772. *Chemistry of Anthanthrone. Part I. The Direct Replacement of Hydrogen by Hydroxyl and Disubstituted Amino-groups.*

By William Bradley and Jeffrey Waller.

Heating with potassium hydroxide alone or with oxidants hydroxylates anthanthrone to the 3 : 9-dihydroxy-derivative. Methylation of this gives 3 : 9-dimethoxyanthanthrone identical with the compound prepared from 5-methoxynaphthostyryl. Morpholine, sodamide, and anthanthrone afford 3 : 9-dimorpholinoanthanthrone, hydrolysed to the 3 : 9-dihydroxy-compound and morpholine. The mechanism of the substitution process is discussed. Several new derivatives of anthanthrene are described.

Previous work has shown that the direct replacement of nuclear hydrogen by hydroxyl, amino-, and mono- and di-substituted amino-groups can be brought about in *meso*benzanthrone (Bradley and Robinson, *J.*, 1932, 1254; Bradley, *J.*, 1937, 1091; Bradley and Jadhav, *J.*, 1937, 1791; Bradley, *J.*, 1948, 1175), 1 : 8 : 9-naphthanthr-10-one (Bradley and Sutcliffe, *J.*, 1951, 2118), benzo-derivatives of *meso*benzanthrone (*idem, J.*, 1952, 1247), and 1 : 9-pyrazoloanthrone (Bradley and Geddes, *J.*, 1952, 1636), and in the present investigation the same reaction has been studied in anthanthrone (I; R = H).

The chemistry of anthanthrone has been actively investigated, mainly on account of its technical interest, but few derivatives of established orientation have been prepared except by cyclisation of substituted dinaphthyldicarboxylic acids. Following Kalb, who synthesised anthanthrone (*Ber.*, 1914, **47**, 1724; G.P. 280,787), Corbellini and Crespi (*Rend. Ist. Lombardo Sci.*, 1936, II, **69**, 429), Scholl and Meyer (*Ber.*, 1934, **67**, 1229), and Clar (*Ber.*, 1939, **72**, 1645) studied its behaviour on reduction, and numerous workers described its nitration, halogenation, and sulphonation (*e.g.*, G.P. 492,446, 458,598, 495,368).

The direct hydroxylation of anthanthrone by means of potassium hydroxide and an oxidant was first described in G.P. 530,497 and later studied by Corbellini and Crespi (*Rend. Ist. Lombardo Sci.*, 1936, II, **69**, 580) who considered that the product was a dihydroxyanthanthrone of uncertain orientation.

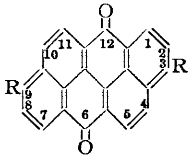
In the present investigation both manganese dioxide and potassium chlorate with copper chloride were employed as oxidants and the product was isolated in good yield through a sparingly soluble potassium salt. The acid product had the composition $C_{22}H_{10}O_4$ and on methylation gave 3 : 9-dimethoxyanthanthrone (I; R = OMe) identical with the authentic derivative prepared by the cyclisation of 5 : 5′-dimethoxy-1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid (G.P. 507,338). The compound $C_{22}H_{10}O_4$ was therefore 3 : 9-dihydroxyanthanthrone (I; R = OH).

In earlier work condensation of piperidine–sodamide with anthanthrone was shown (Bradley, *J.*, 1948, 1175) to give a violet basic product intermediate in composition between a mono- and a di-piperidinoanthanthrone. In the present work morpholine–sodamide and anthanthrone gave a similar violet mixture, which could not be fully purified but when heated with potassium hydroxide and glycol gave morpholine and a phenol. Methylation of the latter gave 3 : 9-dimethoxyanthanthrone from which it was evident that the violet base was mainly 3 : 9-dimorpholinoanthanthrone (II; R = $\cdot NC_4H_8O$). This makes it very probable that the dipiperidinoanthanthrone reported by Bradley (*J.*, 1948, 1175) was the 3 : 9-derivative (II; R = $\cdot NC_5H_{10}$).

