**126.** *The Cyclisation of* 1 : 9-*Benzanthrone-8-carboxylic Acid to* 8 : 11-*Ketobenzanthrone, and of Dibenzanthronedicarboxylic Acid to Diketo-dibenzanthrone.*

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Owing to the indefinite results obtained in a preliminary treatment of benzanthrone-8-carboxylic acid (I) with concentrated sulphuric acid, an extended examination has been made of the behaviour of this compound and its precursor, methyl 8-(*o*-carbomethoxy-phenyl)-1-naphthoate (see previous paper), towards reagents which might be expected to bring about ring closure to 8 : 11-*ketobenzanthrone* (II).

(I.)   (II.)   (III.)
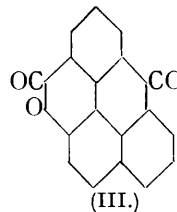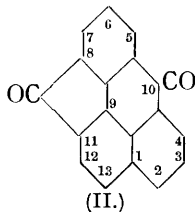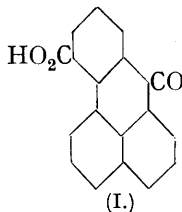
Solutions of the above dimethyl ester in sulphuric acid were maintained for 1 hour at definite temperatures; they were then poured into water, and the products separated. The course of the reaction proved to be unexpectedly complex. The quantities given in the table are those isolated from 1 g. of the dimethyl ester after 1 hour's treatment. Similar results were obtained with methyl benzanthronecarboxylate or the free acid at 130° or higher.

Temp.	Methylbenzanthrone-carboxylate.	Crude benzanthrone.	Benzanthrone-carboxylic acid.	Crude keto-benzanthrone.
16—17°	0·89	—	—	—
50	0·83	—	0·08	—
110	0·13	—	0·74	—
130	—	0·12	0·70	—
150	—	0·19	0·47	0·06
160	—	0·22	0·30	0·13
170	—	0·18	0·16	0·10

Methyl benzanthrone-8-carboxylate was isolated in practically quantitative yield between 15° and 40°. At 50° a little of it underwent hydrolysis, and at 100° benzanthrone-8-carboxylic acid was obtained in 90% yield.

Benzanthrone, produced apparently by decarboxylation of the acid, appeared in small amounts at 120° or higher. The proportion did not increase appreciably with rise in temperature, partly because higher temperatures tended to convert it into a water-soluble sulphonic derivative, which was not isolated, and partly on account of the increasing dehydration of the acid to give ketobenzanthrone (II).

Ketobenzanthrone was formed in small amounts at 135° and upwards, but above 160° disproportionate losses of material occurred by sulphonation. It was always contaminated with a compound, which is provisionally formulated as the *lactone* of 11-*hydroxy-benzanthrone-8-carboxylic acid* (III) and assumed to be formed by oxidation of the acid (the odour of sulphur dioxide is always evident in the sulphuric acid reaction mixture). The lactone may also be prepared in good yield by the oxidation of benzanthrone-8-carboxylic acid with chromic acid. All attempts to confirm the structure by decarboxylation with boiling quinoline and copper bronze, or by methylation to give the methoxy-acid or its ester, failed, the compound being recovered unchanged. Although 1 : 8-naphtholactone also resists decarboxylation by the above method (Rule and Brown, unpublished), no difficulty had been anticipated in methylating the benzanthrone derivative. Nevertheless, this failure is not regarded as excluding the lactone structure, in view of the extremely sparing solubility of the compound and the great tendency of the sodium salt to deposit the neutral product, except in the presence of excess of alkali.

The mixture of lactone and ketobenzanthrone obtained by sulphuric acid treatment

is not easily separated. In organic solvents the lactone is even more difficultly soluble than ketobenzanthrone and it cannot be economically eliminated by recrystallisation. The lactone dissolves in boiling aqueous alkali in a few minutes to give (even a mere trace) an intense purplish-red solution with yellowish-red fluorescence. Ketobenzanthrone, however, also is slowly attacked by hot alkaline solutions, the fluorenone bridge being ruptured with formation of a mixture of benzanthronecarboxylic acids. In spite of the marked disparity in the ease with which the two compounds are attacked, it was not found practicable to purify the crude keto-compound by digestion with hot sodium hydroxide solution, as the separation was always incomplete.

