11. *Reactions of 3-Nitro-1-naphthylamine, including Anil Formation, Bromination, and the Preparation of 1 : 2 : 3 : 4-Tetrabromonaphthalene.*

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3-Nitro-1-naphthylamine readily condenses with aldehydes to form anils, and is di- and not mono-brominated by bromine in chloroform solution; elimination of the amino-group has been effected to give an almost quantitative yield of β-nitronaphthalene.

1 : 2 : 3 : 4-*Tetrabromonaphthalene* has been prepared.

Although 3-nitro-1-naphthylamine is readily mononitrated in the 2-position (Hodgson and Turner, J., 1943, 391), direct bromination in chloroform solution, whether with 1 or 2 equivs. of bromine, always produces 2 : 4-*dibromo-3-nitro-1-naphthylamine*. In this respect 3-nitro- differs from 5-nitro-1-naphthylamine, which is monobrominated in the 2-position (Hodgson and Turner, J., 1942, 723), a result which shows that the 5- exerts a greater direct inhibiting effect than the 3-nitro-group under comparable conditions. 3-Nitro-1-naphthylamine readily condenses with aldehydes to form stable anils. Elimination of the amino-group after diazotisation, and subsequent treatment by the alcohol–cuprous oxide procedure affords an almost quantitative yield of β-nitronaphthalene.

Experimental.

(All m. p.'s are corrected.)

Derivatives of 3-Nitro-1-naphthylamine.—The *benzoyl* derivative, prepared by the Schotten–Baumann reaction in acetone, crystallised from alcohol in lemon parallelepipeds, m. p. 220° (Found : N, 9·6. $C_{17}H_{12}O_3N_2$ requires N, 9·6%). The *toluene*-p-*sulphonyl* derivative, prepared in pyridine solution, crystallised from alcohol in long, colourless needles, m. p. 200° (Found : N, 8·4. $C_{17}H_{14}O_4N_2S$ requires N, 8·2%).

NN′-*Diacetyl-1 : 3-naphthylenediamine* was obtained by reductive acetylation of 3-nitro-1-naphthylamine (1·8 g.) with zinc dust (3 g.) in a mixture of hot acetic anhydride (4 c.c.) and fused sodium acetate (1·6 g.). The hot filtered solutions deposited the diacetyl compound, which crystallised from glacial acetic acid in colourless parallelepipeds, m. p. 264° (Friedländer, *Ber.*, 1895, **28**, 1953, gives m. p. 263°) (Found : N, 11·5. Calc. for $C_{14}H_{14}O_2N_2$: N, 11·6%) ; yield, 0·4 g.

Elimination of the amino-group. 3-Nitro-1-naphthylamine (1·5 g.) was dissolved in glacial acetic acid (15 c.c.), stirred into a solution of sodium nitrite (0·9 g.) in sulphuric acid (10·5 c.c., *d* 1·84) below 20°, and the resulting diazonium solution treated with a mixture of cuprous oxide (1·5 g.) and ethyl alcohol (75 c.c.). After the reaction had ceased, the mixture was either steam-distilled, or diluted with 500 c.c. of water, filtered, and the solid extracted with alcohol (charcoal). Yield of β-nitronaphthalene, 1 g. ; m. p. and mixed m. p. with authentic specimen, 79°.

Anils.—Stoicheiometric proportions of 3-nitro-1-naphthylamine and the aldehyde were dissolved separately in the minimal quantities of glacial acetic acid ; the solutions were then mixed and refluxed. The anil separated on cooling and was recrystallised from glacial acetic acid. The *benzylidene* anil crystallised in small yellow plates, m. p. 122° (Found : N, 10·1. $C_{17}H_{12}O_2N_2$ requires N, 10·2%) ; the o-*nitrobenzylidene* anil, m. p. 194° (Found : N, 13·0. $C_{17}H_{11}O_4N_3$ requires N, 13·1%), the m-*isomer*, m. p. 188° (Found : N, 13·3%), and the p-*isomer*, m. p. 242° (sinters at 235°) (Found :

N, 13·2%), all crystallised in small, yellow parallelepipeds, and the p-*hydroxybenzylidene* anil in long, olive parallelepipeds, m. p. 233° (Found : N, 9·6. $C_{17}H_{12}O_3N_2$ requires N, 9·6%).

Bromination of 3-*Nitro*-1-*naphthylamine.—Attempted monobromination.* When 7 c.c. of a solution of bromine (1 c.c.) in dry chloroform (9 c.c.) were added to a solution of 3-nitro-1-naphthylamine (3 g.) in dry chloroform (20 c.c.), dropwise with stirring, at 40—50°, 2 : 4-dibromo-3-nitro-1-naphthylamine hydrobromide was precipitated; this was removed, basified with ammonia, and the free *amine* (*ca.* 2 g.) crystallised twice from ethyl alcohol (charcoal), forming small, bright yellow plates, m. p. 182° (Found : N, 8·4. $C_{10}H_6O_2N_2Br_2$ requires N, 8·1%). No monobromo-product could be detected.

