87. *Preparation of Diazo-naphthols and Nitration of* 4-*Bromoaceto*-1-*naphthalide.*

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Four methods are described for the preparation of diazo-naphthols (internal diazo-oxides), one of which exemplifies the facilitating action of copper salts for the removal of nitro-groups. The nitration of 4-bromoaceto-1-naphthalide is inhibited by urea. Chromoisomerism is exhibited by 4-chloro- and 4-bromo-2-nitro-1-naphthylamine.

The diazotisation of weak bases such as 2 : 4-dinitro-1-naphthylamine in nitrosylsulphuric acid solution only takes place when a weak acid such as acetic or phosphoric acid is added (Misslin, *Helv. Chim. Acta*, 1920, **3**, 626; Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4531; Hodgson and Walker, J., 1933, 1620), indicating that diazotisation and elimination of the nitro-group take place simultaneously when water is added to the mixture. The two processes have now been separated. If glacial acetic acid alone is added, only diazotisation takes place, the diazo-oxide being precipitated on subsequent dilution (Method I). If, however, cupric carbonate is added to the acetic acid (Method II), diazo-oxide formation begins at once, though dilution with water is necessary to obtain the full yield. The excess of nitrous acid used by Morgan and Evens (J., 1919, **115**, 1126) therefore acts instead of the copper carbonate as an oxidising agent, in the absence of which only diazotisation occurs (compare the formation of 1 : 4 : 6-trichloro-3-bromobenzene in the Sandmeyer reaction on 3-bromo-4 : 6-dinitro-1-benzenediazonium sulphate; Hodgson, *J. Soc. Dyers and Col.*, 1926, **42**, 365). Partial neutralisation of the sulphuric acid solution with ammonia to remove the sulphuric acid alone, may be necessary for the isolation of the diazo-oxide (Method III).

Diazo-oxide formation also takes place in glacial acetic acid by the action of sodium nitrite alone at moderate temperatures (Method IV), to be ascertained separately for each individual amine, and previous procedures (Meldola and Eyre, J., 1902, **81**, 988; Orton, *Proc.*, 1902, **18**, 12; Hodgson and Foster, J., 1942, 30) have been modified accordingly; *e.g.*, 4-*iodonaphthalene*-1 : 2-*diazo-oxide* could only be prepared satisfactorily by Method IV.

Addition of excess of urea to the nitric acid used in the nitration of 4-bromoaceto-1-naphthalide (Morgan and Godden, J., 1910, **97**, 1709) should be avoided, as it inhibits the nitration.

The hydrolysis of the 4-halogeno-2-nitroaceto-1-naphthalides by 50% sulphuric acid and ethyl alcohol requires at least 8 hours for completion, but is completed in 90 minutes in a boiling solution of concentrated hydrochloric and glacial acetic acids.

4-Chloro- and 4-bromo-2-nitro-1-naphthylamines exhibit chromoisomerism, crystallising from aqueous pyridine or chlorobenzene in orange-brown needles, and from anhydrous pyridine in yellow needles, which can be changed into the brown variety.

Experimental.

Nitration of 4-*Chloroaceto*-1-*naphthalide.*—4-Chloroaceto-1-naphthalide prepared by addition of sodium chlorate (12 g.) in water (50 c.c.) to a stirred suspension of aceto-1-naphthalide (37 g.) in glacial acetic acid (120 c.c.) and hydrochloric acid (46 c.c., *d* 1·16) below 40° (yield, 28·5 g.; 65%) was suitable for nitration; it crystallised from alcohol in colourless needles, m. p. 187° (Reverdin and Crépieux, *Ber.*, 1900, **33**, 682, give m. p. 186·5°). A suspension of the naphthalide (85 g.) in glacial acetic acid (450 c.c.) was treated with nitric acid (40 c.c., *d* 1·42) at room temperature, and the mixture heated to 40°; reaction was complete in a few minutes at 50—55°. The 4-chloro-2-nitroaceto-1-naphthalide was filtered off (55 g.) from the almost solid mass and washed with glacial acetic acid (50 c.c.) and with cold water. The mother-liquors afforded another 28 g. (total yield, 81%). The material crystallised from alcohol in pale yellow needles, m.p. 220° (Hodgson and Elliott, J., 1935, 1850, give m. p. 219°) (Found : Cl, 13·3 Calc. : Cl, 13·4%).

