

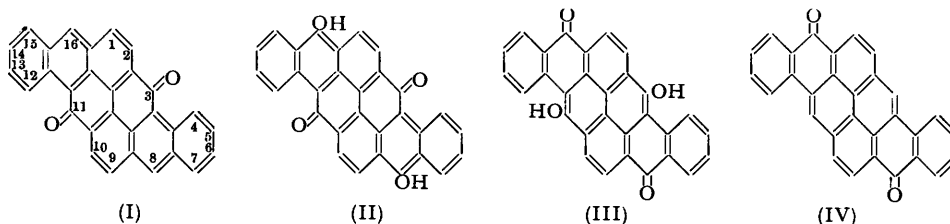
The Direct Hydroxylation of Pyranthrone and *amphi-iso*Pyranthrone.

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Pyranthrone and *amphi-isopyranthrone* yield the same dihydroxy-derivative (3 : 11-dihydro-8 : 16-dihydroxy-3 : 11-dioxopyranthrene) on being heated with potassium hydroxide.

*amphi-iso*PYRANTHRONE (I) (Scholl and Tanzer, *Annalen*, 1923, **433**, 163) was readily hydroxylated on being heated with potassium hydroxide, potassium acetate, and manganese dioxide at 240°. The product afforded a dimethyl derivative on methylation, oxidised by chromium trioxide in acetic acid to 1 : 1'-dianthraquinonyl-2 : 2'-dicarboxylic acid. The absence of methoxyl groups from the oxidation product indicates that the product of hydroxylation is 3 : 11-dihydro-8 : 16-dihydroxy-3 : 11-dioxopyranthrene (II), or the isomer (III), or a resonance hybrid of these. The same dihydroxy-derivative was obtained by the direct hydroxylation of pyranthrone (IV) under similar conditions, although the yield was smaller than with *amphi-isopyranthrone*. The identity of the products confirms the orientation of the entering hydroxyl groups in the two cases and the occurrence of resonance in the anions of the products (II, III). Further, the formation of a dihydroxy-derivative from a diketone in each of the two cases is in agreement with the substitution rule referred to by Bradley and Sutcliffe (*J.*, 1951, 2118).



*amphi-iso*Pyranthrone is more easily hydroxylated than is anthanthrone (Bradley and Waller, *J.*, 1953, 3778), to which it is related as is anthracene to naphthalene. A similar relationship in reactivity was observed between 5 : 6-benzomesobenzanthrone (anthracene structure, more reactive) and mesobenzanthrone (naphthalene structure, less reactive) (Bradley and Sutcliffe, *loc. cit.*). Like 5 : 6-benzomesobenzanthrone *amphi-isopyranthrone* can be hydroxylated even with alcoholic potassium hydroxide at 110°, although the yield of dihydroxy-derivative is reduced under these conditions, in agreement with earlier experience (Bradley, *J.*, 1937, 1091).

## EXPERIMENTAL

*Hydroxylation of amphi-isoPyranthrone.*—*amphi-iso*Pyranthrone (Scholl and Tanzer, *loc. cit.*) crystallised from trichlorobenzene in blue-grey needles which did not melt below 400° and exhibited the colour in concentrated sulphuric acid and alkaline sodium dithionite recorded by these authors. (a) *amphi-iso*Pyranthrone (3 g.) was ground with manganese dioxide (3 g.) and then added during 15 min. to potassium hydroxide (30 g.) and potassium acetate (3 g.) at 220°. The temperature of the melt was raised to 240° and maintained for 1 hr., during which the melt became viscous. Cooling and addition to water (500 c.c.) gave a bright royal-blue filtrate and a solid (0.57 g.), from which unchanged material was recovered by extraction with hot trichlorobenzene. Acidification of the blue solution gave dark, red-brown flocks. These were collected, washed, dried, ground under water, and again collected (2.45 g.). They were redissolved in dilute potassium hydroxide and chromatographed on a column of cellulose powder. A pale brown constituent was rejected and the main blue band was eluted with water. Acidification gave a red-brown solid which did not melt below 400°. It dissolved sparingly in pyridine, and the resulting yellow-brown solution became violet on the addition of morpholine, and greenish-