Dibromination. When 18 c.c. of the above bromine–chloroform solution were employed, the yield of 2 : 4-dibromo-3-nitro-1-naphthylamine obtained was 3·5 g. (almost quantitative). Its *acetyl* derivative crystallised from acetic acid in colourless rhombs, m. p. 202° (Found : N, 7·1. $C_{12}H_8O_3N_2Br_2$ requires N, 7·2%).

Some Halogeno-nitronaphthalenes and -naphthylamines.—1 : 3-*Dibromo*-2-*nitronaphthalene.* A solution of 2 : 4-dibromo-3-nitro-1-naphthylamine (3 g.) in glacial acetic acid (20 c.c.) was stirred below 20° into one of sodium nitrite (0·8 g.) in sulphuric acid (10 c.c., *d* 1·84). After 30 mins., the diazonium solution was stirred into a suspension of cuprous oxide (1 g.) in ethyl alcohol (50 c.c.), and when the reaction had ceased the mixture was poured into ice-water (500 c.c.). The yellowish-white precipitate was filtered off and extracted with ethyl alcohol; from the filtered extract 1 : 3-*dibromo*-2-*nitronaphthalene* separated and, on recrystallisation from ethyl alcohol (charcoal), was obtained in slender, almost colourless parallelepipeds, m. p. 130·5° (Found : N, 4·4; Br, 48·0. $C_{10}H_5O_2NBr_2$ requires N, 4·2; Br, 48·3%); yield, 2 g.

1 : 3-Dibromo-2-naphthylamine was obtained when a solution of this nitro-compound (0·25 g.) in ethyl alcohol (12 c.c.) and water (4 c.c.) was refluxed with sodium hyposulphite (hydros, 0·75 g.) for 60 minutes; inorganic matter was filtered off, and the filtrate concentrated until it deposited long, colourless needles of the amine, m. p. 119·5° (Bell, J., 1932, 2733, gives m. p. 119°) (Found : N, 4·9. Calc. : N, 4·7%); yield, 0·2 g.

1 : 3 : 4-*Tribromo*-2-*nitronaphthalene* was obtained when 2 : 4-dibromo-3-nitro-1-naphthylamine (3·5 g.) was diazotised as above by Hodgson and Walker's method (J., 1933, 1620), and the diazonium solution decomposed by addition, below 20°, to a solution of cuprous bromide (1·5 g.) in hydrobromic acid (10 c.c., *d* 1·7). The tribromo-compound (4·0 g.) which separated crystallised from ethyl alcohol in cream parallelepipeds, m. p. 218° (Found : N, 3·6. $C_{10}H_4O_2NBr_3$ requires N, 3·4%).

1 : 3 : 4-*Tribromo*-2-*naphthylamine*, prepared from the previous nitro-compound (2 g.) by aqueous-alcoholic sodium hyposulphite reduction as above, was obtained in pale straw-coloured plates, m. p. 163° (Found : N, 4·0. $C_{10}H_6NBr_3$ requires N, 3·7%); yield, 1·2 g.

4-*Chloro*-1 : 3-*dibromo*-2-*nitronaphthalene* was prepared by decomposition of the diazonium sulphate from 2 : 4-dibromo-3-nitro-1-naphthylamine (1·5 g.) with a solution of cuprous chloride in hydrochloric acid (*d* 1·16); it separated from ethyl alcohol in almost colourless, spear-shaped crystals, m. p. 198° (Found : N, 3·9. $C_{10}H_4O_2NClBr_2$ requires N, 3·8%); yield, 0·8 g. The corresponding *amine*, obtained by aqueous-alcoholic sodium hyposulphite reduction, as above, of the nitro-compound (0·5 g.), crystallised from ethyl alcohol in fine white needles, m. p. 161° (Found : N, 4·3. $C_{10}H_6NClBr_2$ requires N, 4·2%); yield, 0·3 g.

Preparation of 1 : 2 : 3 : 4-*Tetrabromonaphthalene.*—The diazonium sulphate solution obtained from 1 : 3 : 4-tribromo-2-naphthylamine (1 g.) by Hodgson and Walker's procedure (*loc. cit.*) was decomposed by the cuprous bromide–hydrobromic acid mixture (as above) below 20°, and the whole poured into water; the precipitated brown 1 : 2 : 3 : 4-*tetrabromonaphthalene* crystallised from ethyl alcohol in rosettes of small, pale buff plates, m. p. 196° (Found : Br, 72·0. $C_{10}H_4Br_4$ requires Br, 72%); yield, 0·7 g.

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