168. *Preparation of 2 : 3-Dinitronaphthalene and of 3-Nitro-2-naphthylamine.*

By Herbert H. Hodgson and Harold S. Turner.

2 : 3-Dinitronaphthalene has been readily obtained by deamination of 2 : 3-*dinitro*-1-*naphthylamine*, and reduced to 3-*nitro*-2-*naphthylamine*. NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine* could not be nitrated, and 2 : 3-dinitro-1 : 4-naphthylenediamine could not be deaminated.

Mononitration of 3-nitroaceto-1-naphthalide by nitric acid (*d* 1·5) below —3° gave 2 : 3-dinitroaceto-1-naphthalide, which was hydrolysed in ethyl alcohol–sulphuric acid to 2 : 3-*dinitro*-1-*naphthylamine*, diazotisation and deamination then yielding 2 : 3-dinitronaphthalene. The m. p. 159° could not be raised to that, 170·5—171° (*Chem. Listy*, 1926, **20**, 509), given by Chudozilov. Monoreduction gave 3-*nitro*-2-*naphthylamine*, which, unlike 2-nitro-1- and 1-nitro-2-naphthylamine, is soluble in dilute hydrochloric acid, behaviour which constitutes evidence in favour of single-bond union between the 2- and the 3-carbon atom of the nucleus.

3-Nitro-2-naphthylamine, like all the nitro-2-naphthylamines, is red, although it exhibits chromoisomerism; contrary to expectation, 2 : 3-dinitro-1-naphthylamine also is red, although both 2-nitro- and 3-nitro-1-naphthylamine are yellow.

Experimental.

2 : 3-*Dinitro*-1-*naphthylamine*.—3-Nitro-1-naphthylamine (10 g.), boiled in glacial acetic acid (90 c.c.) and acetic anhydride (10 c.c.) for 3 minutes, was converted into 3-nitroaceto-1-naphthalide (10·6 g.). This compound (10 g.) was stirred gradually into nitric acid (60 c.c., *d* 1·5) below —3° and the mixture kept at —6° for 90 minutes and then poured on ice (300 g.). The precipitated 2 : 3-dinitroaceto-1-naphthalide (9·0 g.), after one crystallisation from glacial acetic acid, had m. p. 275° (Hodgson and Elliott, J., 1936, 1153, give m. p. 275·5°). It (11 g.) was refluxed with 50% sulphuric acid (35 c.c.) and ethyl alcohol (45 c.c.) for 2 hours and the mixture stirred into ice-water (350 c.c.). 2 : 3-*Dinitro*-1-*naphthylamine* (9·4 g.), precipitated in almost theoretical yield, was washed, dried in a vacuum, and crystallised from methyl alcohol containing 5% of acetone, forming deep red needles, m. p. 160—161° (Found : N, 18·0. $C_{10}H_7O_4N_3$ requires N, 18·0%).

2 : 3-*Dinitronaphthalene*.—A solution of 2 : 3-dinitro-1-naphthylamine (5·0 g.) in glacial acetic acid (35 c.c.) was stirred below 20° into one of sodium nitrite (2·0 g.) in sulphuric acid (15 c.c., *d* 1·84); the diazo-solution was kept for 30 minutes and then run into a suspension of cuprous oxide (8·0 g.) in ethyl alcohol (60 c.c.), the temperature rising to 60°. When the reaction had subsided, a further quantity of cuprous oxide (6·0 g.) was added, the mixture stirred for 10 minutes, water (1 l.) added, and the excess of alcohol and ethyl acetate distilled in steam. 2 : 3-Dinitronaphthalene was obtained from the dried precipitate by extraction with hot ethylene dichloride (50 c.c.) and charcoal, concentration of the extract, dilution with ligroin, and distillation at 10—15 mm. of the brown crystalline solid (1·8 g.) which had separated. Two crystallisations from aqueous acetic acid, distillation at 200°/10—15 mm., and further crystallisations from glacial acetic acid and aqueous acetone gave creamy-white needles, m. p. 159° (Found : N, 12·9. Calc. : N, 12·85%).

1 : 2-Dinitronaphthalene, prepared for comparison, crystallised from glacial acetic acid in stout colourless needles, m. p. 161—162° (Veselý and Dvorăk, *Bull. Soc. chim.*, 1923, **33**, 319, describe pale brown needles, m. p. 158°) (Found : N, 12·9. Calc. : N, 12·8%), depressed to 121—122° by 2 : 3-dinitronaphthalene.

