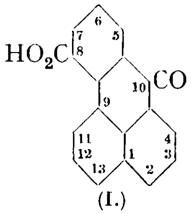
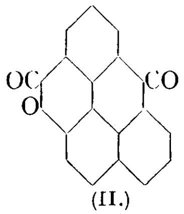
119. *Oxidation Products of Benzanthrone-8-carboxylic Acid.*

By John L. Grieve and H. Gordon Rule.

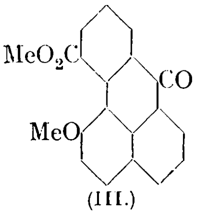
In an earlier communication dealing with the action of hot concentrated sulphuric acid upon benzanthrone-8-carboxylic acid (I), a yellow compound was described which dissolves slowly in alkali to give a brilliant red solution having a vivid green fluorescence. This compound was also isolated in good yield by oxidising the acid with chromic acid and was tentatively formulated (II) as the lactone of 11-hydroxybenzanthrone-8-carboxylic acid (Bigelow and Rule, J., 1935, 573), although it was not found possible to support this structure by the preparation of a methylated or decarboxylated derivative.



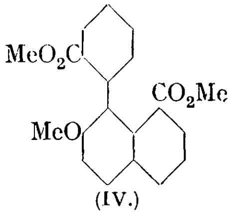
(I.)



(II.)



(III.)

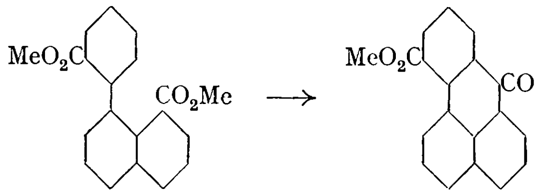


(IV.)

Confirmation of the lactone formula has now been obtained by a synthesis effected in the following stages: *methyl* 8-*bromo*-7-*methoxy*-1-*naphthoate* was condensed with methyl *o*-iodobenzoate in the presence of copper bronze to give an intermediate *phenylnaphthalenedicarboxylate* (IV), which on brief treatment with warm concentrated sulphuric acid was converted quantitatively into a compound identical with the above oxidation product.

Benzanthrone itself is known to undergo oxidation in positions 2 and 12, but the entry of oxygen into position 11 is a somewhat unexpected phenomenon. The reaction is not to be explained by the presence of the 8-carboxyl group, except possibly on the assumption that it is facilitated by the spatial disposition of this group with respect to the rest of the molecule, which is such that a new stable six-membered ring may be formed as a result of oxidation at position 11. Profound modifications in the normal properties of substituent groups undoubtedly occur in molecular structures of this kind where two or more groups of atoms are maintained rigidly in permanent proximity to one another, as is illustrated further by the novel behaviour of the intermediate esters (III) and (IV) towards hydrolysing agents.

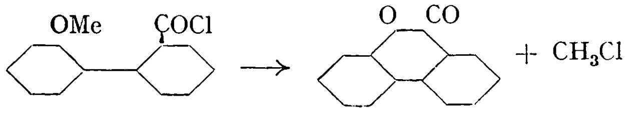
Earlier work has shown that the dimethyl ester of 8-*o*-carboxyphenyl-1-naphthoic acid on treatment for 1 hour at 50° with concentrated sulphuric acid is converted into methyl benzanthrone-8-carboxylate, and that further heating at 100° is required to hydrolyse this ester to the free acid (Bigelow and Rule, *loc. cit.*). By analogy it was hoped to effect a similar series of changes with the methoxy-ester (IV), leading to the isolation of the benzanthrone derivative (III) and its hydrolysis product, 11-methoxybenzanthrone-8-carboxylic acid. This last compound on decarboxylation might have been expected to yield the unknown 11-methoxybenzanthrone. In actual practice, however, the complete transformation could not be achieved, as treatment of (IV) for even a short time with sulphuric acid or other cyclising agent brought about direct conversion into the lactone.



A small yield of the desired *methyl 11-methoxybenzanthrone-8-carboxylate* was eventually isolated together with much lactone by warming the phenylnaphthalene derivative (IV) with an acetic acid solution of sulphuric acid. The product was a brilliantly yellow, crystalline solid which dissolved in the majority of organic solvents to form solutions with a vivid green fluorescence. Brief treatment with cold concentrated sulphuric acid sufficed to convert the ester into lactone. This reaction is the more surprising in view of the resistance to acid hydrolysis normally offered not only by a methoxyl group but also by the ester group of methyl benzanthrone-8-carboxylate, and the facile change appears to be due to the peculiar stereochemical relationship of the interacting groups.

Such a conclusion is supported by the behaviour of the methoxybenzanthronecarboxylic ester towards alkalis, five hours' heating with alcoholic potash converting it largely into the lactone. None of the intermediate 11-methoxybenzanthrone-8-carboxylic acid could be isolated, and this compound would appear to be unstable under the experimental conditions employed, despite the normal stability of a methoxyl group towards alkalis. These results, however, are in complete agreement with the failure of all attempts to methylate the lactone (Bigelow and Rule, *loc. cit.*). On the other hand, the uncyclised ester (IV), in which the phenyl group is able to rotate freely around the bond joining it to the naphthalene nucleus, may be hydrolysed in the usual way with alcoholic alkali to yield the corresponding stable *methoxy-dicarboxylic acid.* All reactions designed to effect a partial cyclisation of the latter to methoxybenzanthronecarboxylic acid again led solely to the production of lactone.

