8. *Decomposition of the Diazonium Salts of 4-Nitro-1-naphthylamine by Sodium Sulphite and Sodium Acetate. Preparation of 4 : 4′-Dinitro-1 : 1′-azonaphthalene.*

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4-Nitronaphthalene-1-diazonium chloride or sulphate is decomposed by sodium sulphite to give mainly 4 : 4′-*dinitro*-1 : 1′-*azonaphthalene* (10—20%) and 4 : 4′-dinitro-1 : 1′-dinaphthyl (*ca.* 50%). Sodium acetate alone initiates an oxidation–reduction reaction from which the above products result, and also a simultaneous decomposition by water or hydroxyl ions to give eventually 4 : 4′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol*. If excess of sodium acetate is added before the sodium sulphite, the product is almost entirely 4 : 4′-dinitro-1 : 1′-azonaphthalene.

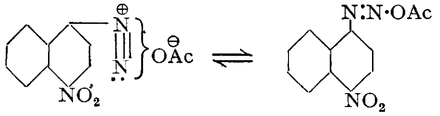
Sulphites in neutral or alkaline solution act on diazo-compounds to give diazosulphonates, Ar·N:N·SO$_3$M, where M is an atom of a univalent metal or its equivalent. This reaction, one of the most general and reliable of those of the diazo-compounds, rarely fails, and crystalline, stable, and easily isolated salts are nearly always obtained. Naphthalene-α- and -β-diazonium salts are among the few exceptions, αα′- (Lange, D.R.-P. 78,225; Friedländer, Vol. 4, 1016) and ββ′-azonaphthalene (Hantzsch and Schmiedel, *Ber.*, 1897, **30**, 80) being formed respectively when these substances are treated with sodium sulphite.

It appeared of interest, therefore, to ascertain whether the sulphonates of substituted diazonaphthalenes would react like the parent compounds, and also to elucidate the mechanism of the reaction in the naphthalene series. The procedure adopted was similar to that of Lange; 4-nitro-1-naphthylamine was diazotised either in hydrochloric acid or by Hodgson and Walker's method (J., 1933, 1620), sodium acetate added in excess of the amount required to react with all the mineral acid, and the requisite amount of an aqueous solution of sodium sulphite then stirred rapidly into the mixture. Reaction commenced immediately, with brisk evolution of nitrogen and precipitation of a mixture of 4 : 4′-*dinitro*-1 : 1′-*azonaphthalene* and sodium 4-nitronaphthalene-1-diazosulphonate; the latter disappeared after several hours, with formation of the former. Only a small amount of 4-nitro-1-naphthol was produced by a side reaction, and in so far as the sulphonate was decomposed, the reaction was nearly quantitative. No azo-dye was formed (compare below), and no α-nitronaphthalene could be detected when either the precipitate or the filtrate therefrom was steam-distilled, the filtrate, however, affording a little more 4 : 4′-dinitro-1 : 1′-azonaphthalene.

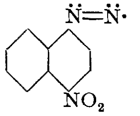
When only sodium acetate was allowed to react with the above diazonium solution, the colour rapidly changed to deep yellow, and after a few minutes formation of a red precipitate occurred and continued for several hours until decomposition of diazoacetate was almost complete. This precipitate consisted mainly of 4 : 4′-dinitro-1 : 1 -dinaphthyl, 4 : 4′-dinitro-1 : 1′-azonaphthalene (I), and 4 : 4′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol* (II), a small amount of naphthalene-1 : 4-diazo-oxide and unidentified oxidation products.

Finally, if sodium sulphite reacts alone with the mineral acid solution of the diazonium compound, there is violent evolution of sulphur dioxide and nitrogen, and formation of numerous products, including 4 : 4′-dinitro-1 : 1′-azonaphthalene (10—20%), 4 : 4′-dinitro-1 : 1′-dinaphthyl, α-nitronaphthalene, sodium 4-nitronaphthalene-1-diazosulphonate, and unidentified substances. No azo-dye (II) was produced.

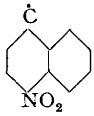
From these experiments it follows that, although 4 : 4′-dinitro-1 : 1′-azonaphthalene is formed whatever the variations, yet a good yield is obtained only when addition of excess of sodium acetate precedes that of sodium sulphite. The mechanism of the latter reaction would appear to be initial formation of an equilibrium mixture of 4-nitronaphthalene-1-diazonium acetate (III*a*) and 4-nitronaphthalene-1-diazoacetate (III*b*), followed by reduction of (III*a*) by electron acceptance from the sodium sulphite to the radicals (IV) and (V), which then unite to form the azo-compound (I). The equilibrium mixture, (III*a*) $\rightleftharpoons$ (III*b*), would then continue to replace (III*a*) until all had reacted. The presence of a very small amount of 4-nitro-1-naphthol would appear to be due to the usual decomposition of diazonium salts by aqueous acids, and the absence of azo-dye (II) would be explained by the slow rate of coupling of the diazo-acetate (III*b*) compared with its rapid rearrangement to (III*a*) and subsequent decomposition as above.