3-*Nitro*-2-*naphthylamine*.—2 : 3-Dinitronaphthalene (1·0 g.), suspended in methyl alcohol (15 c.c.), was refluxed on the water-bath during the dropwise addition of a solution of hydrated sodium sulphide (1·75 g.) and sodium bicarbonate (0·5 g.) in the minimum quantity of water. After boiling for 20 minutes, the mixture was poured on ice (200 g.) and kept for 2 days at 0°; the precipitate was collected and extracted with 10% hydrochloric acid (in 20 c.c. portions) until the extract, on being made alkaline with dilute aqueous ammonia at 0°, ceased to develop colour. The combined extracts were cooled and basified at 0° with dilute aqueous ammonia; after 5 hours, the crude nitro-amine, which had separated in deep red micro-needles (0·32 g.), was collected and dried in a vacuum. 3-*Nitro*-2-*naphthylamine* crystallised from ligroin as a mixture of red and orange-yellow needles, which all became red below the m. p. 86·5° (Found : N, 15·0. $C_{10}H_8O_2N_2$ requires N, 14·9%).

The *picrate*, obtained from the nitro-amine and a slight excess of picric acid in boiling ethyl alcohol, formed grey-green nodules, m. p. 171—172° (decomp. at 205—210°) (Found : N, 17·1. $C_{10}H_8O_2N_2,C_6H_3O_7N_3$ requires N, 16·8%).

3-*Nitroaceto*-2-*naphthalide*, obtained by boiling the nitro-amine (0·1 g.) with glacial acetic acid (1 c.c.) and acetic anhydride (0·15 c.c.) for 2 minutes and pouring the mixture on ice (20 g.), crystallised from aqueous acetic acid (charcoal) in cream needles, m. p. 191·5—192·5° (Found : N, 12·5. $C_{12}H_{10}O_3N_2$ requires N, 12·2%).

NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine*.—Toluene-*p*-sulphon-1-naphthalide (50 g.) in ice-cold aqueous sodium hydroxide solution was coupled with diazotised aniline, and the resulting azo-compound reduced in aqueous-alcoholic medium by the gradual addition of sodium hyposulphite (hydros) in presence of sodium carbonate. After removal of aniline with steam, the light brown precipitate of *N*-monotoluene-*p*-sulphonyl-1 : 4-naphthylenediamine (yield, 44—49 g.; 84—93%) had m. p. 186° after crystallising from aqueous acetic acid (cf. Morgan, E.P. 160,853). NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine* was obtained when the monoacylated compound (85·5 g.) was ground with toluene-*p*-sulphonyl chloride (85 g.), and the mixture heated on the water-bath with water (500 c.c.), sodium carbonate being added as required to remove free acid. After 3 hours' heating, the solid was collected, washed, and extracted, while being heated on the water-bath, with a mixture of 20% aqueous sodium hydroxide (250 c.c.) and water (1500 c.c.). From the filtered extract, the diacylated diamine was precipitated by carbon dioxide as a heavy crystalline powder (93·5 g.; 74·6% yield), which crystallised from glacial acetic acid in pinkish prisms, m. p. 249—250° (Found : N, 6·05. $C_{24}H_{22}O_4N_2S_2$ requires N, 6·00%). It resisted nitration by all the customary methods.

Improved Methods for the Preparation of 2 : 3-*Dinitro*-1 : 4-*naphthylenediamine and Intermediate Compounds*.—*N*-Acetyl-1 : 4-naphthylenediamine (53 g.) was obtained by reduction of 4-benzeneazoaceto-1-naphthalide (80 g.) with sodium hyposulphite (200 g.) in a boiling mixture of ethyl alcohol (360 c.c.) and saturated aqueous sodium carbonate (96 c.c.), followed by passage of steam to remove alcohol and aniline. Acetylation by dissolution in hot glacial acetic acid containing acetic anhydride afforded *NN′*-diacetyl-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, J., 1936, 1764). This compound (10 g.) was stirred during 45 minutes into nitric acid (60 c.c., *d* 1·5) below −5°, and the mixture kept for 2 hours at −5° to −10° and then poured on ice (1000 g.), giving 2 : 3-dinitro-*NN′*-diacetyl-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, J., 1936, 1152). Hydrolysis of the compound (5·0 g.) by 3 hours' refluxing with hydrochloric acid (30 c.c., *d* 1·16) and glacial acetic acid (30 c.c.) gave 2 : 3-dinitro-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, *loc. cit.*), which resisted deamination by the customary methods.

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TECHNICAL COLLEGE, HUDDERSFIELD.

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