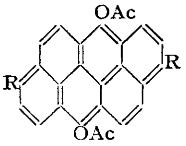
Sodamide reacted with anthanthrone in dimethylaniline to form a blue derivative; amination did not take place and on addition of the mixture to water anthanthrone was regenerated. The blue derivative was probably an addition compound such as has been described for other ketones (Lea and Robinson, *J.*, 1926, 2351).

3 : 9-Dihydroxyanthanthrone is strongly acidic, and yields a diacetyl derivative with acetic anhydride and 3 : 6 : 9 : 12-tetra-acetoxyanthanthrene (II; R = OAc) with acetic anhydride and zinc dust. It does not form a boroacetate, an indication of the absence of substitution *ortho* to a carbonyl group. The hydroxyl groups are not replaced when the

phenol is heated with ammonia, piperidine, or morpholine, but phosphorus pentachloride gives a tetrachloroanthanthrone. Two of the halogen substituents in this compound must occupy the 3 : 9-positions, the hydroxyl groups having been replaced (the product is neutral), but the orientation of the remaining pair has not been ascertained.



(I)



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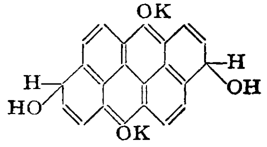

(III)

The action of fused alkali hydroxides on aromatic cyclic carbonyl compounds usually leads to hydrolysis accompanied by ring fission, or to hydroxylation of the nucleus, or to self-coupling of the ketone to a bis-derivative or more complex compound. Anthanthrone resembles anthraquinone in that the main reaction is hydroxylation. Some self-condensation appears to take place, but it has not been definitely established, and only an indication has been obtained of the occurrence of ring fission. Corbellini and Steffenoni (*Rend. Ist. Lombardo Sci.*, 1936, 2, **69**, 429) have indeed shown that anthanthrone results from the action of potassium hydroxide on 7 : 8-benzo*meso*benzanthrone-3′-carboxylic acid. The formation of a *di*hydroxy-compound harmonizes with the *mono*hydroxylation of 1 : 8 : 9-naphthanthr-10-one (Bradley and Sutcliffe, *loc. cit.*) in that each carbonyl group of anthanthrone activates one position in the nucleus. How marked is the effect of the carbonyl groups is shown by the formation of 3 : 9-dihydroxyanthanthrone in the absence of an added oxidant, though the yield is higher when manganese dioxide or potassium chlorate is used. In the absence of oxidant the product contains the reduced (dihydro-)-form which suggests that (III) is an intermediate in the hydroxylation and that 3 : 9-dihydroxyanthrone is formed from it by the oxidants. When heated with amyl-alcoholic potassium hydroxide anthanthrone formed a blue solution but hydroxylation did not take place.

The orientation of the entering groups follows the usual *op*-rule but the absence of substitution *ortho* to the carbonyl groups is noteworthy. This additional example of wholly *para*-substitution emphasises the remarkable character of the direct hydroxylation of anthraquinone to alizarin in which one hydroxyl group enters the nucleus *para* and the other *ortho* to a carbonyl group.

In the course of the work anthanthrone was characterised by reductive acetylation to 6 : 12-diacetoxyanthanthrene (II; R = H), and phosphorus pentachloride and anthanthrone were shown to yield a hexachloroanthanthrene. This compound did not dissolve in alkaline sodium dithionite and the presence of two chlorine substituents at position 6 and two at position 12 appears probable. The absorption spectra of anthanthrone and several of its derivatives have been determined in sulphuric acid.

EXPERIMENTAL

Anthanthrone was prepared by heating 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid with sulphuric acid (Kalb, *loc. cit.*), and also by the action of the same reagent on 7 : 8-benzo*meso*-benzanthrone-3′-carboxylic acid (Kalischer and Zerweck, G.P. 452,063). Both methods were satisfactory. In addition the formation of anthanthrone when the keto-acid (5 g.) was heated for 1 hr. at 200—220° with potassium hydroxide (5 g.) (cf. Corbellini and Steffenoni, *loc. cit.*) was confirmed. The pure compound dissolved in pyridine with a yellow colour, changed to green on the addition of a drop of 30% methanolic potassium hydroxide. The solution in sulphuric acid exhibited maximum light absorption at 335 (*E* 38,850), 432 (*E* 20,800), and 675 mµ (*E* 9800).

