28. *Nitration of* m-*Methoxycinnamic Acid.*

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Contrary to the predictions of the current theories, 4-*nitro*-3-*methoxycinnamic acid*, m. p. 296°, is the main product of nitration of *m*-methoxycinnamic acid. Its constitution has been established by its oxidation to 4-nitro-3-methoxybenzaldehyde and 4-nitro-3-methoxybenzoic acid, and by synthesis. 6-*Nitro*-3-*methoxycinnamic acid*, m.p. 227°, and 2-*nitro*-3-*methoxycinnamic acid*, m. p. 265°, also formed during the nitration, have been synthesised.

As bromination of *m*-methoxycinnamic acid (Davies and Davies, J., 1928, 602; see also Jones and James, J., 1935, 1602) gives exclusively 6-bromo-3-methoxycinnamic acid, it was hoped that 6-nitro-3-methoxycinnamic acid, required for synthetical work on alkaloids, might be obtained in good yield by its nitration. The main product, however, formed under a variety of conditions was, contrary to the predictions of the current theories, 4-*nitro*-3-*methoxycinnamic acid*, m. p. 296°, giving on oxidation 4-nitro-3-methoxybenzaldehyde and 4-nitro-3-methoxybenzoic acid. 6-*Nitro*- and 2-*nitro*-3-*methoxycinnamic acids* were formed only in small quantities. The constitutions of the three nitro-compounds were established by synthesis.

Much of the older work (see Reiche, *Ber.*, 1889, **22**, 2358) on the nitration of *m*-hydroxycinnamic acid and *m*-methoxycinnamic ester requires revision and correction: this will form the subject of a future communication.

EXPERIMENTAL.

m-Methoxycinnamic acid was nitrated with an excess of nitric acid (*d* 1·42, 1·48, or 1·52), alone or in presence of glacial acetic acid or sulphuric acid. Fuming nitric acid produced dinitration. Mononitration was best carried out as follows: *m*-Methoxycinnamic acid (10 g.) was gradually added to nitric acid (50 c.c., *d* 1·48) at 0° and after 15 minutes' stirring the mixture was poured into cold water. The precipitated acids were washed with water and fractionally crystallised from acetic acid. The first acid to separate (yield, 70—80%) had m. p. 296° (shrinking at 280°) (Found: C, 53·8; H, 4·2; N, 6·5. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·0; N, 6·3%) and formed a methyl ester, m. p. 163°. From the mother-liquor, an acid, m. p. 265°, and an acid, m. p. 227°, were ultimately isolated (methyl esters, m. p. 116° and 128° respectively): separation of the acids in the form of their methyl esters also necessitated tedious fractional crystallisations.

Identification of the Acid, m. p. 296°.—(a) The acid (1 g.) was dissolved in sodium carbonate solution and treated with potassium permanganate (1·2 g. in 20 c.c. of water), and the whole boiled until the colour of the permanganate vanished. On acidification of the cooled filtered solution, 4-nitro-3-methoxybenzoic acid was precipitated; it crystallised from water in long needles, m. p. 233° alone or mixed with an authentic specimen prepared from 4-nitro-3-methoxybenzaldehyde.

(b) The acid (0·5 g.), dissolved in dilute sodium carbonate solution, was gradually treated with a 2% solution of potassium permanganate (45 c.c.) in presence of benzene, in which the resulting aldehyde dissolved as soon as it was formed. When the permanganate was decolorised, the liquids were filtered, the precipitate washed several times with benzene, and the combined benzene solutions dried over sodium sulphate and evaporated. The residue crystallised in needles of 4-nitro-3-methoxybenzaldehyde, m. p. and mixed m. p. 104° (oxime, m. p. 147°).

The above proofs that the acid, m. p. 296°, is 4-*nitro*-3-*methoxycinnamic acid* were confirmed by the synthesis of the acid.

The 6-nitro-compound was obtained in better yields by the nitration of *m*-methoxycinnamic ester than by the nitration of the acid itself.

Synthesis of the Nitro-m-*methoxycinnamic Acids.*—*m*-Hydroxybenzaldehyde was nitrated (Pschorr, *Ber.*, 1901, **34**, 4400) and 4-nitro- and 6-nitro-3-hydroxybenzaldehyde were isolated (Friedländer and Schenck, *Ber.*, 1914, **47**, 3046), and methylated, the former with methyl sulphate and sodium bicarbonate solution, and the latter with methyl sulphate and sodium hydroxide solution. 2-Nitro-3-methoxybenzaldehyde was prepared by nitrating *m*-methoxybenzaldehyde under conditions similar to those used by Hinkel, Ayling, and Morgan (J., 1932, 1115).

The above three nitro-*m*-methoxybenzaldehydes were converted into the corresponding cinnamic acids in almost quantitative yields by the following method: The aldehyde (13 g.), malonic acid (16 g.), pyridine (25 c.c.), and piperidine (1 c.c.) were heated on the steam-bath for 1½ hours and then boiled for 10 minutes. When the product was poured into dilute hydrochloric acid, the cinnamic acid was precipitated. It was crystallised from acetic acid.

4-*Nitro*-3-*methoxycinnamic acid*, m. p. 296° (shrinking at 280°) (Found: N, 6·5. Calc.: N, 6·3%), was converted into its *methyl* ester, m. p. 163° (Found: N, 6·1. $C_{11}H_{11}O_5N$ requires N, 5·9%). 2-*Nitro*-3-*methoxycinnamic acid*, m. p. 265° (Found: C, 53·9; H, 4·3. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·0%), gave a *methyl* ester, m.p. 116° (Found: N, 6·0%). 6-*Nitro*-3-*methoxycinnamic acid*, m. p. 227° (Found: C, 53·7; H, 4·2%), formed a methyl ester, m. p. 128°. In all three cases the m. p.'s of the acid and its ester were not depressed by the corresponding nitration acid and its methyl ester respectively.

4-*Nitro*-3-*hydroxycinnamic acid*, m. p. 248° (Found: N, 6·9. $C_9H_7O_5N$ requires N, 6·7%), and 6-*nitro*-3-*hydroxycinnamic acid*, m. p. 221° (Found: N, 6·8%), also were synthesised by the malonic acid–pyridine method.

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