115. *Decompositions of Diazonium Salts by Sodium Sulphite and Sodium Acetate. Part II.* 3-*Nitro*-1-*naphthylamine.*

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3-Nitronaphthalene-1-diazonium chloride is decomposed by sodium acetate to give mainly 3 : 3′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol,* and 3-nitronaphthalene-1-diazoacetate is converted almost entirely into 3 : 3′-*dinitro*-1 : 1′-*azonaphthalene* by sodium sulphite.

Previous work on the decompositions of 4-nitronaphthalene-1-diazonium salts by sodium sulphite and sodium acetate (Hodgson, Nicholson, and G. Turner, J., 1944, 15) has now been extended to the decompositions of 3-nitronaphthalene-1-diazonium chloride. In this case the action of sodium acetate on the diazonium chloride forms almost entirely 3 : *3′-dinitronaphthalene-1′* : *2-azo-1-naphthol* with a little 3 : 3′-dinitro-1 : 1′-azonaphthalene and a trace of β-nitronaphthalene; no 3 ; 3′-dinitrodinaphthyl was formed. According to the mechanism discussed for the 4-nitro-isomerides (Hodgson, Nicholson, and Turner, *loc. cit.*), the nitro-group in the *p*-position to the diazo-group restrains the attack of anionoid water at the significant carbon to which the diazo-group is attached and so enables the other simultaneous reactions to occur, whereas the relatively slight influence of the nitro-group in the 3-(*m*-)position cannot prevent the course of the reaction falling mainly into line with that of 3-nitronaphthalene-1-diazonium chloride in the presence of calcium carbonate, where the above azo-compound is the sole product (cf. also Hodgson and Marsden, J., 1943, 379). The velocity of the sodium acetate reaction was considerably less than in the case of the 4-nitro-compound and would appear to indicate that 3-nitronaphthalene-1-diazonium acetate is more stable than its 4-nitro-isomeride. On analogy with the coupling of diazotised amines to 3-nitro-1-naphthylamine (Hodgson and Hathway, this vol., p. 123) and from the insolubility of 3 : 3′-dinitronaphthalene-1′ : 2-azo-1-naphthol in hot aqueous alkalis, it is assumed that the coupling of 3-nitronaphthalene-1-diazohydroxide with 3-nitro-1-naphthol is in the 2-position.

The action of sodium sulphite on 3-nitronaphthalene-1-diazoacetate is to form almost entirely 3 : *3′-dinitro-1* : *1′-azonaphthalene* with but a trace of β-nitronaphthalene, and the mechanism of this reaction, which follows the lines of that previously discussed for the 4-nitro-compound (*loc. cit.*), also appears to involve the intermediate formation of sodium 3-nitronaphthalene-1-diazosulphonate.

EXPERIMENTAL.

Action of Sodium Acetate on 3-Nitronaphthalene-1-diazonium Chloride.—A chilled and filtered solution of the diazonium chloride, prepared by addition of an aqueous solution of sodium nitrite (2·5 g.) with constant stirring to a chilled finely divided suspension of the naphthylamine hydrochloride (from 4·7 of base) in 6% aqueous hydrochloric acid (175 c.c.), was treated with an aqueous solution of sodium acetate (*ca.* 45 g.) in 50% excess over that required to neutralise all the mineral acid present. The solution became red very slowly with simultaneous liberation of nitrogen until eventually a scarlet precipitate resulted, which was filtered off, and dried in a vacuum over concentrated sulphuric acid (yield, 4·4 g.). No 3-nitro-1-naphthol was obtained from the acidified filtrate. The precipitate was treated with steam to remove β-nitronaphthalene (0·02 g.; m. p. and mixed m. p. with authentic specimen, 79°) and successively extracted with boiling ethyl alcohol, boiling acetone, and cold ethyl-alcoholic potassium hydroxide, each of which removed some 3 : *3′-dinitronaphthalene-1′* : *2-azo-1-naphthol*; the azo-naphthol was reprecipitated from the last extract (3 g., 60%) by acidification and when crystallised twice from toluene formed crimson needles, m. p. and mixed m. p. with authentic specimen 125° (Found : N, 14·6. $C_{20}H_{12}O_5N_4$ requires N, 14·4%). Many extractions of another reaction specimen with acetone still left a mixture whose colour reactions, however, showed it to contain a trace of 3 : 3′-dinitro-1 : 1′-azonaphthalene. Since the last compound is attacked by alcoholic potassium hydroxide, the residue from the former set of extractions did not give the colour reactions found before the use of the alcoholic alkali. No 3 : 3′-dinitro-1 : 1′-dinaphthyl was ever found in any of the extractions, and the bulk of the reaction mixture appeared to be the above azonaphthol, since more was still forthcoming after the 60% had been removed by further extractions with the cold alcoholic alkali.

