of diffusion of the reduced forms of anthanthrone and its derivatives were studied by means of the device described by Brown (*Nature*, 1939, **143**, 377). The several compounds were dissolved in alkaline sodium dithionite, and the solutions poured into the central hole of the cover plate. Diffusion occurred and the addition of further alkaline dithionite led to the separation of bands. The ratio (R_F) of the distances travelled by the concentric rings of solvent-front and solution was determined. White blotting paper was used as the substrate. Clear separations of mixtures were generally obtained and the following values of R_F are typical: anthanthrone 0·25; 2 : 8- 0·1, and 4 : 10-dibromoanthanthrone 0·1; 3 : 9- 0·4, and 4 : 10-dihydroxyanthanthrone 0·4; 3 : 9-dimethoxyanthanthrone 0·2. In practice the values obtained in particular experiments depended in some degree on the concentration of salts.

EXPERIMENTAL

4 : 10-*Dibromoanthanthrone*.—(*a*) This compound was synthesised from naphthalic anhydride by way of 8-hydroxymercuri-1-naphthoic acid (Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1831), 8-bromo-1-naphthoic acid (Rule, Purcell, and Brown, *J.*, 1934, 170), 5 : 8-dibromo-1-naphthoic acid and its methyl ester, and dimethyl 4 : 4'-dibromo-1 : 1'-dinaphthyl-8 : 8'-dicarboxylate (for cyclisation see Rule and Smith, *loc. cit.*).

4 : 10-Dibromoanthanthrone crystallised from nitrobenzene in red needles, m. p. >360° (Found: C, 56·6; H, 2·0; Br, 34·1. Calc. for $C_{22}H_8O_2Br_2$: C, 56·9; H, 1·7; Br, 34·5%). Sublimation at low pressure from a bath at 350° gave a single red zone. The dibromo-compound dissolved in concentrated sulphuric acid with a green colour [absorption maxima at 345 (*E* 34,400), 460 (*E* 13,000) and 745 (*E* 10,700)]. It dissolved in alkaline sodium dithionite with a blue-violet colour, and the solution when absorbed on cellulose, gave a single blue zone changed

to reddish-orange on aeration. It was recovered unchanged after being heated at the b. p., for 12 hr. with aniline, for 24 hr. with 20% methyl-alcoholic potassium hydroxide, or for 10 hr. with a solution of sodium (5 g.) in methanol (50 c.c.).

(*b*) 1 : 1′-Dinaphthyl-8 : 8′-dicarboxylic acid was dissolved in concentrated sulphuric acid, and the resulting anthanthrone was further brominated by the method of F.I.A.T. Final Report, No. 1313, Vol. II, p. 90. The product, purified from concentrated sulphuric acid and crystallised from nitrobenzene, formed lustrous, red needles, m. p. >360° (Found: Br, 34·2. Calc. for $C_{22}H_8O_2Br_2$: Br, 34·5%). The green solution in concentrated sulphuric acid exhibited light absorption maxima at 345 (*E* 34,000), 460 (*E* 13,000), and 745 mμ (*E* 10,300).

4 : 10-*Dimorpholinoanthanthrone*.—A suspension of 4: 10-dibromoanthanthrone [1 g.; prep. (*a*)] in morpholine (25 c.c.) was heated under reflux for 6 hr. The solution which had changed in colour from yellow to red-violet was added to water. The resulting tarry precipitate was collected, dried, and crystallised from chlorobenzene. 4 : 10-*Dimorpholinoanthanthrone* was obtained as a violet powder which dissolved in concentrated sulphuric acid to a violet solution which showed light absorption maxima at 500 (*E* 23,800), 565 (*E* 12,800), and 620 mμ (*E* 18,100) (Found: C, 76·0; H, 5·1; N, 5·5. $C_{30}H_{24}O_4N_2$ requires C, 75·6; H, 5·1; N, 5·9%). The violet solution in pyridine remained almost unchanged on the addition of methanolic potassium hydroxide.

A parallel experiment with 4 : 10-dibromoanthanthrone from prep. (*b*) gave similar material with absorption maxima at 500, 565, and 620 mμ. The compound dissolved with a blue-violet colour in alkaline sodium dithionite.

