372. *An Improved Method for the Preparation of the 3-Halogeno-4-nitrophenols.*

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ALL the 3-halogenophenols, when nitrated by the usual method with dilute nitric acid, yield about 50% of the 3-halogeno-6-nitrophenol, which is removed from the reaction mixture by steam distillation. The non-volatile residue is the 4-nitro-isomeride mixed with a considerable amount of tar (Hodgson and Moore, J., 1925, **127**, 1599; 1926, 155; 1927, 630; Hodgson and Nixon, J., 1928, 1879).

In view of the difficulty of obtaining the 3-halogeno-4-nitrophenols, particularly 3-iodo-4-nitrophenol, free from tar, the nitration of the 3-halogenophenyl 3-nitrobenzenesulphonates has now been investigated. These esters were selected because *p*-toluenesulphonyl chloride failed to react with the 3-halogenophenols under conditions under which the 3-nitrobenzenesulphonates were easily and rapidly produced.

The action of excess of nitric acid (*d* 1·5) between − 5° and −10° converted the above sulphonates into the 3-halogeno-4-nitrophenyl 3-nitrobenzenesulphonates in approximately 72% yield. The remainder of the product was the 6-nitro-isomeride, the yield of which is thus considerably diminished by nitration of the sulphonic esters instead of the free phenol. The products in each case were identified by comparison with synthetic specimens produced by the action of *m*-nitrobenzenesulphonyl chloride on the 3-halogeno-4-nitrophenols.

The 3-halogeno-4 : 6-dinitrophenyl 3-nitrobenzenesulphonates were formed quantitatively when a mixed acid was employed at room temperature, with the single exception of 3-iodophenyl 3-nitrobenzenesulphonate, which was only nitrated in the 4-position and resisted further nitration.

Contrary to expectation based on electronic considerations, the nitrated esters were hydrolysed readily by aqueous-alcoholic sodium hydroxide at 25° without displacement of the halogen.

De Kiewiet and Stephen (J., 1931, 84), in describing the preparation of 3-chloro-6-nitro- and 3-chloro-4-nitro-phenol, overlooked the work of Hodgson and Moore (J., 1925, **127**, 1600) on the nitration of *m*-chlorophenol.

EXPERIMENTAL.

Preparation of the 3-*Halogenophenyl* 3-*Nitrobenzenesulphonates*.—A solution of the halogenophenol ($\frac{3}{4}$ g.-mol.) in 20% aqueous sodium hydroxide (42 c.c.) and water (170 c.c.) was heated to 60°, *m*-nitrobenzenesulphonyl chloride (22 g.) added, and the mixture shaken at 60—70° until the product preserved its solidity at and above 70°; it was then washed with water, and crystallised from glacial acetic acid. The following 3-*nitrobenzenesulphonates* were thus prepared; all were colourless: *Phenyl*, plates, m. p. 91—92° (Found: S, 11·5. $C_{12}H_9O_5NS$ requires S, 11·5%); 3-*fluorophenyl*, plates, m. p. 90—91° (Found: S, 10·8. $C_{12}H_8O_5NFS$ requires S, 10·8%); 3-*chlorophenyl*, prisms, m. p. 111—112° (Found: S, 10·1. $C_{12}H_8O_5NClS$ requires S, 10·2%); 3-*bromophenyl*, elongated prisms, m. p. 135—136° (Found: S, 8·7. $C_{12}H_8O_5NBrS$ requires S, 8·9%); 3-*iodophenyl*, elongated plates, m. p. 143—144° (Found: S, 7·7. $C_{12}H_8O_5NIS$ requires S, 7·9%).

Nitration of the 3-*Halogenophenyl* 3-*Nitrobenzenesulphonates*.—The finely powdered 3-halogenophenyl 3-nitrobenzenesulphonate ($\frac{1}{5}$ g.-mol.) was added with stirring to nitric acid (48 c.c., *d* 1·5) at − 10°. After 10 minutes, the clear solution was poured on ice, and the precipitated product filtered off, washed with water, and crystallised from glacial acetic acid. The following 3-*nitrobenzenesulphonates* were thus prepared: 3-*Fluoro*-4-*nitrophenyl*, colourless needles, m. p. 113—114° (Found: S, 9·3. $C_{12}H_7O_7N_2FS$ requires S, 9·4%); 3-*chloro*-4-*nitrophenyl*, colourless elongated prisms, m. p. 104—105° (Found: S, 8·5. $C_{12}H_7O_7N_2ClS$ requires S, 8·9%); 3-*bromo*-4-*nitrophenyl*, colourless needles, m. p. 109—110° (Found: S, 7·6. $C_{12}H_7O_7N_2BrS$ requires S, 7·9%); 3-*iodo*-4-*nitrophenyl*, very pale yellow needles, m. p. 135—136° (Found: S, 6·9. $C_{12}H_7O_7N_2IS$ requires S, 7·1%).