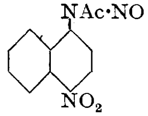
(III*a*.) (III*b*.)



(IV.)



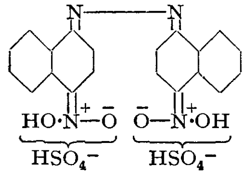
(V.)



(VI.)

When only sodium acetate is added to the diazonium salt solution, the equilibrium (III*a*) $\rightleftharpoons$ (III*b*) will first be set up, but the following simultaneous reactions then occur : (1) Decomposition of (III*a*) by anionoid water or hydroxyl ions in the normal manner to form 4-nitro-1-naphthol, which will then couple with (III*b*) to form azo-dye (II). (2) Decomposition of (III*a*) by an oxidation–reduction process, doubtless facilitated by the equilibrium disturbance necessitated by reaction (1), whereby radicals (IV) and (V) result on the one hand, and oxidation products on the other. Combination of (IV) and (V) will afford (I), whereas union of two (IV) affords 4 : 4′-dinitrodinaphthyl. The latter reaction is closely allied to those reported by Hodgson and Marsden (J., 1940, 208), and by Elks, Haworth, and Hey (J., 1940, 1284) for the preparation of biaryl compounds. The oxidation products were all soluble in acetone. After being kept overnight, the sodium acetate mixture still contained undecomposed diazo-compound, although coupling with alkaline β-naphthol was very slow and might well indicate the presence of the *anti*-form of (III*b*), or even the nitrosoamine form (VI). Hydrochloric acid, however, at once converts the slow-coupling compound into 4-nitronaphthalene-1-diazonium chloride.

The most complex case is when sodium sulphite is added alone to the mineral acid solution of the diazonium salt, since there is now present free sulphur dioxide, which could not be detected when the solution had been previously saturated with sodium acetate. About 25% of the product, extracted by boiling alcohol, melted below 200°, but could not be purified. Also, after several days the mixture still contained undecomposed sulphonate, which could be reoxidised to 4-nitronaphthalene-1-diazonium salt, and subsequently coupled with alkaline β-naphthol to give 4′-nitronaphthalene-1′ : 1-azo-2-naphthol (VII).



(VIII.)

4 : 4′-Dinitro-1 : 1′-azonaphthalene gives a bright pure blue colour with concentrated sulphuric acid, which suggests that salt formation has produced a di-indamine-like structure (VIII). Dilution with water changes the blue to a bright yellow, and these colours afford a characteristic qualitative test for the presence of the azo-compound. The great stability of (I) was also shown by a marked tendency to sublime when heated.

In all the reactions described the formation of 4 : *4′-dinitronaphthalene-*1′ : 2-*azo*-1-*naphthylamine* (IX), though expected, was never observed.

EXPERIMENTAL.

Action of Sodium Sulphite on 4-*Nitronaphthalene*-1-*diazonium Chloride* (*or Sulphate*).—4-Nitro-1-naphthylamine (4·7 g.) was ground with hydrochloric acid (10 c.c., *d* 1·16) and water (15 c.c.), ice (5 g.) added, and a solution of sodium nitrite (2 g.) in water (10 c.c.) stirred into the mixture as rapidly as possible. Most of the paste passed into solution, and after a further addition of water (10 c.c.), the liquid was filtered and treated at 0° with hydrated sodium sulphite (4 g.) in water (20 c.c.). Sulphur dioxide and nitrogen were evolved, and after being kept cold overnight, the red-brown solid (4—5 g.) was collected and washed with cold water until the washings were only pale yellow. The filtrate did not couple with alkaline *β*-naphthol, but did so after cautious treatment with bromine water, or with potassium chromate preceded by neutralisation, to give 0·3 g. of 4′-nitronaphthalene-1′ : 1-azo-2-naphthol (VII), thereby showing the presence of unchanged sulphonate; when excess of bromine water is used, 4-nitronaphthalene-1-diazoperbromide is precipitated. If the initial reaction mixture was kept for 3 days before the filtrate was oxidised and coupled with alkaline *β*-naphthol, the weight of (VII) decreased to 0·2 g., indicating a very gradual decomposition of the diazosulphonate. Steam distillation of the red-brown solid removed *a*-nitronaphthalene (0·12 g., *i.e.*, 2—3%), and the flask liquor still contained diazosulphonate, as established by its oxidation with bromine water and hydrochloric acid to 4-nitronaphthalene-1-diazonium chloride.