Traces of the supposed lactone are sometimes produced from the ester used as initial material, even when the sulphuric acid treatment is conducted at lower temperatures, as is shown by the purplish-red colour given by the crude benzanthronecarboxylic acid on solution in alkali. By fractional precipitation the lactone, accompanied by a small amount of the acid, may be completely precipitated from such a solution. The purified solution of sodium benzanthrone-8-carboxylate thus obtained on filtration is then orange-yellow and on dilution exhibits a characteristic brilliant yellow-green fluorescence.

Pure 8 : 11-ketobenzanthrone was prepared more simply and in almost theoretical yield by dehydrating the lactone-free carboxylic acid in phthalic anhydride solution at 200° with phosphoric oxide. It was also obtained in small amount by ring closure of the acid chloride by means of aluminium chloride.

The keto-derivative dissolves in concentrated sulphuric acid to a reddish-violet solution having no fluorescence. It gives a deep green solution with dilute alkaline sodium hydrosulphite, the salt of the leuco-compound being sparingly soluble. This solution is readily oxidised in air to deposit the original compound, but the latter is of no value as a dye owing to its instability towards alkalis. This difference from fluorenone, which is not appreciably attacked by aqueous alkalis, probably arises from the greater tension in the 8 : 11-ring in the benzanthrone derivative. In fluorenone the strain in the five-membered ring may be relieved by a slight adjustment of the loose diphenyl system, a distortion which is not so readily tolerated by the more rigid benzanthrone molecule.

Dibenzanthronedicarboxylic acid (see previous paper) exhibited even less tendency than benzanthronecarboxylic acid to undergo ring closure by dehydration when heated with sulphuric acid. In phthalic anhydride solution, however, it reacted with phosphoric oxide to give diketodibenzanthrone, a small amount of the acid being recovered unchanged. The somewhat greater stability of the dibenzanthronedicarboxylic acid towards dehydrating agents is in keeping with the greater rigidity of its molecular structure as compared with that of the corresponding benzanthrone derivative. Diketodibenzanthrone is attacked by boiling aqueous alkalis only with extreme slowness, presumably on account of its insolubility.

<div align="center">EXPERIMENTAL.</div>

The analyses recorded below are micro-determinations carried out by Dr. A. Schoeller, Berlin. All melting points are corrected.

Treatment of Methyl 8-(o-*Carbomethoxyphenyl*)-1-*naphthoate with Sulphuric Acid.*—The ester (1 g.) was dissolved in concentrated sulphuric acid, $d_4^{20°}$ 1·823 (32 c.c. at 16°, or 8 c.c. in other cases), and maintained at the stated temperature ($\pm$ 1°) for 1 hour (see table). The blood-red mixture was then poured into water and the precipitated solids were filtered off and digested for a few minutes with dilute aqueous sodium hydroxide at 60°. The resulting purplish-red suspension was filtered. *Filtrate.* This was treated carefully with sulphuric acid until the first small precipitation discharged the red colour, leaving an orange solution of sodium benzanthronecarboxylate. Precipitated lactone of 11-hydroxybenzanthrone-8-carboxylic acid was filtered off, and the clear liquor acidified with sulphuric acid; it then deposited lactone-free benzanthrone-8-carboxylic acid. *Solids.* These were recrystallised from alcohol, by which means ketobenzanthrone and lactone were readily separated from benzanthrone.

Methyl benzanthrone-8-carboxylate crystallised from alcohol in long yellow needles, m. p. 159—160° (Found : C, 79·3; H, 4·2. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%), sparingly soluble in hot alcohol or benzene. In concentrated sulphuric acid it forms a deep orange solution having a yellow fluorescence.

