54. *Preparation of* 1 : 5- *and* 1 : 8-*Naphthylenediamine and Related Compounds.*

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New methods are described for the preparation of 1 : 5- and 1 : 8-naphthylenediamine, both from 1 : 5- and 1 : 8-dinitronaphthalene separately and also from the mixture of diamines obtained by reduction of a mixture of 1 : 5- and 1 : 8-dinitronaphthalene. Improved methods of preparation of these dinitro-compounds are included.

The preparation of 1 : 5- and 1 : 8-naphthylenediamine from the corresponding dinitronaphthalenes, described somewhat scantily in the literature, is readily effected by iron powder (Hodgson and Marsden, J., 1944, 398) in neutral aqueous suspension containing either ferrous or ferrous ammonium sulphate as catalyst. When a mixture of 1 : 5- and 1 : 8-dinitronaphthalene has been thus reduced, the diamines can be readily separated by preliminary conversion into a mixture of naphthalene-1 : 5- and -1 : 8-di-*p*-toluenesulphonamides, which is either (*a*) treated with aqueous potassium hydroxide to dissolve the 1 : 5-isomeride, or (*b*) extracted with toluene to dissolve the 1 : 8-compound.

Experimental.

1 : 5-*Naphthylenediamine.*—A mixture of pure 1 : 5-dinitronaphthalene (20 g.), iron powder (pin-dust, 60 g.), crystallised ferrous sulphate (6·0 g.), and water (200 c.c.) was refluxed for 3 hours, and then cooled in ice-water with continuous shaking. After filtration, the residue was extracted with boiling alcohol (200 c.c., charcoal), and the extract filtered hot; 1 : 5-naphthylenediamine (7 g.) separated from the filtrate in colourless needles, m. p. 190·5°, after recrystallisation from alcohol or pyridine (Bucherer and Uhlmann, *J. pr. Chem.*, 1909, **80**, 212, give m. p. 189·5°) (Found: N, 17·8. Calc.: N, 17·7%). The diamine was stable when pure and dry, but the presence of moisture promoted oxidation. The diacetyl and the dibenzoyl derivative had m. p. above 360° and 350°, respectively, agreeing with those recorded by Kunckell and Schneider (*Chem.-Ztg.*, 1912, **36**, 1021) and Sachs (*Ber.*, 1906, **39**, 3024).

1 : 5-*Diformamidonaphthalene*, formed by heating the diamine (0·8 g.) in 90% formic acid on the water-bath for 30 mins., was deposited, on cooling, in colourless rods, m. p. 280° after recrystallisation from 90% formic acid (Found: N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%).

1 : 5-*Dibenzylideneaminonaphthalene* separated immediately in fine needles when a solution of the diamine (1 g.) in alcohol (18 c.c.) and glacial acetic acid (6 c.c.) was treated dropwise with benzaldehyde; it crystallised from pyridine in pale yellow rhombs, m. p. 193° (Found: N, 8·45. $C_{24}H_{18}N_2$ requires N, 8·4%).

Naphthalene-1 : 5-*di*-p-*toluenesulphonamide* was formed when 1 : 5-dinitronaphthalene (20 g.) was reduced and extracted as above with alcohol (250 c.c., charcoal), and the hot extract stirred with finely powdered *p*-toluenesulphonyl chloride (20 g.), followed dropwise by pyridine (20 c.c.); it separated in almost colourless needles (22 g.), m. p. 318°, after recrystallisation either from pyridine, diluted subsequently with an equal volume of water, or from nitrobenzene (Found: N, 6·25. $C_{24}H_{22}O_4N_2S_2$ requires N, 6·0%).

Naphthalene-1 : 5-*di*-m-*nitrobenzenesulphonamide*, obtained similarly, crystallised in colourless needles (24 g.), m. p. 302°, from pyridine or nitrobenzene (Found : N, 10·5. $C_{22}H_{14}O_8N_4S_2$ requires N, 6·0%).

These two disulphonamides may also be purified by solution in the minimum quantity of 10% aqueous potassium hydroxide, followed by addition of solid potassium hydroxide until the separation of the crystalline dipotassium salts is complete. The crystalline mass is collected, dissolved in water, and decomposed.

Naphthalene-1 : 5-*di*-p-*toluenesulphondimethylamide* was obtained when the above sulphonamide in 2N-sodium hydroxide was stirred with methyl sulphate for 1 hour; the precipitate, after extraction with 2N-sodium hydroxide to remove any unmethylated compound, crystallised from nitrobenzene in small colourless plates, m. p. 275° (Found : N, 5·8. $C_{26}H_{26}O_4N_2S_2$ requires N, 5·7%).