After steam distillation, the red-brown solid had m. p. 145—150°; extraction by ethyl alcohol (Soxhlet) removed 25% of it, and the residue then had m. p. 229°; the extract on cooling deposited a microcrystalline mixture, m. p. 140—152° (Found : N, 11·4%), but no constituent could be identified. Boiling 8% aqueous sodium hydroxide also extracted about 25%. The residue from the alcoholic extraction was extracted by acetone (Soxhlet), a further 50% being removed, and the m. p. of the residue rising to 318—320°. This 4 : *4′-dinitro-*1 : 1′-*azonaphthalene* crystallised from boiling nitrobenzene in short red needles, m. p. 334° (Found : N, 15·3. $C_{20}H_{12}O_4N_4$ requires N, 15·1%), almost insoluble in boiling alcohol, slightly soluble in boiling glacial acetic acid to give a yellow solution, and sparingly soluble in acetone and boiling benzene or chlorobenzene; its colour reactions are described above and in the table. When carefully heated to the m. p., preferably in a vacuum, this azo-compound gave a sublimate of orange needles, m. p. 334°; and alcoholic potassium hydroxide apparently reduced it very readily to a chocolate-brown powder which no longer gave a blue colour with concentrated sulphuric acid, indicating that the nitro-groups had been attacked.

The acetone extract (above), when concentrated, deposited micro-crystals of impure 4 : 4′-dinitro-1 : 1′-dinaphthyl, m. p. 230—240°, raised by several recrystallisations from acetone and benzene to 246° (Found : N, 8·3. Calc. : N, 8·1%). The fraction removed by acetone, when refluxed with boiling glacial acetic acid containing a little concentrated hydrochloric acid and treated with zinc dust in small quantities until a clear solution was obtained, afforded a small amount of 4 : 4′-di(acetamido)-1 : 1′-dinaphthyl, which crystallised from the hot filtered solution on cooling; m. p. 364° (Cumming and Howie, J., 1932, 530, give m. p. 363—364°) (Found : N, 7·8. Calc. : N, 7·6%). No colour reactions (see **table**) were obtained for (II).

Colour Reactions of the Azo-compounds described.

Compound.	Conc. H_2SO_4.	$COMe_2$, followed by NaOH.	Alcoholic KOH.
(I), m. p. 334°	Pure blue, with yellow halo on standing. Dilution with water changes blue to bright yellow	Very sparingly soluble in acetone. No colour when NaOH added	Insoluble but rapidly reduced, especially on heating, to a chocolate-brown powder
(II), m. p. 278°	Initial blue-violet, changing to red-violet which persists on addition of water	Red, changing to blue-violet with NaOH	Permanganate-violet solution, unchanged on gentle heating
(VII), m. p. 258°	Purple, but bluer than (II). Vanishes on addition of water	Scarlet, changing to reddish-blue. Red on dilution	Violet
(IX), m. p. 274°	Initial blue, changing to red-violet and purple. Colour vanishes on addition of water	Scarlet solution, changing to blue-green with NaOH, and to green on standing	Blue-violet, changing to blue and then to deep green on heating

Action of Sodium Acetate on 4-*Nitronaphthalene*-1-*diazonium Chloride* (*or Sulphate*).—A solution of the diazonium chloride, obtained as above from 4-nitro-1-naphthylamine (4·7 g.), was mixed rapidly with a solution of sodium acetate in amount sufficient to provide 50% excess over the hydrochloric acid. The deep yellow solution produced began to redden rapidly after a few minutes and then to deposit a dull maroon-brown precipitate, m. p. 250—256° (Found : N, 9·2%), which crystallised from nitrobenzene in a mixture of micro-crystals, m. p. 288—290° (with red sublimate of m. p. 280°). This mixture gave colour reactions for both (I) and (II); and although several recrystallisations from nitrobenzene failed to effect a clear separation, nevertheless the m. p. was raised to 316°. When the mixture was heated in the vacuum sublimator, (I) was obtained pure in small quantity as an orange sublimate, m. p. 334° (Found : N, 15·3%), but the red sublimate of (II) was admixed with (I). Of the initial precipitate above, boiling alcohol extracted only *ca.* 5—10%, and this extract on cooling deposited micro-crystals of 4 : 4′-dinitro-1 : 1′-dinaphthyl, which, when recrystallised several times from benzene or glacial acetic acid, had m. p. 246° (Found : N, 8·3. Calc. : N, 8·1%). Subsequent extraction with acetone (Soxhlet) removed *ca.* 50% more of the mixture, the final residue (40%) having m. p. 292° (Found : N, 14·1%). The acetone extract on concentration deposited 4 : 4′-dinitro-1 : 1′-dinaphthyl, m. p. 200—240°, raised to 246° after several recrystallisations from acetone and benzene (Found : N, 8·2%), but the compounds still dissolved in the acetone could not be resolved and were probably the oxidation products of the original oxidation–reduction process.