Benzanthrone was obtained as the more readily soluble neutral fraction from sulphuric acid treatment above 120°. After successive recrystallisation from alcohol, ligroin, and benzene it melted at 170—171·5°, and at 170—173° in admixture with a specimen, m. p. 172—173°, prepared from anthranol and glycerol (Found : C, 88·6; H, 4·4; M, in boiling benzene by the Menzies–Wright method, 246, 237, 243. Calc. for $C_{17}H_{10}O$: C, 88·7; H, 4·3%; M, 230).

The lactone of 11-*hydroxybenzanthrone*-8-*carboxylic acid* (?). This was first separated in small amount as a very difficultly soluble fraction in an attempt to dissolve in alcohol the carboxylic acid resulting from an experiment at 135°. It crystallised from hot alcohol (0·5 g. dissolves in 450 c.c.), with addition of animal charcoal, in fine golden-yellow needles, m. p. 355—356°.

A solution of benzanthrone-8-carboxylic acid (0·5 g.) in 5 c.c. of concentrated sulphuric acid was poured into 40 c.c. of water, chromium trioxide (2 g.) added, and the mixture heated at 97° with stirring for 4 hours. The pink powder (0·27 g.) obtained by filtration was recrystallised from alcohol, giving the *lactone* (0·16 g.), m. p. 353—355° (softening at 342°), practically unchanged in admixture with the above sample (Found : C, 79·4; H, 2·8. $C_{18}H_8O_3$ requires C, 79·4; H, 2·9%). About 45% loss of material always occurred during these oxidations, but no anthraquinonecarboxylic acid or other product of oxidation could be isolated.

The compound is not soluble in cold aqueous sodium carbonate; at higher temperatures it acquires a pink tint without appreciably dissolving. From a benzene solution the lactone can be extracted only extremely slowly by shaking with aqueous caustic soda. In concentrated sulphuric acid it dissolves to a light orange solution showing strong yellow-green fluorescence.

Methylation was attempted, (*a*) by treating the lactone in alkaline solution with methyl sulphate, (*b*) by evaporating the slightly alkaline solution to dryness in a vacuum, removing the remaining water as completely as possible by repeated distillation with toluene, and heating the residual red solid with methyl sulphate, (*c*) with silver oxide and methyl iodide. In all these cases the lactone was largely recovered unchanged.

Cyclisation of Benzanthrone-8-*carboxylic Acid with Phosphoric Oxide.*—The lactone-free acid (4 g.) (see above) was dissolved with stirring in phthalic anhydride (80 g.) at 200°, and phosphoric oxide (4·7 g.) added in two portions at an interval of 30 minutes. After 2 hours the dark red mixture was cooled somewhat and poured into a solution of 50 g. of sodium hydroxide in 450 c.c. of water. The orange precipitate was collected hot, washed liberally with hot water (yield, 3·45 g.), and recrystallised from hot benzene, giving stout orange needles (3·07 g.) of 8 : 11-*ketobenzanthrone*, m. p. 327—328° (softening at 325°, and resolidifying in needles at 323°) (Found : C, 84·2; H, 3·2. $C_{18}H_8O_2$ requires C, 84·4; H, 3·1%). Both the lactone and keto-benzanthrone have normal molecular weights in boiling benzene.

Diketodibenzanthrone.—Purified dibenzanthronedicarboxylic acid (2·0 g.), dissolved in 100 g. of phthalic anhydride, was heated with stirring for 3 hours at 210°, phosphoric oxide (6 g.) being added in portions during the first 1½ hours. The warm mixture was poured into 450 c.c. of 10% sodium hydroxide solution, and the suspension warmed and filtered. The blue solid was extracted with hot dilute alkali until the filtrate was no longer coloured. It was practically insoluble in boiling quinoline, but dissolved extremely sparingly in boiling nitrobenzene, giving a blue solution with dark red fluorescence. Yield, 1·2 g. The compound formed a purplish-blue vat with alkaline sodium hydrosulphite solution, which dyed cotton a pure blue colour. When the dyed material was boiled for 30 minutes with 1% soap solution, no colour was removed.