Naphthalene-1 : 5-*di*-m-*nitrobenzenesulphondimethylamide*, prepared similarly, crystallised from nitrobenzene in small colourless plates, m. p. 315° (Found : N, 10·2. $C_{24}H_{18}O_8N_4S_2$ requires N, 10·1%).

1 : 8-*Naphthylenediamine*.—Pure 1 : 8-dinitronaphthalene (30 g.) was boiled for 3 hours with iron powder (90 g.), ferrous sulphate (9 g.), and water (200 c.c.), alcohol (120 c.c.) and charcoal added, and boiling continued for 30 minutes. The liquid was filtered and cooled in ice-water, and the colourless needles of 1 : 8-naphthylenediamine recrystallised from 30% alcohol; m. p. 66°, in agreement with De Aguias (*Ber.*, 1864, **7**, 309) and Meyer and Müller (*Ber.*, 1897, **30**, 775) (Found : N, 17·8. Calc. : N, 17·7%). The sulphate was precipitated in over 80% yield by extracting the dried residue from the dried reduction residue with boiling ether (1·1) and adding concentrated sulphuric acid in the required amount, or, alternatively, by adding alcohol to the reduction mixture so as to bring the solution to 30% strength, boiling it, filtering it hot, and precipitating the sulphate with dilute sulphuric acid.

Naphthalene-1 : 8-*di*-p-*toluenesulphonamide* was prepared by addition of *p*-toluenesulphonyl chloride (26·5 g., 10% excess) to a hot solution of the diamine (10 g.) in 30% alcohol (200 c.c.) with subsequent addition of anhydrous sodium carbonate until the mixture was just permanently alkaline; the reaction required *ca.* 30 minutes. The sodium derivative which separated (26 g.) was heated with 10% hydrochloric acid (30 c.c.) on the water-bath for an hour; the disulphonamide thus obtained crystallised from toluene in colourless rhombs and from glacial acetic acid in colourless needles, m. p. 207° (Found : N, 5·9. $C_{24}H_{22}O_4N_2S_2$ requires N, 6·07%).

Naphthalene-1 : 8-*di*-m-*nitrobenzenesulphonamide* crystallised from toluene or ethylene dichloride in clusters of rods, m. p. 200° (Found : N, 10·4. $C_{22}H_{14}O_8N_4S_2$ requires N, 10·6%).

Separation of 1 : 5- *and* 1 : 8-*Naphthylenediamine*.—*Method* (1). The mixture of 1 : 5- and 1 : 8-dinitronaphthalene (10 g.) obtained by nitration of naphthalene or 1-nitronaphthalene was reduced as described, the solid residue extracted with boiling pyridine (75 c.c.), the filtered extract treated with *p*-toluenesulphonyl chloride (10 g.), and the mixture heated on the water-bath for 3 hours, cooled, and poured into 15% hydrochloric acid. The precipitate of naphthalene-1 : 5- and -1 : 8-toluenesulphonamide was removed and stirred with water (200 c.c.) during the gradual addition of a solution of potassium hydroxide (10 g.) in water (30 c.c.). The mixture was heated to 75° during 30 minutes, and the two phases then separated by filtration or decantation. The oily phase (? potassium salt) was rendered solid (5·5 g.) by keeping it in contact with hydrochloric acid (15%) on a water-bath for 6 hours or with the cold acid overnight and finally heating on the water-bath for 1 hour; the resulting naphthalene-1 : 8-di-*p*-toluenesulphonamide, crystallised from toluene and then from glacial acetic acid, formed colourless needles, m. p. 207° (Found : N, 5·9%). The filtered or decanted aqueous alkaline phase was acidified with dilute acetic acid, the precipitated naphthalene-1 : 5-di-*p*-toluenesulphonamide (2·6 g.) extracted with 70% acetic acid (20 c.c.), and the solid sulphonamide washed with water and dried; it crystallised from pyridine, on cautious dilution with water, in colourless needles, m. p. 324° (Found : N, 6·3%).

Method (2). The dried mixture of 1 : 5- and 1 : 8-disulphonamides, prepared as above, was boiled with toluene (60 c.c.), and the liquid filtered hot; the filtrate contained almost all of the 1 : 8- and the residue almost all of the 1 : 5-isomeride. Both compounds were purified and crystallised as above.