6 : 12-*Diacetoxyanthanthrene*.—(*a*) Anthanthrone (1 g.), suspended in water at 60°, was reduced and dissolved by the addition of sodium dithionite (0·4 g.) and 10% sodium hydroxide solution (3 c.c.). The red-violet solution was filtered, the filtrate acidified by the addition of acetic acid, and the precipitated yellow 6 : 12-dihydroxyanthanthrene was collected, washed,

dried between filter paper, and then heated with boiling acetic anhydride. The resulting solution gave a brown precipitate on addition to water and this, crystallised from chlorobenzene, gave 6 : 12-diacetoxyanthanthrene identical with the compound prepared by the following method.

(*b*) An intimate mixture of anthanthrone (3 g.) and zinc dust (10 g.) was added in small successive amounts to boiling acetic anhydride (100 c.c.), and the heating was continued for 30 min. The solution, which changed in colour from orange to yellow, was filtered, and the residue was crystallised first from glacial acetic acid and then from chlorobenzene. 6 : 12-*Diacetoxyanthanthrene* forms yellow needles, m. p. 299° (decomp.) (Found: C, 78·9; H, 4·0; Ac, 22·4. $C_{26}H_{16}O_4$ requires C, 79·6; H, 4·1; Ac, 22·0%). It is sparingly soluble in hot alcohol or ethyl acetate, forming yellow solutions with red-violet fluorescence. In chlorobenzene it shows a turquoise fluorescence. In concentrated sulphuric acid it dissolves with a brown colour which slowly becomes green; addition of water precipitates anthanthrone. The diacetate was relatively slowly decomposed by hot 5% sodium hydroxide, more rapidly in the presence of alcohol, forming a solution of the sodium salt of dihydroanthanthrone; anthanthrone separated from the solution after contact with air.

*Action of Phosphorus Pentachloride on Anthanthrone. Formation of Hexachloro-*6 : 12-*dihydroanthanthrene.*—An intimate mixture of anthanthrone (10 g.) and phosphorus pentachloride (10 g.) was heated for 3 hr. at 150°. Hydrogen chloride was liberated, phosphorus oxychloride distilled, and a red solid remained. This was added to ice, and the solid material was collected, washed, and then stirred with concentrated sulphuric acid (200 c.c.). The resulting suspension was filtered. The green filtrate gave anthanthrone on addition to water. The red residue was washed with concentrated sulphuric acid, then in turn with water, aqueous sodium carbonate, and water. After drying (4·1 g.), a portion heated under reduced pressure at 325° gave a single red band of a sublimate. The main portion crystallised from trichlorobenzene in deep red needles of *hexachloro*-6 : 12-*dihydroanthanthrene* which were unaffected by hot alkaline sodium dithionite (Found: C, 54·9; H, 1·7; Cl, 43·5. $C_{22}H_8Cl_6$ requires C, 54·4; H, 1·7; Cl, 43·9%).

Action of Potassium Hydroxide on Anthanthrone.—(*A*) Finely divided anthanthrone (10 g.) (obtained by the addition to water of a solution of anthanthrone in concentrated sulphuric acid) was added during 15 min. to molten potassium hydroxide (100 g.) at 180°, and then the mixture was stirred for 1 hr. at 240°. Working up as in (*B*) gave anthanthrone (4·5 g.), 3 : 9-dihydroxyanthanthrone (2·8 g.), and a dark residue which formed a blue-violet solution in alkaline sodium dithionite.

