DERIVATIVES OF SALICYLIC ACID.

Part XII. Nitro-Salicylic Acids and their Methyl Ethers.

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Investigation of the nitro-salicylic acids* has been here continued as their amides and the amides of their methyl ethers were required for a study of their chloralamides. A new method for the synthesis of 3 : 5-dinitro-salicylic acid by nitration of salicylic acid is described; it gives a better yield and does not require the same temperature control as the method of Meldola, Foster and Brightman.¹

The 3 : nitro and 5 : nitro-salicylic acids give a red colour with ferric chloride; the 3 : 5-dinitro-salicylic-acid responds to the test feebly, though its ester and amide give deep red colours.

Unlike the 3 : bromo-salicylic acid, the 3 : nitro-acid, like ortho-cresotic acid, yields an ester by simple alcoholysis. The phenolic group in these three acids is not affected by the phosphorus pentachloride; like the 3 : bromo-acid, no amide of 3 : nitro-salicylic acid could be obtained through the phosphorus pentachloride reaction.

The methyl ethers of these acids are unstable, and the instability is more pronounced with increase in the number of nitro groups. Thus the methyl ethers of 3 : nitro- and 5 : nitro-salicylic acids are hydrolysed by warm but not by cold alkali; while that of 3 : 5-dinitro-salicylic acid is easily hydrolysed by cold alkali. It has thus not been possible to prepare these methyl ethers by direct methylation. These have therefore been prepared by the direct nitration of the methyl ethers of salicylic acid.

The method of Froelicher and Cohen² is found to be better for the 3 : nitro-2-methoxy-benzoic acid, while that of Simonsen and Rau,³ coupled with a new modification for the separation of the two isomeric acids, works well for the preparation of 5 : nitro-2-methoxy-benzoic acid. A new method has been described for the preparation of 3 : 5-dinitro-2-methoxy-benzoic acid from the 0-methoxy-benzoic acid by direct nitration.

Experimental.

3 : Nitro-salicylic acid—was prepared according to Meldrum and Hirwe (loc. cit.).

Calcium-3-nitro-salicylate—crystallised from hot water in needles with two molecules of water. [Found: H₂O, 8.5; Ca, 9.1; C₁₄H₈O₁₀N₂Ca, 2H₂O requires H₂O, 8.2; Ca, 9.1 per cent.]

5 : Nitro-salicylic acid—was prepared according to Meldrum and Hirwe (loc. cit.).

Sodium-5-nitro-salicylate—crystallises from water in yellow microscopic needles with one molecules of water. [Found: H₂O, 8.2; Na, 10.3; C₇H₄O₅Na, H₂O requires H₂O, 8.1; Na, 10.3 per cent.]

3 : Nitro-2-methoxy-benzoic acid—was prepared according to Froelicher and Cohen.

Calcium-3-nitro-2-methoxy benzoate—crystallised from water in yellow cubic plates. [Found: Ca, 9.0; C₁₆H₁₂O₁₀N₂Ca requires Ca, 9.3 per cent.]

Barium-3-nitro-2-methoxy-benzoate—crystallised from water in yellow needles with four molecules of water, which could not be removed as the compound decomposes on heating. [Found: Ba, 22.6; C₁₆H₁₂O₁₀N₂Ba, 4H₂O requires Ba, 22.8 per cent.]

Sodium-3-nitro-2-methoxy-benzoate—crystallised from water in yellowish crystals with three molecules of water. [Found: H₂O, 19.6; Na, 8.3; C₉H₈O₅NNa, 3H₂O requires H₂O, 19.8; Na, 8.4 per cent.]

Methyl-3-nitro-2-methoxy-benzoate.—A mixture of 3 : nitro-2-methoxy-benzoic acid (5 g.), alcohol (absolute; 20 c.c.) and sulphuric acid (conc. 4 c.c.) was kept for twelve hours and heated under reflux for five hours; on dilution a solid was obtained which, crystallised from alcohol in white needles, m.p. 60°. [Found: N, 6.8; C₉H₈O₅N requires N, 6.6 per cent.]

3 : Nitro-2-methoxy-benzamide.—A mixture of 3 : nitro-2-methoxy-benzoic acid (10 g.) and phosphorus pentachloride (15 g.) was heated on a water-bath until a clear liquid is obtained, which on being poured into strong ammonia (sp. gr., 0.888) gave a solid which crystallised from water in yellowish needles, m.p. 124°. [Found: N, 14.3; C₈H₆O₄N₂ requires N, 14.3 per cent.]

5 : Nitro-2-methoxy-benzoic acid—the nitration was carried out according to Simonsen and Rau. M.p. = 160°–161°.

Method for separation.—The mixture of 3 : nitro-2-methoxy and 5 : nitro-2-methoxy-benzoic acids obtained in the nitration of the 2 : methoxy-benzoic acid was neutralised with hot potassium carbonate solution. Potassium-