406. *The Nitration of 3-Methoxyacenaphthenequinone and 2-Methoxynaphthalic Anhydride.*

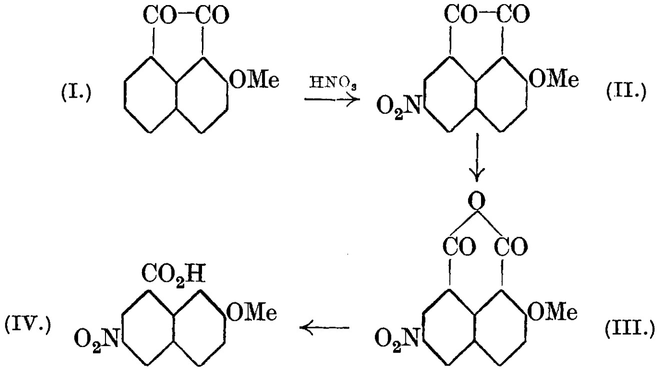
By R. I. Davies, I. M. Heilbron, and F. Irving.

Whereas 4-nitronaphthalic anhydride is obtained when acenaphthenequinone is nitrated and then oxidised with chromic acid (Rowe and Davies, J., 1920, **117**, 1344; Mayer and Kaufmann, *Ber.*, 1920, **53**, 289), the nitration of naphthalic anhydride itself gives the 3-nitro-isomeride (Graebe and Briones, *Annalen*, 1903, **327**, 84). By the nitration of 3-methoxyacenaphthenequinone (I) we have obtained a mononitro-derivative, m. p. 264—265°, which on oxidation with potassium dichromate in glacial acetic acid yields a *nitromethoxynaphthalic anhydride*, m. p. 297—298°, identical with that obtained by the direct nitration of 2-methoxynaphthalic anhydride itself, a result indicating that the substitution reaction is controlled in both cases by the methoxyl in the β-position.

In order to establish the position taken up by the nitro-group in the naphthalene nucleus an attempt was made to remove the carboxyl radicals by distilling the nitromethoxynaphthalic anhydride with soda-lime, but under these conditions extensive decomposition took place. The desired result was, however, achieved in stages. By application of the mercuration process of Leuck, Perkins, and Whitmore (*J. Amer. Chem. Soc.*, 1929, **51**, 1831) a single nitromethoxynaphthoic acid, m. p. 240—241°, was first produced, from which, by heating in boiling quinoline in presence of copper-bronze according to the method applied by Sheppard, Winslow, and Johnson (*J. Amer. Chem. Soc.*, 1930, **52**, 2083) to derivatives of furoic acid, 6-nitro-2-methoxynaphthalene was obtained (Davis, *Chem. News*, 1896, **74**, II, 302). It thus follows that the nitration of 3-methoxyacenaphthenequinone and 2-methoxynaphthalic anhydride gives respectively 7-*nitro*-3-*methoxyacenaphthenequinone* (II) and 6-*nitro*-2-*methoxynaphthalic anhydride* (III).

The mercuration process was also applied to 2-methoxynaphthalic anhydride itself, and led to the sole production of 7-methoxy-1-naphthoic acid in excellent yield. It may be concluded, therefore, by analogy that the decarboxylation of 6-nitro-

2-methoxynaphthalic anhydride by means of mercury leads to 3-*nitro*-7-*methoxy*-1-*naphthoic acid* (IV).



EXPERIMENTAL.

2-Methoxynaphthalic anhydride, previously obtained by Dziewoński and Kocwa (*Chem. Abstracts*, 1929, **23**, 2435) from acenaphthene-3-sulphonic acid, was prepared from 3-methoxyacenaphthenequinone (Staudinger, Goldstein, and Schlenker, *Helv. Chim. Acta*, 1921, **4**, 342). The quinone (15 g.) was boiled in suspension with $K_2Cr_2O_7$ (15 g.) in AcOH (150 c.c.) under reflux for 1½ hr. The product crystallised from AcOH or HNO_3 (*d* 1·4) in colourless needles, m. p. 255° (yield, 85%) (Found : C, 68·5; H, 3·6. Calc. for $C_{13}H_8O_4$: C, 68·4; H, 3·5%).