(*B*) Anthanthrone (20 g.), obtained in a finely divided condition as in (*A*), was collected, washed with sodium carbonate solution, then water, and finally dried by suction. The filter cake (35 g.) was intimately mixed with manganese dioxide (35 g.) and added during 15 min. to molten potassium hydroxide (200 g.) at 180°. The temperature was raised to 240° and maintained thereat for 1 hr. At first the melt was viscous, later it became more fluid. It was added to water, the resulting suspension was aerated, and the undissolved material was collected and washed with 20% potassium hydroxide solution. The filter cake was extracted with hot water (800 c.c.), and the resulting permanganate-red solutions were filtered from undissolved solid (6 g.); this crystallised from chlorobenzene and was identified as anthanthrone. The permanganate-red extracts were combined and acidified by adding glacial acetic acid, and the resulting red-brown precipitate was collected, washed, and dried (yield, 7·4 g.). It did not melt below 360°. It was insoluble in boiling nitrobenzene or trichlorobenzene but crystallised from pyridine or quinoline in small red-brown needles. The red-violet solution in pyridine remained unaltered on the addition of methanolic potassium hydroxide, but a similar solution in aqueous sodium hydroxide became bluer on the addition of sodium dithionite. Heated *in vacuo* in a bath at 425° a small quantity sublimed (Found: C, 78·0; H, 3·2. Calc. for $C_{22}H_{10}O_4$: C, 78·1; H, 3·0%) but the main bulk remained as an alkali-insoluble product. It dissolved sparingly in hot acetic anhydride, forming a yellow solution. The same result was obtained with acetic anhydride containing boroacetic anhydride. On the addition of water (15 c.c.) to a solution of the product (10 g.) in concentrated sulphuric acid (100 c.c.) a black solid separated. This was collected, washed with 85% sulphuric acid, and then stirred with water (400 c.c.). 3 : 9-Dihydroxyanthanthrone was precipitated as a red-brown solid which exhibited the following light absorption maxima in concentrated sulphuric acid solution; 340 (*E* 30,800), 380 (*E* 27,000), 449 (*E* 22,300), 475 (*E* 35,200), 570 (*E* 14,400), and 620 mμ (*E* 18,300).

(*C*) Anthanthrone (10 g.), potassium chlorate (10 g.), and copper chloride (2 g.) were added to potassium hydroxide (60 g.) at 150° and the mixture was stirred at 240° for 1 hr. (cf. Corbellini and Crespi, *loc. cit.*). The product contained anthanthrone (3 g.) and 3 : 9-dihydroxyanthanthrone (3·6 g.). On methylation the latter gave a derivative which exhibited the same light absorption in concentrated sulphuric acid as the 3 : 9-dimethoxyanthanthrone described below.

3 : 9-Dihydroxyanthanthrone was recovered unaltered after 12 hr.' heating with aqueous ammonia (*d* 0·880) at 220°. It was also unchanged by hot morpholine.

Methylation of 3 : 9-*Dihydroxyanthanthrone.*—(*a*) 3 : 9-Dihydroxyanthanthrone was recovered unchanged when 1 g. was dissolved in water (25 c.c.) containing sodium hydroxide (0·2 g.) and heated and stirred with methyl sulphate (1 c.c.) during 3 hr., sodium carbonate being added at intervals.

(*b*) 3 : 9-Dihydroxyanthanthrone (5 g.) was dissolved in a 2% solution (100 c.c.) of potassium hydroxide, and potassium hydroxide (20 g.) was then stirred in. The potassium salt which separated was collected and dried. It was a dark purple solid with a green lustre. The potassium salt (1 g.) was heated for 12 hr. at 130° with methyl iodide (8 c.c.). The product was extracted by means of dilute sodium hydroxide, then dried and crystallised from trichlorobenzene. Orange needles of 3 : 9-dimethoxyanthanthrone separated. The same product (Found : C, 78·7; H, 4·0. Calc. for $C_{24}H_{14}O_4$: C, 78·7; H, 3·8%) [light absorption maxima in concentrated sulphuric acid at 340 (*E* 33,000), 380 (*E* 17,400), 451 (*E* 22,700), 475 (*E* 35,200), 570 (*E* 15,200), and 620 mμ (*E* 21,500)] also resulted, in better yield (0·6 g.), when 3 : 9-dihydroxyanthanthrone (1 g.) was heated under reflux for 12 hr. with anhydrous potassium carbonate (2 g.), methyl toluene-*p*-sulphonate (2 g.), and trichlorobenzene (200 c.c.). In concentrated sulphuric acid both products formed blue-violet solutions which exhibited the same light absorption maxima as the 3 : 9-dimethoxyanthanthrone prepared from 5-methoxynaphthastyryl (G.P. 504,342).