A somewhat analogous phenomenon to the above has previously been recorded in the case of 2-methoxydiphenyl-2′-carboxylic acid, the acid chloride of which passes spontaneously even at low temperatures into the lactone of the 2-hydroxy-acid, with elimination of methyl chloride (Rule and Bretscher, J., 1927, 925) :



As the acid oxidation of benzanthrone-8-carboxylic acid gave no isolable product apart from the lactone, an examination was made of its reaction towards alkaline permanganate as employed by Allen and Overbaugh (*J. Amer. Chem. Soc.*, 1935, **57**, 740) and Charrier and Ghigi (*Ber.*, 1936, **69**, 2211). By use of this reagent a small amount of the hitherto unknown *anthraquinone*-1 : 8-*dicarboxylic acid* has now been isolated, the structure of which has been confirmed by sublimation in the presence of copper bronze to give anthraquinone.

EXPERIMENTAL.

8-Bromo-7-methoxy-1-naphthoic acid was prepared by the method of Davies, Heilbron, and Irving (J., 1932, 2715), but modified by use of alkaline hydrogen peroxide (Whiston, *J. Soc. Chem. Ind.*, 1924, **43**, 370) for converting the intermediate methoxyacenaphthenequinone into 2-methoxynaphthalic acid (yield, 92%). *Methyl* 8-*bromo*-7-*methoxy*-1-*naphthoate*, obtained by way of the acid chloride, crystallised from light petroleum in stout needles, m. p. 79° (Found : Br, 27·0. $C_{13}H_{11}O_3Br$ requires Br, 27·1%).

A mixture of the above ester (20 g.) with methyl *o*-iodobenzoate (40 g.) was heated with stirring to 150°. Copper bronze (25 g.) was then added during 1 hour, and the temperature maintained at 175° for 3 hours. The cooled product was extracted with acetone (150 c.c.), and after removal of the solvent under diminished pressure the syrupy residue was treated with ether (25 c.c.). The solid deposited, on recrystallisation from ligroin, gave colourless prisms (11·0 g.) of *methyl* 7-*methoxy*-8-(o-*carbomethoxyphenyl*)-1-*naphthoate*, m. p. 137° (Found: C, 71·9; H, 5·2. $C_{21}H_{18}O_5$ requires C, 72·0; H, 5·2%).

The above dimethyl ester was examined as follows : (*a*) 1·5 G., treated for 5 minutes at room temperature with concentrated sulphuric acid, gave a theoretical yield of the lactone of 11-hydroxybenzanthrone-8-carboxylic acid, m. p. 356°, unchanged on admixture with the product obtained by oxidising benzanthrone-8-carboxylic acid with chromic acid. (*b*) Mild fusion with zinc chloride, warming with thionyl chloride, or boiling with phosphoric oxide in nitrobenzene, again effected cyclisation to the lactone. (*c*) 0·5 G. in 10 c.c. of glacial acetic acid was treated with 2 c.c. of concentrated sulphuric acid and maintained at 80° for 15 minutes. On pouring into water, and boiling for 10 minutes with alkali to dissolve lactone, a small residue of *methyl* 11-*methoxybenzanthrone*-8-*carboxylate* remained. This crystallised from alcohol in brilliant yellow needles (0·06 g.; 13%), m. p. 194° (Found : C, 75·4; H, 4·4. $C_{20}H_{14}O_4$ requires C, 75·1; H, 4·5%). The ester (0·56 g.), on being boiled for 5 hours with potassium hydroxide (10 g.) in alcohol (50 c.c.), gave a solution from which only lactone (0·32 g.) and unchanged starting material (0·1 g.) could be isolated.

7-*Methoxy*-8-(o-*carboxyphenyl*)-1-*naphthoic Acid.*—The ester (IV) (1 g.) was boiled for 24 hours with alcoholic potassium hydroxide. Acidification gave a precipitate of 7-*methoxy*-8-(o-*carboxyphenyl*)-1-*naphthoic acid* (0·75 g.; 82%), which crystallised from alcohol in colourless rhombs containing alcohol of crystallisation. After being heated at 150° for 30 minutes, these melted at 239° (Found : C, 70·8; H, 4·4. $C_{19}H_{14}O_5$ requires C, 70·8; H, 4·4%). The acid dissolves in concentrated sulphuric acid to a red solution, being rapidly converted into the lactone. The cyclising agents mentioned above, including a dilute solution of sulphuric acid in acetic acid, also led to the formation of lactone, no other products being isolated.

Alkaline Oxidation of Benzanthrone-8-carboxylic Acid.—The acid (1 g.), sodium hydroxide (1 g.), and potassium permanganate (2 g.) were dissolved in water (150 c.c.), and the mixture boiled for 20 hours. Filtration, followed by acidification, threw out 0·2 g. of unchanged starting material; this was removed, and the clear liquid evaporated almost to dryness. A small yield of *anthraquinone*-1 : 8-*dicarboxylic acid* was obtained, readily soluble in hot water and in alcohol, crystallising from the latter solvent in light yellow octahedra (0·04 g.), m. p. 316—317° (decomp.) (Found : C, 65·0; H, 2·9. $C_{16}H_8O_6$ requires C, 64·9; H, 2·7%). When the acid (0·1 g.), mixed with a trace of copper bronze, was heated for 5 minutes at 320°, and the product sublimed under reduced pressure, neutral yellow needles of anthraquinone were obtained (0·06 g.; 85%), m. p. and mixed m. p. 285°.

Grateful acknowledgement is made to the Carnegie Trust for a Scholarship (to J. L. G.) and a Teaching Fellowship (to H. G. R.), and to Imperial Chemical Industries, Ltd., for a grant.

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[*Received, February* 17*th*, 1937.]