Nitration of 4-*Bromoaceto*-1-*naphthalide with and without Urea.*—4-Bromoaceto-1-naphthalide was obtained in 95% yield when a solution of aceto-1-naphthalide (56 g.) in glacial acetic acid (360 c.c.) was treated at 18—20° with bromine (48 g.) in glacial acetic acid (192 c.c. of a 25% solution); it was collected (75 g.) after 30 minutes, washed with glacial acetic acid (50 c.c.) and with water, and was then suitable for nitration. It crystallised from alcohol in colourless needles, m. p. 193° (Meldola, *Ber.*, 1878, **11**, 1906, gives m. p. 193°).

4-Bromoaceto-1-naphthalide (75 g.), suspended in glacial acetic acid (320 c.c.), was treated at room temperature with nitric acid (30 c.c., *d* 1·42); reaction began at 50° and was completed at 60—65°. The 4-bromo-2-nitroaceto-1-naphthalide obtained (70 g.; 79% yield), after being washed with glacial acetic acid (100 c.c.) and with cold water, crystallised from alcohol in pale yellow needles, m. p. 231—233° (Morgan and Godden, *loc. cit.*, give m. p. 230°) (Found: Br, 25·8. Calc.: Br, 25·9%).

In a similar experiment in which the nitrating solution contained urea the m. p. of the product indicated that nitration was very incomplete.

Hydrolysis of 4-*Halogeno*-2-*nitroaceto*-1-*naphthalides*.—The naphthalide (25 g.) was refluxed with hydrochloric acid (125 c.c., *d* 1·16) and glacial acetic acid (375 c.c.) for 90 minutes. The amine crystallised on cooling; the total yield was obtained by dilution with water. 4-Chloro-2-nitro-1-naphthylamine (20·2 g.; 96% yield) separated from aqueous pyridine or chlorobenzene in orange-brown needles, m. p. 205° (Hodgson and Elliott, *loc. cit.*, give m. p. 202°) (Found: Cl, 15·7. Calc.: Cl, 15·9%). 4-Bromo-2-nitro-1-naphthylamine (20·2 g.; 93% yield) crystallised from either solvent in orange-brown needles, m. p. 200° (Morgan and Godden, *loc. cit.*, give m. p. 200°) (Found: Br, 29·8. Calc.: Br, 29·9%), and from anhydrous pyridine in bright yellow needles, m. p. 197° (Found: Br, 29·8%).

Preparation of Internal Diazo-oxides (*Diazo-naphthols*).—*Method I* (compare Morgan and Evens, *loc. cit.*). 2 : 4-Dinitro-1-naphthylamine (46·6 g.) was gradually added to sulphuric acid (200 c.c., *d* 1·84) below 10°, followed by sodium nitrite (14·0 g.) in sulphuric acid (100 c.c., *d* 1·84) at such a rate that the temperature did not rise above 10°. The mixture was added to ice-cooled glacial acetic acid (300 c.c.) below 20°, stirred for 30 minutes, and run into water (2 l.) containing ice (1 kg.) during 30 minutes. The precipitated orange-yellow diazo-oxide was filtered off, washed three times with cold water (5 l.), and dried at *ca.* 50°. Yield, 41 g. (95%); m. p. 130—133° (decomp.).

Method II. 2 : 4-Dinitro-1-naphthylamine (7 g.), dissolved in sulphuric acid (30 c.c., *d* 1·84), was treated as above with a solution of sodium nitrite (2·2 g.) in sulphuric acid (15 c.c., *d* 1·84), and the mixture added below 25° to a solution of copper carbonate (15 g.) in glacial acetic acid (120 c.c.). Rapid precipitation of 4-nitronaphthalene-1 : 2-diazo-oxide occurred, which was completed by dilution with water. Yield, 6·1 g. (95%).