Action of Sodium Sulphite on 3-Nitronaphthalene-1-diazoacetate.—3-Nitro-1-naphthylamine (4·7 g.) was diazotised as above, and the chilled and filtered solution of the diazonium chloride at 0° was treated rapidly with an aqueous solution of sodium acetate (*ca.* 45 g.) and then immediately with a solution of sodium sulphite (2·5 g.) in water (125 c.c.) containing ice. (Speed is essential in order to obviate the reactions caused by sodium acetate alone.) Nitrogen was evolved, but no sulphur dioxide, and the solution, which had assumed an orange colour on the addition of sodium acetate and sodium sulphite, began to redden gradually as a solid separated. If collected too soon and dried, the precipitate exploded on heating, showing the presence of diazosulphonate. No 3-nitro-1-naphthol could be detected in the colourless filtrate, but both filtrate and precipitate afforded a small amount of β-nitronaphthalene (*ca.* 0·1 g. in all) when steam-distilled; when crystallised from ethyl alcohol, this had m. p. and mixed m. p. 79° with an authentic specimen. The residue (4·4 g.) was removed and dried at 100°, but when boiled with 5% aqueous sodium hydroxide in order to remove any naphthol, the compound had considerably deteriorated; so it was first refluxed for 1 hour with glacial acetic acid (200 c.c.) and the mixture filtered hot; the residue was then refluxed with nitrobenzene (20 c.c.) and charcoal for 2 hours and filtered hot. On cooling 3 : *3′-dinitro-1* : *1′-azonaphthalene* (2 g.) separated in lustrous red-brown needles, which were removed, washed with light petroleum, and dried at 200°; m. p. 315° (Found : N, 15·3. $C_{20}H_{12}O_4N_4$ requires N, 15·1%); with concentrated sulphuric acid they afforded a Prussian-blue colour which was permanent for days, and changed to bright yellow on dilution with water. No other substance except 3 : 3′-dinitro-1 : 1′-azonaphthalene was recovered from the glacial acetic acid extract. The compound was sparingly soluble in acetone, and the solution gave an intense emerald colour with aqueous sodium hydroxide; prolonged boiling with alcoholic potassium hydroxide produced a brown powder which did not respond to the concentrated sulphuric acid test above. Reductive acetylation (see Hodgson and Nicholson, J., 1940, 206) gave 1 : 3-diacetylnaphthylenediamine, m. p. and mixed m. p. with authentic specimen, 263° (Friedländer, *Ber.*, 1895, **28**, 1953, gives m. p. 263°) (Found : N, 11·7. Calc. : N, 11·5%).

Preparation of 3 : 3′-Dinitronaphthalene-1′ : 2-azo-1-naphthol.—3-Nitro-1-naphthylamine (1·8 g.) was diazotised as described above, and the filtered solution stirred at 0° into one of 3-nitro-1-naphthol (2 g.) in water (100 c.c.) containing sodium hydrogen carbonate (5 g.). Immediate precipitation of the dye occurred, and after 30 minutes it was filtered off, washed, and dried; recrystallisation from toluene with addition of light petroleum afforded crimson needles, m. p. 125° (Found : N, 14·6%), which gave a blue-green colour with concentrated sulphuric acid changing to scarlet on dilution; the scarlet solution in acetone changed to claret with aqueous sodium hydroxide, and the violet solution in alcoholic potassium hydroxide remained unchanged on boiling. Alternatively, this compound was obtained when 3-nitronaphthalene-1-diazonium chloride was allowed to decompose at room temperature in the presence of calcium carbonate (cf. Hodgson and Marsden, *loc. cit.*).

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