Improved Preparation of 1 : 5- *and* 1 : 8-*Dinitronaphthalene*.—*Method* (1) *for* 5-*nitro*-1-*naphthylamine and* 1 : 8-*dinitronaphthalene*. 1-Nitronaphthalene (100 g.), dissolved in cold sulphuric acid (350 c.c., *d* 1·84), was nitrated by the dropwise addition of a mixed acid containing nitric acid (37 c.c., *d* 1·42) and sulphuric acid (144 c.c., *d* 1·84) initially at 0°. Three-fourths of the mixed acid were added slowly and the last quarter more rapidly so long as a temperature of 35° was not exceeded. The mixture, from which crystals commenced to separate immediately nitration was complete, was heated gradually until solution had occurred (at 90—100°) and then run in a thin stream into water (1 kg.) containing ice (2 kg.). After 1 hour's stirring, the fine paste (essential for subsequent operations) was removed, washed with water, then with 5% aqueous ammonia until the washings were slightly alkaline, and again with water; finally water was added to bring the volume to 850 c.c. This suspension was heated to boiling with vigorous agitation, and treated with two-thirds of a hot solution of crystallised sodium sulphide (60 g.) and sulphur (15 g.) in water (120 c.c.), the remaining third being added gradually after the initial violent ebullition had abated. The mixture was kept boiling for 30 minutes and cooled, and the residue removed, boiled with hydrochloric acid (100 c.c., *d* 1·16) and water (600 c.c.), washed, and dried. The filtrate was neutralised with ammonia at 0° and kept for 12 hours for the 5-nitro-1-naphthylamine (10 g.) to separate. The residue of 1 : 8-dinitronaphthalene (45 g.), m. p. above 165°, was boiled with benzene (800 c.c.) and charcoal; the cooled filtrate yielded pure 1 : 8-dinitronaphthalene (45 g.), m. p. 170·5°.

Method (2), *for* 1 : 5-*dinitronaphthalene*. The procedure of method (1) was varied at the point where crystals began to separate, in that the mixture was not heated to effect solution before the pouring into water. The coarser neutral paste thus obtained was boiled with water (450 c.c.) during the portionwise addition during 1 hour of finely powdered, crystalline sodium sulphite (85 g.). All the 1 : 8-isomeride passed into solution, the coarser 1 : 5-isomeride being secured from attack.

Alternatively, when the sulphuric acid solution of the dinitro-compounds in method (1) at 90—100° was allowed to cool gradually to 70—80°, almost complete crystallisation of 1 : 5-dinitronaphthalene occurred; this was collected on asbestos and washed with 70% sulphuric acid and with water (yield, 20—30 g.; m. p. 200—205°, raised to 216° by recrystallisation from pyridine). The hot filtrate, which contained almost all the 1 : 8-dinitronaphthalene, was heated again to 90—100°, and run into ice and water, the resulting paste collected, washed as before, mixed with water to bring the volume to 700° c.c. and treated as in method (1) for 30 minutes with a solution of crystallised sodium sulphide (30 g.) and sulphur (7·5 g.) in water (50 c.c.); the hot mixture was cooled and after filtration the residue was extracted with hydrochloric acid as in method (1) to remove 5-nitro-1-naphthylamine (2·4 g.); the residue of 1 : 8-dinitronaphthalene, when crystallised from benzene, had m. p. 166°.

Setting Points of Mixtures of 1 : 5- *and* 1 : 8-*Dinitronaphthalene.*

1 : 5-Compound, %	100	90	80	70	60	50	40	30	20	10	0
1 : 8-Compound, %	0	10	20	30	40	50	60	70	80	90	100
S. p.	216°	196°	180°	168·5°	159°	151°	145°	141°	140°	152°	170°

Quantitative Mononitration of 1-*Nitronaphthalene to show the Distribution of* 1 : 5- *and* 1 : 8-*Dinitronaphthalene.*—1-Nitronaphthalene (5 g., recrystallised from glacial acetic acid) was dissolved in sulphuric acid (25 c.c., *d* 1·84) at 0° and treated during vigorous stirring with a solution at 0° of dried potassium nitrate (2·919 g.) in sulphuric acid (15 c.c., *d* 1·84). The mixture was maintained at 0° throughout the reaction, and kept at 0° for 24 hours before being allowed to warm gradually to room temperature. After filtration (sintered glass), the solid was washed with sulphuric acid (7 c.c., *d* 1·84), and air sucked through it for 1 hour; it was then washed with water and air-dried. The setting point (average of six readings) was 143° and corresponded, as shown by a composition–setting point diagram, to a mixture containing 36% of 1 : 5- and 64% of 1 : 8-dinitronaphthalene. The filtrate, when diluted with water, gave a negligible amount of precipitate, indicating that the solid collected contained the whole of the dinitration product.

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