Method III. A solution of 4-bromo-2-nitro-1-naphthylamine (26·7 g.) in hot glacial acetic acid (200 c.c.) was chilled rapidly, and the paste added between 10° and 20° to a solution of sodium nitrite (8 g.) in sulphuric acid (56 c.c., *d* 1·84), 25 c.c. of glacial acetic acid being used during manipulation. After 15 minutes' stirring, a mixture of ice and water (300 c.c.) was added, the temperature rising to *ca.* 20°. After removal of a brown precipitate the filtrate was diluted with more ice and water (400 g.) and then, during 1 hour, neutralised in part below 20° by the addition of aqueous ammonia (120 c.c., *d* 0·880) in water (120 c.c.), which is the amount required to neutralise the sulphuric but not the acetic acid. When the addition was not too rapid, 4-bromonaphthalene-1 : 2-diazo-oxide separated as a heavy, orange, granular precipitate (22 g., 90% yield), which was air-dried in the dark; m. p. 120°. Too rapid addition precipitated the compound as a tar, which, however, was slowly transformed into yellow needles with evolution of gas. This method is also admirable for the preparation of 4-chloronaphthalene-1 : 2-diazo-oxide, which is obtained in 90% yield as an orange-yellow compound, m.p. 130°. It is not convenient to prepare 4-iodonaphthalene-1 : 2-diazo-oxide by this procedure, since tar formation during the partial neutralisation could not be prevented, however slowly the ammonia was added.

Method IV (cf. Meldola and Eyre, *loc. cit.*). 4-Iodo-2-nitro-1-naphthylamine (6·3 g.) (Hodgson and Elliott, *loc. cit.*) was suspended in glacial acetic acid (40 c.c.) and stirred at *ca.* 30° for 30 minutes with sodium nitrite (1·6 g.; slight excess); the mixture was then heated to 40—45°, and sodium nitrite (0·2 g.) added to complete the diazotisation, denoted by complete dissolution of the amine. (This further addition was unnecessary in the preparation of 4-chloro- and 4-bromo-naphthalene-1 : 2-diazo-oxides.) The solution was filtered, cooled, and diluted with ice and water, whereby 4-*iodonaphthalene*-1 : 2-*diazo-oxide* was precipitated (5·6 g.; 95% yield), which crystallised from boiling water (very sparingly soluble in the cold) in felted yellow needles, m. p. 142° (decomp.) (Found: N, 9·6; I, 42·7. $C_{10}H_5ON_2I$ requires N, 9·5; I, 42·9%).

4-*Chloronaphthalene*-1 : 2-*diazo-oxide*, prepared in like manner, but at 25—30° throughout (95% yield), crystallised from boiling water in pale yellow, feathery needles, m. p. 138° (decomp.) (Found: N, 6·9; Cl, 17·2. $C_{10}H_5ON_2Cl$ requires N, 6·8; Cl, 17·3%).

4-Bromonaphthalene-1 : 2-diazo-oxide, similarly prepared in 96% yield (initially at room temperature, finally at 40° to complete the dissolution of the amine), crystallised from hot water in yellow needles, m. p. 133° (decomp.) (Orton, *Proc.*, 1902, **18**, 252, gives m. p. 132—133°) (Found: Br, 32·0. Calc.: Br, 32·1%).

Preparation of 4-*Nitronaphthalene*-1 : 2-*diazo-oxide by Method IV*.—2 : 4-Dinitro-1-naphthylamine (4·7 g.), suspended in glacial acetic acid (100 c.c.), was stirred for several hours with sodium nitrite (2 g.) at room temperature, but no diazo-oxide appeared to be formed. When the temperature was gradually raised to 90°, and more sodium nitrite (2—3 g.) added, dissolution to a deep red solution occurred. After filtration, cooling, and dilution with ice-water, 4-nitronaphthalene-1 : 2-diazo-oxide was precipitated as a bright yellow powder (3·5 g.; 81·5% yield), m. p. 120° (decomp.).

The authors thank I.C.I (Dyestuffs) Ltd. for various gifts, and G. Turner, B.Sc., for some analyses.

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[*Received, February 5th*, 1943.]