3 : 9-*Diacetoxyanthanthrone.*—3 : 9-Dihydroxyanthanthrone (5 g.) was prepared in a finely divided state by precipitation from sulphuric acid, then dried in air and heated under reflux for 4 hr. with acetic anhydride (150 c.c.). The acetylated compound separated. It was filtered off and crystallised from trichlorobenzene. The resulting reddish-orange needles of 3 : 9-*diacetoxyanthanthrone* did not melt below 360° (Found : C, 73·4; H, 3·5; Ac, 20·45. $C_{26}H_{14}O_6$ requires C, 73·9; H, 3·3; Ac, 20·29%).

3 : 6 : 9 : 12-*Tetra-acetoxyanthanthrene.*—Finely divided 3 : 9-dihydroxyanthanthrone (2 g.) was heated under reflux with zinc dust (10 g.) in acetic anhydride (50 c.c.). The dark colour became lighter and a green-blue fluorescence developed. After 30 min. the mixture was filtered through sintered glass, and the orange yellow prisms of 3 : 6 : 9 : 12-*tetra-acetoxyanthanthrene* which separated from the filtrate were recrystallised from ethyl acetate, in which it formed a yellow solution with a blue fluorescence. It decomposed before melting (Found : C, 70·4; H, 3·7; Ac, 33·6. $C_{30}H_{20}O_8$ requires C, 70·8; H, 3·9; Ac, 33·8%). It dissolved slowly in aqueous sodium hydroxide to a red-violet solution, and in pyridine to a yellow solution with a green fluorescence. On the addition of a drop of methanolic potassium hydroxide a red colour developed, changing to red-violet.

5-*Acetoxy*-N-*acetylnaphthastyryl.*—By the method of G.P. 504,342 (Example 1), 1-cyanonaphthalene-4 : 8-disulphonic acid (10 g.) afforded 8 g. of a product which sublimed *in vacuo* from a bath at 250° and gave pure 5-hydroxynaphthastyryl (3·5 g.), m. p. >300°. A slight improvement in yield (to 4·0 g.) resulted when the conditions of Example 3 were used (Found : C, 71·2; H, 3·9; N, 7·4. Calc. for $C_{11}H_7O_2N$: C, 71·4; H, 3·8; N, 7·5%). The *diacetyl* derivative was obtained by heating 0·3 g. of 5-hydroxynaphthastyryl with 5 c.c. of acetic anhydride under reflux for 30 min. Crystallisation from alcohol gave colourless needles of 5-*acetoxy*-N-*acetylnaphthastyryl*, m. p. 210—211° (Found : C, 66·6; H, 3·9; N, 5·2. $C_{15}H_{11}O_4N$ requires C, 66·9; H, 4·1; N, 5·2%).

The crude product prepared from 5-methoxynaphthastyryl by hydrolysis, diazotisation, coupling (cf. Macrae and Tucker, *J.*, 1933, 1520), and ring-closure was sublimed *in vacuo* from a bath at 325°. It yielded a reddish-orange powder, m. p. >350° (Found : C, 78·5; H, 4·1. Calc. for $C_{24}H_{14}O_4$: C, 78·7; H, 3·8%). It exhibited the properties of the dimethoxyanthanthrone referred to in G.P. 507,338, Example 1. The green solution in concentrated sulphuric acid exhibited light absorption maxima at 340 (*E* 31,600), 380 (*E* 16,800), 451 (*E* 21,000), 475 (*E* 34,200), 470 (*E* 14,900), and 620 mμ (*E* 20,200).

