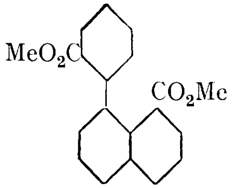
125. 1 : 9-*Benzanthrone*-8-*carboxylic Acid and Dibenzanthronedicarboxylic Acid from* 8-*Bromo*-1-*naphthoic Acid.*

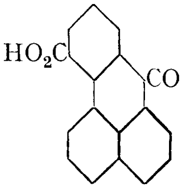
By H. Gordon Rule, William Pursell, and (in part) A. John G. Barnett.

The preparation of 8-bromo-1-naphthoic acid in good yield from naphthalic acid (Rule, Pursell, and Brown, J., 1934, 170) has opened up a ready approach to a number of more complex cyclic compounds, which may be obtained by taking advantage of the reactivity of the halogen atom and the carboxyl group. Several new benzanthrone derivatives thus synthesised are described in this and the following communication.

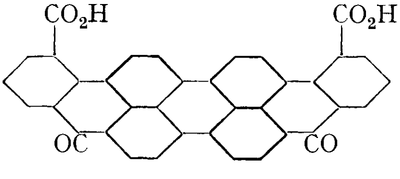
The condensation of methyl 8-bromo-1-naphthoate and methyl *o*-iodobenzoate with the aid of copper bronze led to the isolation of *methyl* 8-(o-*carbomethoxyphenyl*)-1-*naphthoate* (I), which, on being heated with sulphuric acid, was converted into 1 : 9-*benzanthrone*-8-*carboxylic acid* (II). The acid is orange-yellow, dissolves in sulphuric acid to a deep blood-red solution, and in dilute aqueous alkali yields a yellow solution having a brilliant yellowish-green fluorescence. When boiled with quinoline in the presence of copper bronze, it is readily decarboxylated to form benzanthrone.



(I.)



(II.)



(III.)

Dibenzanthrone dicarboxylic acid (III) was obtained in an attempt to convert the very difficultly hydrolysable ester (I) into the corresponding dicarboxylic acid by fusion with alkali : reaction occurred between 265° and 280° to give the deep blue salt of (III); above 280°, carbon dioxide was eliminated. The compound is much more readily prepared from benzanthrone-8-carboxylic acid by fusing with alkali at 230°. The dibenzanthronedicarboxylic acid is a pure blue vat dye, which is, however, not fast to washing owing to the presence of the free carboxyl groups. Crude violanthrone prepared by the alkali fusion of benzanthrone is a mixture of products, which may be more or less completely separated by taking advantage of their different solubilities in alkali and in acetic acid and their different behaviour towards hydrosulphite (cf. Maki, *J. Soc. Chem. Ind. Japan*, 1932, **35**, 577 B). Such methods were not applicable to the dicarboxy-derivative under discussion, but the product obtained by fusing benzanthronecarboxylic acid with alkali is undoubtedly a mixture, as is indicated by the removal of a more soluble salt on treatment with cold saturated sodium bicarbonate solution, in which the disodium dicarboxylate scarcely dissolves. The purified acid was decarboxylated with quinoline and copper bronze, and the product identified as dibenzanthrone (violanthrone A; cf. Maki) by an examination of the absorption spectrum of a sulphuric acid solution.

Among copper bronzes employed in the Ullmann condensations, the most effective were those exhibiting in bulk a red copper colour; less active specimens were of a brownish or brassy tint. Gattermann's precipitated copper powder was found even more active than the best copper bronze.

EXPERIMENTAL.

Methyl 8-(o-*carbomethoxyphenyl*)-1-*naphthoate* * was prepared from 25 g. of methyl 8-bromo-1-naphthoate, 38 g. of methyl *o*-iodobenzoate, and 18 g. of copper bronze, heated for 2 hours in an oil-bath at 215—220°. The product was boiled with 175 c.c. of acetone, and insoluble matter filtered off. Acetone was removed from the filtrate by heating in a vacuum, and the warm syrupy residue treated with 25 c.c. of ether; crystals were immediately deposited. After 12 hours, these were filtered off and washed with 30 c.c. of ether (yield of mixed esters, 22 g., m. p. 115—127°, consisting almost entirely of phenylnaphthyl and dinaphthyl derivatives).

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* Modified preparation by L. A. Bigelow.