Action of Amyl-alcoholic Potassium Hydroxide on 4 : 10-*Dibromoanthanthrone*.—4 : 10-Dibromoanthanthrone (4 g.) was heated under reflux for 24 hr. with a solution of potassium hydroxide (20 g.) in amyl alcohol (400 c.c.). The resulting blue solution was added to water, and the amyl alcohol was distilled off in steam. A brown solid remained. This was collected and extracted with water. A green solution was obtained and this gave a reddish-brown precipitate on acidification. Though soluble in dilute sodium hydroxide the product was insoluble in more concentrated alkali. It dissolved in alkaline dithionite, forming a violet solution. The red-violet solution in pyridine became green on the addition of 30% methanolic potassium hydroxide, unaltered on the further addition of water. It sublimed under reduced pressure from a bath at 350°, forming a single brown zone. The compound dissolved in concentrated sulphuric acid, forming a green solution [light absorption maxima: 343 (*E* 34,200), 450 (*E* 15,100), and 815 mμ (*E* 8300) (Found: C, 80·1; H, 2·7. $C_{22}H_{10}O_3$ requires C, 82·0; H, 3·1. $C_{22}H_{10}O_4$ requires C, 78·1; H, 3·0%).

Part of the original reaction product which was insoluble in sodium hydroxide was dissolved in alkaline dithionite solution and chromatographed on cellulose; one band gave anthanthrone on aeration. Another portion was sublimed *in vacuo*. Two bands resulted of which the more volatile exhibited the reactions and absorption spectrum of anthanthrone; the lower band contained a bromo-compound.

Action of Potassium Hydroxide on 4 : 10-*Dibromoanthanthrone*.—4 : 10-Dibromoanthanthrone (10 g.) was added during 15 min. to potassium hydroxide (100 g.) and water (10 c.c.) at 170°. The temperature was raised to 200° and the whole was stirred for 2 hr. The violet product was added to water (500 c.c.), and the suspension was aerated and then filtered. The residue was extracted twice with hot water (300 c.c.) and finally with 1% potassium hydroxide. The combined extracts were acidified with hydrochloric acid, and the precipitate (2·4 g.) was collected. A portion of this product was dissolved in alkaline sodium dithionite, the reduction product was chromatographed on cellulose, and the resulting bands were aerated. The main constituent was a red-violet compound, but a trace of a green product was present also which gave the reactions of 4 : 10-dihydroxyanthanthrone.

The unseparated mixture of hydroxy-compounds was methylated in *o*-dichlorobenzene with methyl toluene-*p*-sulphonate and potassium carbonate (see methylation of 3 : 9-dihydroxyanthanthrone, preceding paper, p. 3781). The violet product, crystallised from *o*-dichlorobenzene and then sublimed *in vacuo* from a bath at 350°, gave an orange-red compound identical with authentic 3 : 9-dimethoxyanthanthrone [light absorption in concentrated sulphuric acid: max. at 340 (*E* 31,200), 380 (*E* 16,800), 451 (*E* 21,700), 475 (*E* 33,600), 570 (*E* 14,700), and 620 mμ (*E* = 20,700)].

2 : 8-*Dibromoanthanthrone*.—Prepared from 1 : 6-dibromo-2-naphthylamine by Rule and Smith's method (*J.*, 1937, 1096) (Found: C, 56·6; H, 1·9; Br, 33·8. Calc. for $C_{22}H_8O_2Br_2$: C, 56·9; H, 1·7; Br, 34·5%), this sublimed *in vacuo* from a bath at 350° to give a single orange zone. It gave a yellow solution in pyridine, changed to green on the addition of a drop of 30% methanolic

potassium hydroxide. It formed a green solution in concentrated sulphuric acid and dissolved in alkaline sodium dithionite with a blue-violet colour. It was recovered unaltered after 12 hours heating with aniline at the b. p.

When 2 : 8-bromoanthanthrone (0·5 g.) was heated under reflux for 6 hr. with morpholine (25 c.c.) and then added to water a dark precipitate was formed and this separated from chlorobenzene as a violet, crystalline powder. It formed a red-violet solution in concentrated sulphuric acid which did not exhibit any marked maximum light absorption. The red-brown solution in pyridine became green on the addition of methanolic potassium hydroxide. In the presence of a small volume of pyridine it dissolved in alkaline sodium dithionite, forming a blue solution.

Fusion of 2 : 8-*Dibromoanthanthrone with Potassium Hydroxide. Formation of* 3 : 9-*Dimethoxyanthanthrone*.—2 : 8-Dibromoanthanthrone (5 g.) was added to potassium hydroxide (50 g.) and water (5 c.c.) at 170°, and then the mixture was stirred at 200° for 3 hr. The violet product was added to water (250 c.c.), and the suspension so formed was aerated and then filtered. The residue was extracted with hot water and the resulting permanganate-red solution was filtered and acidified. The precipitate was collected, dried, and methylated with potassium carbonate and methyl toluene-*p*-sulphonate. The alkali-insoluble product was sublimed *in vacuo*; a solution of the sublimate in concentrated sulphuric acid exhibited light absorption maxima at 340 (*E* 32,000), 380 (*E* 16,700) 451 (*E* 21,700), 475 (*E* 32,400), 570 (*E* 14,800), and 620 mμ (*E* 20,000).

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