

115. Preparation of 1:3-Dinitronaphthalene.

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Details are given for the preparation of 1:3-dinitronaphthalene from 2:4-dinitro-1-naphthylamine by the action of cuprous oxide on the diazo-compound in glacial acetic-sulphuric acid solution.

FAILURE to diazotise 2:4-dinitro-1-naphthylamine with preservation of the nitro-groups (Morgan and Evens, J., 1919, 115, 1126) prevented the preparation of 1:3-dinitronaphthalene from this amine, and it was obtained by Veselý and Dvorák (*Bull. Soc. chim.*, 1923, 33, 323,328) *via* the oxidation of 1:3-dinitrotetralin. The diazotisation method of Hodgson and Walker (J., 1923, 123, 1620) enabled 2:4-dinitronaphthalene-1-diazonium sulphate to be prepared free from 4-nitronaphthalene-1:2-diazo-oxide, and its decomposition by ethyl alcohol gave 1:3-dinitronaphthalene in yields of *ca.* 50%. 1:3-Dinitronaphthalene is a potentially useful intermediate and an improved preparation is now described.

The hydrolysis of 2:4-dinitro-*p*-toluenesulphon-1-naphthalide by concentrated sulphuric acid at room temperature gives 2:4-dinitro-1-naphthylamine in almost theoretical yield; hydrolysis at 70° (Morgan and Evens, *loc. cit.*) or 80° (Hodgson and Smith, J., 1935, 1854) gives a less pure product. The diazonium salt is much more effectually decomposed by cuprous oxide than by ethyl alcohol; this decomposition, however, must be complete, otherwise, when the reaction mixture is poured into water, some 4-nitronaphthalene-1:2-diazo-oxide may be formed (detected by treatment with alcohol; the 4-nitro-2-naphthol thus formed will couple with any unchanged diazo-oxide present). The best ratio of sulphuric acid to glacial acetic acid in the solution of the diazonium salt is *ca.* 1:3, the solution then being not too viscous to prevent the cuprous oxide from reacting with reasonable speed. Freshly precipitated or commercial cuprous oxide may be used. Reaction above 25° appears to promote slight reduction of the nitro-groups, since diazotisable amine has been detected in some cases. Cupric copper, if present in the cuprous oxide, causes conversion of some of the 2:4-dinitronaphthalene-1-diazonium sulphate into 4-nitronaphthalene-1:2-diazo-oxide (Hodgson and Birtwell, this vol., p. 321).

1:3-Dinitronaphthalene is obtainable from 2:4-dinitro-*p*-toluenesulphon-1-naphthalide without isolation of the intermediate 2:4-dinitro-1-naphthylamine.

2:4-Dinitronaphthalene-1-diazonium sulphate is practically unaffected by hydrazine or hydroxylamine sulphate.

EXPERIMENTAL.

Improved Preparation of 2:4-Dinitro-1-naphthylamine.—2:4-Dinitro-*p*-toluenesulphon-1-naphthalide was prepared (Hodgson and Smith, *loc. cit.*) from *p*-toluenesulphon-1-naphthalide (75 g.), washed with water, and stirred into sulphuric acid (200 c.c., *d* 1.84) at such a rate that the temperature could be maintained below 20° by external cooling. After 45 minutes the solution was slowly poured on ice, and the bright lemon-yellow 2:4-dinitro-1-naphthylamine collected, washed with water (10 l.), and dried at 65°. The product had m. p. 238—242° and was therefore almost pure (Hodgson and Smith, *loc. cit.*, give m. p. 242° for the recrystallised compound); yield, theoretical. Alternatively, dried 2:4-dinitro-*p*-toluenesulphon-1-naphthalide was added to sulphuric acid (185 c.c. of acid, *d* 1.84, and 15 c.c. of water), the subsequent procedure being as described above.

Preparation of 1:3-Dinitronaphthalene.—(a) *From 2:4-dinitro-1-naphthylamine.* Finely powdered 2:4-dinitro-1-naphthylamine (23.5 g.) was dissolved in well-stirred sulphuric acid (90 c.c., *d* 1.84) below 10°, and the solution treated with one of sodium nitrite (7.5 g.) in sulphuric acid (35 c.c., *d* 1.84), the temperature being maintained at or below 10°. The mixture was stirred gradually into glacial acetic acid (375 c.c.) kept below 20°, stirring being continued for 30 minutes thereafter. Cuprous oxide (25 g.) was then vigorously stirred into the solution, initially at 5°, during 15 minutes, the temperature rising to 25—30°; after further stirring for 15 minutes, the evolution of gas ceased. The thick brownish-white liquid was stirred into a mixture of ice (500 g.) and water (2 l.), and the precipitated 1:3-dinitronaphthalene collected, washed, and pressed. The moist cake was dissolved in hot pyridine (200 c.c.) and filtered hot from the insoluble copper oxide, which was washed several times with hot pyridine (75 c.c. in all); the hot filtrates, after addition of water (75 c.c.), deposited 1:3-dinitronaphthalene (16 g.), m. p. 146—147°, on cooling; further dilution with water afforded 2 g. more (m. p. 138—140°). Total yield, 18 g. (82%). 1:3-Dinitronaphthalene crystallised from aqueous pyridine in pale yellow parallelepipedes having a silvery lustre, m. p. 148° (Veselý and Dvorák, *loc. cit.*, describe brownish needles, m. p. 144—145°) (Found: N, 12.9. Calc.: N, 12.8%).

(b) *From 2:4-dinitro-*p*-toluenesulphon-1-naphthalide.* The naphthalide (38.7 g.) was dissolved below 10° in sulphuric acid (90 c.c., *d* 1.84) and mixed at this temperature with nitrosylsulphuric acid prepared from sodium nitrite (8 g.) and sulphuric acid (35 c.c., *d* 1.84). This solution was stirred dropwise into glacial acetic acid (375 c.c.) below 20°. The mixture, after being stirred for 30 minutes to complete the hydrolysis of the 2:4-dinitro-*p*-toluenesulphon-1-naphthalide and subsequent diazotisation, was treated with cuprous oxide (25 g.), added during 15—20 minutes; the temperature, which rose to *ca.* 40°, was allowed to fall slowly, evolution of gas ceasing in *ca.* 1 hour. The solution was then poured into ice and water, and the precipitate collected, washed, dried, and extracted with hot ethylene dichloride (250 c.c.). After partial removal of solvent (200 c.c.) from the extract by distillation, 1:3-dinitronaphthalene (14.2 g., m. p. 144—146°) separated; it crystallised from ethylene dichloride (charcoal) in pale yellow needles, m. p. 148°. The mother-liquors (above), on evaporation to dryness, afforded a further 2.9 g., the total yield thus being 17.1 g. (78%).

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