

128. *Union of Aryl Nuclei. Part III. 3'-Hydroxymesobenzanthrone.*

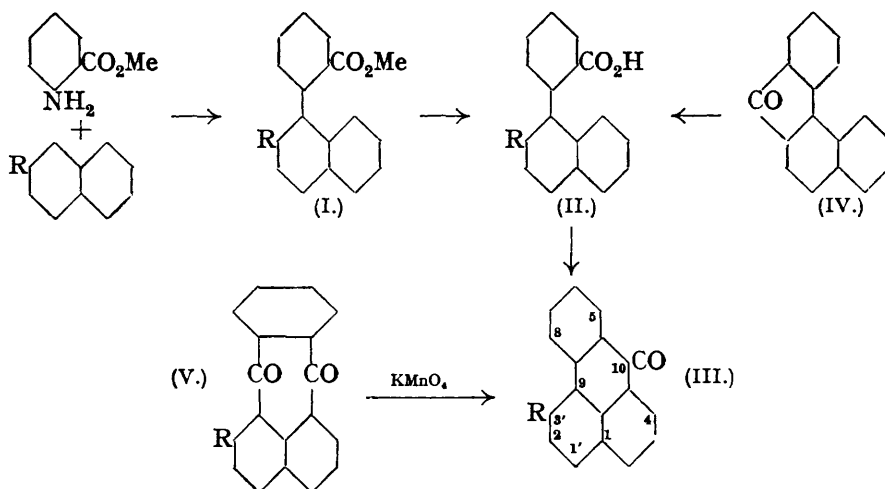
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The extension of the Gomberg reaction to include the use of solid reactants in solution (as shown in Part I) is applied to the reaction between diazotised methyl anthranilate and a solution of 2-methoxynaphthalene in chloroform. The product, *methyl 2-methoxy-1-phenylnaphthalene-2'-carboxylate*, is converted, by the action of aluminium chloride on the acid chloride, into 3'-hydroxymesobenzanthrone, which is methylated to give 3'-methoxymesobenzanthrone. The hydroxybenzanthrone thus obtained is identical with that prepared by the oxidation of 1:8-phthaloyl-2-naphthol with permanganate.

IN Part I (this vol., p. 108) it was shown that the method for the synthesis of biaryl compounds due to Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372) could be extended to include the use of solid reactants dissolved in a suitable solvent; *e.g.*, from diazotised methyl anthranilate and a solution of naphthalene in carbon tetrachloride, methyl *o*- α -naphthylbenzoate (I, R = H) was obtained. The free acid (II, R = H) derived from this ester was converted by ring closure into *mesobenzanthrone* (III, R = H), a reaction which had been carried out previously by Schaarschmidt and Georgeacopol (*Ber.*, 1918, **51**, 1085), who obtained their acid, however, by the alkaline fusion of 3:4-benzfluorenone (IV).

Since the yield of the naphthylbenzoic ester (I, R = H) was low and some of the diazo-compound from the methyl anthranilate obviously reacted with the solvent with formation of methyl *o*-chlorobenzoate, a more reactive component was sought and the present

communication deals with the reaction between diazotised methyl anthranilate and 2-methoxynaphthalene.



In the reaction between diazotised methyl anthranilate and naphthalene there was no indication of condensation at the β -positions in the naphthalene molecule. It is now shown that in the case of 2-methoxynaphthalene condensation takes place to a preponderating extent at position 1, giving rise to *methyl 2-methoxy-1-phenylnaphthalene-2'-carboxylate* (I, R = OMe), which on ring closure by the action of aluminium chloride on the acid chloride yields 3'-hydroxymesobenzanthrone (III, R = OH). Methylation with methyl iodide or methyl sulphate gives 3'-methoxymesobenzanthrone (III, R = OMe). The yield of the ester (I, R = OMe) from 2-methoxynaphthalene was approximately 20%, calculated on the weight of methyl anthranilate. Chloroform was used throughout as solvent, since it appeared to react with the diazo-compound to a smaller extent than did carbon tetrachloride.

A compound stated to be 3'-hydroxymesobenzanthrone (III, R = OH) was obtained by Rieche, Sauthoff, and Müller (*Ber.*, 1932, **65**, 1371) from the oxidation of 1 : 8-phthaloyl-2-naphthol (V, R = OH) with potassium permanganate. The constitution of the phthaloyl- β -naphthol, which was obtained from the condensation of phthalic anhydride with β -naphthol in the presence of sulphuric acid (Rieche and Frühwald, *Ber.*, 1931, **64**, 1603) or aluminium chloride (Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 3546), was questioned by Fieser (*loc. cit.*), but later accepted (*ibid.*, 1933, **55**, 3010). The manner in which 3'-hydroxymesobenzanthrone is obtained on oxidation, however, remains somewhat obscure, but there can now be little doubt about the constitution of this compound, since a repetition of the permanganate oxidation of the phthaloyl- β -naphthol yielded a product identical with that obtained from the methoxynaphthylbenzoic acid (II, R = OMe) resulting from the Gomberg reaction. In addition the preparation of 3'-hydroxymesobenzanthrone by the oxidation of 1 : 8-phthaloyl-2-naphthol with alkaline potassium ferricyanide has also been described (I.G., D.R.P. 555,938), and the product is stated to be identical with that obtainable from 7-hydroxy-1-benzoylnaphthalene.

EXPERIMENTAL.