blue with methanolic potassium hydroxide. It was sparingly soluble in hot acetic anhydride; there was no change in colour on the addition of boroacetic anhydride. It dissolved in aqueous sodium carbonate and in concentrated sulphuric acid forming blue solutions. (b) A similar product was obtained by heating *amphi-isopyranthrone* (2 g.) with potassium hydroxide (20 g.) and potassium acetate (2 g.). After 1 hr. at 240° the yield was 0.6 g.; 1.0 g. of unchanged *amphi-isopyranthrone* was recovered. (c) *amphi-isoPyranthrone* (2 g.) was stirred and heated for 1 hr. at 110° with a paste prepared from potassium hydroxide (10 g.) and ethanol (20 c.c.), and then added to water (500 c.c.). Air was bubbled through the resulting suspension for 12 hr., the solids were filtered off, and the pale blue solution was acidified. The precipitated hydroxy-compound (0.05 g.) was identical with that described in (a).

3 : 11-*Dihydro-8* : 16-*dimethoxy-3* : 11-*dioxopyranthrene* (*Dimethoxyamphi-isopyranthrone*) (II; OMe for OH).—The hydroxy-compound (0.5 g.) prepared as in (a) was finely ground, suspended in trichlorobenzene (50 c.c.), and refluxed 12 hr. with methyl toluene-*p*-sulphonate (1 g.) and anhydrous potassium carbonate (1 g.). The suspension was filtered hot, the residue was washed with the hot solvent, and the combined filtrates were concentrated. Fine, red-brown needles separated which were insoluble in aqueous sodium hydroxide or carbonate and did not melt below 400° [Found: OMe, 12.5.  $C_{30}H_{12}O_2(OMe)_2$  requires OMe, 13.7%]. The *dimethoxy*-derivative gave a blue solution in concentrated sulphuric acid, and a pale yellow solution in pyridine which became violet on the addition of aqueous alkaline sodium dithionite; on aeration a red-brown precipitate formed.

*Oxidation.* *Dimethoxyamphi-isopyranthrone* (0.2 g.) was refluxed for 0.5 hr. with chromium trioxide (0.2 g.) in glacial acetic acid (10 c.c.). Chromium trioxide (0.2 g.) and glacial acetic acid (2 c.c.) were added and the refluxing continued for 0.5 hr. The resulting solution was filtered, the filtrate was added to water (100 c.c.), and the yellow precipitate was collected. It was extracted with dilute sodium hydroxide, and the solution was treated with charcoal, filtered, and acidified. A precipitate was formed. This was collected, washed, dried, and recrystallised from alcohol. Yellow needles (0.1 g.), m. p. 352—355°, not depressed on admixture with authentic 1 : 1'-*dianthraquinonyl-2* : 2'-*dicarboxylic acid* were obtained. The two samples of the acid were also identical in their light absorption in EtOH, max. at 271 ( $10^{-3} \epsilon$  59, 62), 391 ( $10^{-3} \epsilon$  13);  $\lambda_{min.}$  at 335 m $\mu$  ( $10^{-3} \epsilon$  6).

*Hydroxylation of Pyranthrone.*—This was carried out with potassium hydroxide, potassium acetate, and manganese dioxide as for *amphi-isopyranthrone* (a) except that the quantities used were five times larger. The cooled melt was added to water (1 l.), and the suspension was filtered from the dark brown alkaline solution, then added to water and boiled. A deep royal-blue solution resulted, and this gave 0.55 g. of a precipitate on acidification. Methylation of 0.5 g. with methyl toluene-*p*-sulphonate (1 g.) and potassium carbonate (1 g.) in 1 : 2 : 4-trichlorobenzene (100 c.c.) gave after 12 hr. fine, red-brown needles (0.2 g.) identical in reactions and in light absorption in concentrated sulphuric acid with the *dimethoxyamphi-isopyranthrone*; max. at 227 ( $10^{-3} \epsilon$  53, 50), 282 ( $10^{-3} \epsilon$  55, 52), 531 ( $10^{-3} \epsilon$  24, 23), 630 ( $10^{-3} \epsilon$  38.5, 37);  $\lambda_{min.}$  at 255 ( $10^{-3} \epsilon$  32, 31) and 560 m $\mu$  ( $10^{-3} \epsilon$  15, 14)]; values for the *dimethoxy*-derivative from *amphi-isopyranthrone* are given first.

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