Synthetic Preparation of the Nitro-3-*halogenophenyl* 3-*Nitrobenzenesulphonates*.—The preceding four esters were readily prepared by shaking the corresponding phenols, dissolved in aqueous sodium carbonate, with a slight excess of *m*-nitrobenzenesulphonyl chloride at 90°.

The following 3-*nitrobenzenesulphonates* were prepared by this method and were crystallised from glacial acetic acid : 2-*Nitrophenyl*, colourless needles, m. p. 88—89° (Found : S, 9·8. $C_{12}H_8O_7N_2S$ requires S, 9·9%) ; 3-*nitrophenyl*, clusters of colourless micro-prisms, m. p. 110·5—111·5° (Found : S, 9·7%) ; 4-*nitrophenyl*, colourless plates, m. p. 131—132·5°, almost insoluble in boiling ligroin (Found : S, 9·8%) ; 2 : 4-*dinitrophenyl*, colourless micro-prisms, m. p. 122—123° (Found : S, 8·6. $C_{12}H_7O_9N_3S$ requires S, 8·7%) ; 3-*fluoro*-6-*nitrophenyl*, colourless needles (from methyl alcohol), m. p. 72—72·5° (Found : S, 9·2. $C_{12}H_7O_7N_2FS$ requires S, 9·4%) ; 3-*chloro*-6-*nitrophenyl*, colourless needles, m. p. 99·5—100·5° (Found : S, 8·8. $C_{12}H_7O_7N_2ClS$ requires S, 8·9%) ; 3-*bromo*-6-*nitrophenyl*, colourless needles, m. p. 110—110·5° (Found : S, 7·5. $C_{12}H_7O_7N_2BrS$ requires S, 7·9%) ; 3-*iodo*-6-*nitrophenyl*, pale yellow needles, m. p. 130—131° (Found : S, 7·0. $C_{12}H_7O_7N_2IS$ requires S, 7·1%).

Dinitration of the 3-*Halogenophenyl* 3-*Nitrobenzenesulphonates*.—3-Chlorophenyl 3-nitrobenzenesulphonate (7 g.) was added gradually to a mixture of nitric acid (20 c.c., *d* 1·5) and sulphuric acid (20 c.c., *d* 1·84) at 30°. After 1 hour, the solution was poured on ice, and the 3-*chloro*-4 : 6-*dinitrophenyl* 3-*nitrobenzenesulphonate* filtered off (yield, quantitative), washed with water, and crystallised from glacial acetic acid; it formed almost colourless needles, m. p. 127—127·5° (Found : S, 7·8. $C_{12}H_6O_9N_3ClS$ requires S, 7·9%). In like manner were prepared 3-*fluoro*-4 : 6-*dinitrophenyl* 3-*nitrobenzenesulphonate*, almost colourless needles, m. p. 148—149·5° (Found : S, 8·0. $C_{12}H_6O_9N_3FS$ requires S, 8·3%), and 3-*bromo*-4 : 6-*dinitrophenyl* 3-*nitrobenzenesulphonate*, almost colourless needles, m. p. 137—138·5° (Found : S, 6·9. $C_{12}H_6O_9N_3BrS$ requires S, 7·1%).

Experiments on the nitration of 3-iodo-6-nitrophenyl 3-nitrobenzenesulphonate were unsuccessful, this substance being recovered unchanged.

Hydrolysis of the 3-*Halogeno*-4-*nitrophenyl* 3-*Nitrobenzenesulphonates*.—The following description is typical : The crude nitration product from 3-iodophenyl 3-nitrobenzenesulphonate (16 g.) was dissolved in boiling alcohol (*ca.* 150 c.c.) or cellusolve (*ca.* 100 c.c.), the solution cooled to 25°, and 20% aqueous sodium hydroxide added until no further deepening of the colour of the solution took place. When all the material had dissolved, the solution was acidified with dilute hydrochloric acid, the alcohol or cellusolve removed by distillation, and the mixture steam-distilled until 3-iodo-6-nitrophenol (1·2 g.) ceased to pass over. The non-volatile phenol, which crystallised on cooling, was almost pure 3-iodo-4-nitrophenol (7·4 g.), and no tar was produced in the hydrolysis.

Hydrolysis of the 3-*Halogeno*-4 : 6-*dinitrophenyl* 3-*Nitrobenzenesulphonates*.—These esters were hydrolysed by alkali even more readily than the mononitrated compounds. The 3-halogeno-4 : 6-dinitrophenols were isolated by steam distillation and identified by m. p. and mixed m. p. determinations with authentic specimens. The esters were also hydrolysed by concentrated sulphuric acid at room temperature in 1 week; the phenols were precipitated on dilution with water.

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