Action of Sodamide on Anthanthrone.—A suspension of anthanthrone (6 g.) in dimethylaniline (50 c.c.) was stirred with finely powdered sodamide (8 g.) at 160°. The colour changed from yellowish-orange to blue. After 4 hr. the blue solid was filtered off and added to water. Ammonia was liberated, and an orange suspension and a red-violet solution were formed. The whole was aerated, and the orange-brown solid was collected and washed with water and acetone.

Crystallisation from nitrobenzene afforded anthanthrone, identified by the absorption spectrum of its solution in concentrated sulphuric acid.

Action of Morpholine and Sodamide on Anthanthrone.—Finely divided anthanthrone (10 g.), sodamide (5 g.), and morpholine (100 c.c.) were heated under reflux. The colour changed from orange to blue-violet. After 4 hr. the product was cooled and added to water; there was no evidence of unchanged sodamide. The suspension was aerated, and the solid was collected and extracted with hot 20% hydrochloric acid (3 × 500 c.c.). The first and second extracts were violet, the third was feebly coloured. On addition to 9 l. of water the combined, filtered extracts afforded a deep violet precipitate.

This product, after being washed and dried (0·4 g.), crystallised from pyridine in deep violet, impure needles (Found: N, 5·0. Calc. for $C_{30}H_{16}O_4N_2$: N, 6·0%). It decomposed without subliming when heated *in vacuo*. It gave a greenish-brown solution in concentrated sulphuric acid, exhibiting no marked light absorption maxima. On the addition of water the solution became orange, then red-violet. The product was difficultly soluble in alkaline dithionite, more easily on the addition of pyridine, forming a red-violet solution. The hydrochloric acid-insoluble part (8 g.) of the product was identified as anthanthrone.

The crude 3 : 9-dimorpholinoanthanthrone (0·2 g.) was heated under reflux for 3 hr. with potassium hydroxide (2 g.) and glycol (10 c.c.). Morpholine was eliminated. After addition to water (100 c.c.) and filtration, a tar was obtained and a violet filtrate. The latter was acidified with acetic acid, and the resulting precipitate was collected, dried, and methylated as described for 3 : 9-dihydroxyanthanthrone. The product exhibited light absorption maxima in concentrated sulphuric acid at 340 (*E* 32,100), 380 (*E* 15,900), 451 (*E* 21,000), 475 (*E* 31,900), 570 (*E* 14,900), and 625 mμ (*E* 20,300).

The same 3 : 9-dihydroxyanthanthrone was obtained together with morpholine when the crude dimorpholinoanthanthrone (0·1 g.) was fused with potassium hydroxide (5 g.) and water (0·3 c.c.).

Tetrachloroanthanthrone.—3 : 9-Dihydroxyanthanthrone (10 g.) was intimately mixed with phosphorus pentachloride (20 g.) and heated in an oil-bath at 160°. A reaction proceeded for 3 hr. during which phosphorus oxychloride distilled and hydrogen chloride was evolved. The brown product was stirred with ice, then collected and stirred with concentrated sulphuric acid. The resulting green solution was filtered, then added to water, and the brown precipitate was collected, washed, and dried. It was then extracted with trichlorobenzene at the b. p.; an orange solid separated from the filtered solution on cooling. Recrystallisation from the same solvent gave orange needles of a *tetrachloroanthanthrone* (Found: Cl, 30·1. $C_{22}H_6O_2Cl_4$ requires Cl, 32·0%). These dissolved in concentrated sulphuric acid, forming a solution which exhibited light absorption maxima at 347 (*E* 30,800), 469 (*E* 22,800), and 667 mμ (*E* 11,200). The product dissolved in pyridine with a yellow colour, changed to green on the addition of methanolic potassium hydroxide. It dissolved in alkaline sodium dithionite forming a blue-violet solution.

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