2-Methoxy-1-phenylnaphthalene-2'-carboxylic Acid (II, R = OMe).—Molten methyl anthranilate (50 g.) was poured with rapid stirring into dilute hydrochloric acid (83 c.c., *d* 1.16, in 40 c.c. of water) and the resulting fine paste was diazotised in the normal manner with aqueous sodium nitrite (25 g. in 40 c.c.). Aqueous sodium hydroxide (30 g. in 100 c.c.) was added gradually to a vigorously stirred mixture of the diazonium solution and a solution of 2-methoxynaphthalene (100 g., prepared by the method of Hiers and Hager, "Organic Syntheses," IX, p. 13) in chloroform (400 c.c.) at 0–5°. Stirring was continued for about 12 hours, during which the temperature was gradually raised to 25°. The chloroform layer was separated, washed with hydrochloric acid

and with water, dried over sodium sulphate, and distilled. The excess of 2-methoxynaphthalene was recovered at 130—150°/15 mm. and crude methyl 2-methoxy-1-phenylnaphthalene-2'-carboxylate was collected at 185—195°/15 mm. as a pale yellow oil, leaving a considerable quantity of high-boiling tar. The ester was boiled under reflux with 20% alcoholic potassium hydroxide, and the solution poured into water, filtered from impurities, and acidified with hydrochloric acid. The precipitated acid (17 g.) was boiled in alcoholic solution (charcoal), repeatedly crystallised from the same solvent, sublimed in a high vacuum, and finally crystallised from absolute alcohol, giving fine colourless needles of 2-methoxy-1-phenylnaphthalene-2'-carboxylic acid, m. p. 218—220° (Found : C, 77.6; H, 5.3. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.0%). The methyl and the ethyl ester, prepared by the Fischer-Speier method, had m. p. 85—86° (Found : C, 78.4; H, 5.3. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%) and 83—84° (Found : C, 78.6; H, 6.1. $C_{20}H_{18}O_3$ requires C, 78.4; H, 5.9%), respectively.

Reactions were also carried out (a) with 60% sulphuric acid and solid sodium nitrite, (b) at temperatures varying from 0° to 25°, and (c) with carbon tetrachloride as solvent, but no improvement in yield resulted.

3'-Hydroxymesobenzanthrone (III, R = OH).—A mixture of 2-methoxy-1-phenylnaphthalene-2'-carboxylic acid (3 g.), dry benzene (40 c.c.), and phosphorus pentachloride (2.3 g.) was boiled under reflux for $\frac{1}{2}$ hour. Finely powdered aluminium chloride (7 g.) was added to the cold mixture, which was then heated at 60° for 2 $\frac{1}{2}$ hours. The product was poured into water, the benzene removed in steam, the residual brownish solid extracted with aqueous sodium carbonate, and the filtered extract acidified with hydrochloric acid. The precipitated 3'-hydroxymesobenzanthrone sublimed in a high vacuum as a bright orange-yellow powder, m. p. 290—292° (Found : C, 82.6; H, 4.15. Calc. for $C_{17}H_{10}O_2$: C, 82.9; H, 4.1%) (cf. Rieche, Sauthoff, and Müller, *loc. cit.*).

3'-Methoxymesobenzanthrone (III, R = OMe).—A mixture of 3'-hydroxymesobenzanthrone (1 g.), methyl iodide (0.6 g.), and potassium carbonate (0.3 g.) was boiled under reflux with acetone (50 c.c.) for 10 hours. After removal of the acetone by distillation, the residue was boiled with water. The yellow insoluble residue (1 g.), on sublimation in a high vacuum, yielded 3'-methoxymesobenzanthrone as a light yellow powder, m. p. 147—148° (Found : C, 82.5; H, 4.8. $C_{18}H_{12}O_2$ requires C, 83.1; H, 4.6%).

1 : 8-Phthaloyl-2-naphthol (V, R = OH).—Two methods of preparation were used, both of which gave low yields. (i) A mixture of β -naphthol (20 g.), phthalic anhydride (20 g.), boric acid (20 g.), and concentrated sulphuric acid (100 c.c.) was heated with stirring at 160° for 6 hours (cf. Rieche and Frühwald, *loc. cit.*). The solution was poured on ice; the yellow precipitate, after being washed with water (yield 4 g.) and sodium carbonate solution and crystallised from glacial acetic acid, had m. p. 195—196°. (ii) When β -naphthol (15 g.) had been added gradually to a fused mass of phthalic anhydride (250 g.) and aluminium chloride (100 g.), the mixture became too stiff to stir even at 250°. The solidified melt was crushed, and the phthaloyl- β -naphthol (8 g.) isolated as described above (cf. Bayer and Co., D.R.P. 298,345; Fieser, *J. Amer. Chem. Soc.*, 1931, 53, 3546; Rieche, Sauthoff, and Müller, *loc. cit.*).

Oxidation of 1 : 8-Phthaloyl-2-naphthol.—An aqueous solution of potassium permanganate (5 g.) was added during 6 hours to a stirred solution of 1 : 8-phthaloyl-2-naphthol (7 g.) in aqueous sodium hydroxide (23 g. in 280 c.c.) heated on the water-bath. Stirring and heating were continued for a further 2 hours, and the solution then cooled, filtered, and acidified. The yellow precipitate was washed and extracted repeatedly with aqueous sodium bicarbonate. Acidification of the extracts precipitated 3'-hydroxymesobenzanthrone as a yellow powder. After purification by sublimation it melted at 290°, both alone and on admixture with the specimen prepared from the methoxynaphthylbenzoic acid. The methyl ethers of the two specimens also showed no depression of m. p.

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