From the ethereal mother-liquor, methyl diphenate (5 g.) and the excess of iodo-ester were recovered.

A solution of the mixed esters (22 g.) in 250 c.c. of boiling ligroin was allowed to cool, the clear liquor quickly decanted after 2 hours (longer standing may result in the deposition of methyl dinaphthyldicarboxylate), and the remaining crystals recrystallised from 165 c.c. of ligroin, giving 12·1 g. of methyl 8-(*o*-carbomethoxyphenyl)-1-naphthoate, m. p. 132—133° (Found : C, 75·2; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). A considerable quantity of the ester is retained in the mother-liquors and may be isolated as benzanthronecarboxylic acid by treating the mixed solids with sulphuric acid at 100°.

A small portion of the methyl ester was hydrolysed for 16 hours with concentrated alcoholic potash; 8-(o-*carboxyphenyl*)-1-*naphthoic acid* thus prepared separated from alcohol in colourless plates, m. p. 231—232° (Found : C, 74·0; H, 4·3. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%). The use of less concentrated alcoholic potash for 24 hours gave, in addition to some dicarboxylic acid, a colourless *methyl hydrogen* ester, crystallising from ligroin in compact prisms, m. p. 150—151° (Found : C, 74·4; H, 4·6. $C_{19}H_{14}O_4$ requires C, 74·6; H, 4·3%). When treated in the cold for 30 minutes with sulphuric acid, this compound gave a quantitative yield of benzanthrone-8-carboxylic acid. Hence the unhydrolysed ester group in the ester-acid is that attached to the naphthalene residue, as the isomeric carbomethoxyphenylnaphthoic acid would have been converted into methyl benzanthrone-8-carboxylate under the above treatment (see succeeding paper, p. 573).

1 : 9-*Benzanthrone*-8-*carboxylic acid*, prepared in almost quantitative yield from methyl 8-(*o*-carbomethoxyphenyl)-1-naphthoate by heating it for an hour at 100° in sulphuric acid solution, and precipitated by dilution with water, crystallised from alcohol in yellow leaflets, m. p. 273° (Found : C, 78·6; H, 3·8. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%). (For purification of the acid from traces of colouring matter and for its behaviour towards dehydrating agents, see following paper.)

The acid (0·5 g.) was decarboxylated by solution in dry boiling quinoline (5 c.c.), with subsequent addition of copper bronze (0·5 g.). After 20 minutes' boiling, the liquid was filtered, the residue washed with ether, and the mixed filtrates were washed with dilute acid, followed by dilute aqueous alkali. Evaporation of the ether gave crude benzanthrone (0·25 g.), which gave yellow crystalline benzanthrone, m. p. and mixed m. p. 170—171°, on sublimation.

Dibenzanthronedicarboxylic Acid.—Benzanthrone-8-carboxylic acid was fused for 30 minutes at 225—230° with ten times its weight of potassium hydroxide and a few drops of water. The cooled melt dissolved in water to a blue solution, from which a deep blue solid was precipitated on acidification. The crude acid (1·5 g.) was boiled with alcohol, in which it was practically insoluble, and shaken with a cold saturated solution of sodium bicarbonate (50 c.c.), which extracted an impurity forming a brown solution with a brilliant green fluorescence. The bulk of the *dibenzanthronedicarboxylic acid* remained undissolved as the sodium salt, which was filtered off and dissolved in water, and the clear blue solution acidified (yield, 85% of the theoretical) (Found : C, 79·5; H, 2·8. $C_{36}H_{16}O_6$ requires C, 79·4; H, 2·9%).

The compound was readily decarboxylated with quinoline and copper bronze to give dibenzanthrone, as confirmed by appearance and the absorption spectrum of the product in sulphuric acid solution (concn., 1 in 10,000). For the purpose of comparison, commercial violanthrone was separated by the method of Maki (*loc. cit.*) into " violanthrone A " (dibenzanthrone) and " violanthrone B." In sulphuric acid solution the product obtained by decarboxylation transmitted light over the narrow range 5800—6562 Å., as compared with 5950—6680 Å. for dibenzanthrone. Violanthrone B solution transmitted relatively weakly over the wider range 4500—6000 Å. The small observed differences between the first two solutions may conceivably arise from the presence in the dicarboxylic acid of a small amount of an impurity which eventually appears in the final product as " violanthrone B."

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