NOTE.

The Preparation of 1 : 2 : 3-*Trinitronaphthalene.*

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The ease with which toluene-*p*-sulphon-1-naphthalide is dinitrated in the 2- and the 4-position (Hodgson and Walker, J., 1934, 180) has been utilised for the preparation of 2 : 3 : 4-*trinitrotoluene*-p-*sulphon*-1-*naphthalide* from 3-nitrotoluene-*p*-sulphon-1-naphthalide (Hodgson and Hathway, this vol., p. 21). Homonuclear dinitration was established by oxidation of the above compound to phthalic acid with neutral aqueous potassium permanganate. Subsequent hydrolysis by concentrated sulphuric acid to 2 : 3 : 4-*trinitro*-1-*naphthylamine* (cf. Hodgson and Birtwell, J., 1943, 433), diazotisation by Hodgson and Walker's procedure (J., 1933, 1620), and decomposition by cuprous oxide in ethyl alcohol (Hodgson and Turner, J., 1942, 748) afforded 1 : 2 : 3-*trinitronaphthalene.*

Dinitration of 3-*Nitrotoluene*-p-*sulphon*-1-*naphthalide.*—Nitric acid (3 c.c., *d* 1·42) in which a crystal of sodium nitrite had been dissolved, was added with vigorous stirring at 50° to a finely divided suspension of 3-nitrotoluene-*p*-sulphon-1-naphthalide (6 g.) in glacial acetic acid (12 c.c.), and the mixture heated to 75°; dinitration then occurred, the temperature rising to 100°. On cooling, 2 : 3 : 4-*trinitrotoluene*-p-*sulphon*-1-*naphthalide* (4 g.) slowly crystallised in fine, cream, felted needles, which were filtered off, washed successively with glacial acetic acid, methyl alcohol, and ligroin, and finally dissolved in hot glacial acetic acid, from which it crystallised on cooling in buff-coloured rods, m. p. 190° (Found : N, 12·95. $C_{17}H_{12}O_8N_4S$ requires N, 12·96%).

Orientation of the Nitro-groups. The trinitro-compound (1·2 g.) was boiled for 5 hours with a solution of potassium permanganate (3·5 g.) in water (50 c.c.). Sulphur dioxide was then passed through the chilled acidified solution to dissolve the manganese oxides, and the mixture was heated, filtered from insoluble organic material, and the filtrate evaporated to dryness; the residue of crude phthalic acid was purified by dissolution in ether, removal of the ether from the extract, and crystallisation of the residual phthalic acid from hot water; m. p. and mixed m. p. 195°.

2 : 3 : 4-*Trinitro*-1-*naphthylamine* was formed when a cold solution of the naphthalide (1 g.) in sulphuric acid (5 c.c., *d* 1·84) was heated at 30° for 15 minutes, the mixture poured on ice, triturated with aqueous ammonia, and the free amine (0·7 g.) removed; it crystallised from ethyl alcohol–acetone (1 : 2) in orange-yellow, micro-crystals, m. p. 220° (Found : N, 20·3. $C_{10}H_6O_6N_4$ requires N, 20·2%).

1 : 2 : 3-*Trinitronaphthalene.*—The trinitro-naphthalide (1·3 g.) was stirred into sulphuric acid (7 c.c., *d* 1·84) below 10°, a solution of sodium nitrite (0·3 g.) in sulphuric acid (2 c.c., *d* 1·84) added, and the mixture stirred into glacial acetic acid (25 c.c.) below 20°. Stirring was continued for 30 minutes, after which the diazotised solution was stirred into a suspension of red cuprous oxide (0·8 g.) in ethyl alcohol (50 c.c.). After the reaction had subsided, the mixture was poured on ice (300 g.), filtered, the filtrate steam-distilled to remove volatile compounds, and the flask liquor extracted with ethylene dichloride (100 c.c.) to remove the 1 : 2 : 3-trinitronaphthalene, the extract being washed with aqueous sodium carbonate followed by water. On partial removal of the ethylene dichloride from the dried extract, the 1 : 2 : 3-*trinitronaphthalene* (0·3 g.) was deposited; it recrystallised from chloroform in pale orange parallelepipeds, m. p. 190° (Found : N, 16·0. $C_{10}H_5O_6N_3$ requires N, 16·0%). This compound can be sublimed, and also gives a blood-red colour with aqueous acetone containing sodium hydroxide, but no pronounced coloration with alcoholic potassium hydroxide.

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