7-*Methoxy*-1-*naphthoic Acid.*—A solution of sodium 2-methoxynaphthalate, prepared by dissolving the anhydride (10·3 g.) in H_2O (220 c.c.) containing the calc. amount of NaOH, was treated with HgO (10 g.) dissolved in 20% AcOH (27·5 c.c.), and the resulting suspension was boiled under reflux until the solid product was completely sol. in cold alkali (100 hr.). The resulting 8-hydroxymercuri-7-methoxy-1-naphthoic anhydride (16 g.) was washed with H_2O, dissolved in the min. amount of dil. NaOH aq., and the filtered solution stirred with excess of 3*N*-HCl (300 c.c.) on the water-bath for 3 hr. The crude 7-methoxy-1-naphthoic acid crystallised from EtOH aq. in colourless needles (7 g.), m. p. 167—168° (Found : C, 71·9; H, 4·8. Calc. for $C_{12}H_{10}O_3$: C, 71·3; H, 4·9%).

7-*Hydroxy*-1-*naphthoic Acid.*—A suspension of the methoxy-acid (10 g.) in conc. HCl (400 c.c.) was heated under reflux with stirring for 3 hr. The hydroxy-acid separated from the cooled solution and crystallised from H_2O in needles, m. p. 253—254° (cf. Royle and Schedler, J., 1923, **123**, 1641).

8-*Bromo*-7-*methoxy*-1-*naphthoic Acid.*—A suspension of 8-hydroxymercuri-7-methoxy-1-naphthoic anhydride (6 g.) in boiling AcOH (80 c.c.) was treated with a solution of Br (2·8 g.) in NaBr aq., the excess of Br destroyed with bisulphite, and the solution cooled. The *bromo-acid* crystallised from EtOH aq. in pale yellow needles (2·5 g.), m. p. 195° (decomp.) (Found : Br, 27·9. $C_{12}H_9O_3Br$ requires Br, 28·5%).

7-*Nitro*-3-*methoxyacenaphthenequinone* (II).—A solution of 3-methoxyacenaphthenequinone (10 g.) in conc. H_2SO_4 (50 c.c.) was treated with a mixture of HNO_3 (*d* 1·51; 2 c.c.) and H_2SO_4 (4 c.c.) during 1 hr. at 10°. After 1 hr.'s warming at 30° the solution was poured into ice-water, and the product recryst. from AcOH. 7-*Nitro*-3-*methoxyacenaphthenequinone* formed dark yellow needles, m. p. 264—265°, very sparingly sol. in the common org. solvents (Found : N, 5·6. $C_{13}H_7O_5N$ requires N, 5·4%).

6-*Nitro*-2-*methoxynaphthalic Anhydride* (III).—(a) 7-Nitro-3-methoxyacenaphthenequinone, oxidised by the method given for the prepn. of 2-methoxynaphthalic anhydride, gave a product which had m. p. 288—289° even after repeated crystn. from both AcOH and HNO_3 and for complete purification required partial pptn. from Na_2CO_3 aq. and crystn. from conc. HNO_3.

(b) 2-Methoxynaphthalic anhydride in conc. H_2SO_4 was treated with 1 mol. of fuming HNO_3 or KNO_3 under similar conditions to those employed in the nitration of 3-methoxyacenaphthenequinone. 6-*Nitro*-2-*methoxynaphthalic anhydride* crystallised from conc. HNO_3 in almost colourless needles, m. p. 297—298° (Found : C, 57·3; H, 2·7; N, 5·0. $C_{13}H_7O_6N$ requires C, 57·15; H, 2·6; N, 5·1%).

3-*Nitro*-7-*methoxy*-1-*naphthoic acid*, prepared by the mercuration method as described under 7-methoxy-1-naphthoic acid, crystallised from EtOH aq. in brown needles, m. p. 240—241° (Found : N, 5·9. $C_{12}H_9O_5N$ requires N, 5·7%).

6-*Nitro*-2-*methoxynaphthalene*.—When a solution of 3-nitro-7-methoxy-1-naphthoic acid (1 g.) in dry boiling quinoline (1 c.c.) was treated with copper-bronze (0·5 g.), a violent evolution of CO_2 immediately commenced. After 15 min.'s heating, the mixture was cooled, taken up in Et_2O, and the solution washed with dil. HCl and then with Na_2CO_3 aq. and H_2O. The solid obtained after removal of solvent was repeatedly crystallised from EtOH aq., and the pure *ether* obtained in yellow needles, m. p. 134° (Found : N, 6·8. $C_{11}H_9O_3N$ requires N, 6·9%). The nitromethoxynaphthalene was reduced with Sn and HCl, and the product acetylated, 6-acetamido-2-methoxynaphthalene, m. p. 183°, being obtained (cf. Davis, *loc. cit.*).

The authors thank Imperial Chemical Industries Ltd. for a grant.

THE UNIVERSITY, LIVERPOOL. [*Received, September* 10*th*, 1932.]