When either the initial product or the residue after acetone extraction was shaken vigorously for a few seconds with alcoholic potassium hydroxide, and the liquid rapidly filtered and rendered acid, 4 : 4′-*dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol* (II) was precipitated; after two crystallisations from nitrobenzene it was obtained in short, red parallelepipeds, m. p. 278° (Found : N, 14·5. $C_{20}H_{12}O_5N_4$ requires N, 14·4%). The undissolved part containing the 4 : 4′-dinitro-1 : 1′-azonaphthalene was attacked by the alcoholic potash and no longer gave the colour reactions of (I). When the reaction product with sodium acetate was treated in the cold with 20 times its weight of fuming nitric acid (*d*, 1·5), kept for 20 minutes, and then poured on ice, the precipitate contained 2 : 4-dinitro-1-naphthol and the filtrate from it coupled with alkaline β-naphthol to give (VII).

This reaction with sodium acetate started fairly rapidly but soon became slow, and a solution of the diazonium chloride was always obtained on acidification with hydrochloric acid after precipitation had practically ceased. Only a small amount of naphthalene-1 : 4-diazo-oxide was formed, which, when dissolved in a mixture of glacial acetic and sulphuric acids, was deaminated to α-naphthol by alcoholic cuprous oxide (Hodgson and H. S. Turner, J., 1942, 748).

Action of Sodium Sulphite on 4-*Nitronaphthalene*-1-*diazoacetate* (in part with J. Habeshaw).—4-Nitro-1-naphthylamine (18·8 g.) was diazotised as above, and also by the method of Hodgson and Walker (*loc. cit.*) : the amine was dissolved in glacial acetic acid (188 c.c.), the solution added below 20° to sulphuric acid (60 c.c., *d* 1·84) in which sodium nitrite (7 g.) had been dissolved, and ice (600 g.) added. Both diazo-solutions were rapidly treated with an aqueous solution of sodium acetate in 50% excess over that required to react with all the mineral acid, and then as quickly as possible mixed with a solution of neutral sodium sulphite (10 g.) in water (500 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 a solid separated, the light orange colour of which deepened on keeping. If filtered off too soon and dried, the precipitate exploded on heating, showing the presence of diazosulphonate, but after being kept overnight, when filtered off and dried (15·9 g.), it had m. p. 305—312°. The deep red filtrate contained a little 4-nitro-1-naphthol, and on heating deposited a small amount of 4 : 4′-dinitro-1 : 1′-azonaphthalene. No α-nitronaphthalene could be obtained by steam distillation of either filtrate or precipitate, but a little 4-nitro-1-naphthol was extracted from the latter by 10% aqueous sodium hydroxide; the residue of almost pure 4 : 4′-dinitro-1 : 1′-azonaphthalene then crystallised from nitrobenzene in red needles, m. p. 334° (Found : N, 15·3%); reductive acetylation (see Hodgson and Nicholson, J., 1940, 206) gave 1 : 4-diacetylnaphthylenediamine in colourless crystals, m. p. 304° (Kleeman, *Ber.*, 1886, **19**, 334, gives m. p. 303—304°) (Found : N, 11·7. Calc. : N, 11·6%). The colour reactions for (II) were not observed.

Preparation of 4 : 4′-*Dinitronaphthalene*-1′ : 2-*azo*-1-*naphthol* (II).—4-Nitro-1-naphthylamine (1·8 g.) was diazotised as described above, and the filtered solution stirred at 0° into one of 4-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, dried, and recrystallised from nitrobenzene, separating in copper-coloured needles, m. p. 278° (Found : N, 14·4%). When sodium hydroxide was used instead of the bicarbonate, only partial precipitation occurred, but on cautious neutralisation of the alkaline filtrate with acetic acid the remainder of the dye was obtained : the stronger alkali had probably converted part of the 4-nitronaphthalene-1-diazonium chloride into the sodium salt of the less reactive (*anti*-) form of 4-nitronaphthalene-1-diazotate.

Preparation of 4 : 4′-*Dinitronaphthalene*-1′ : 2-*azo*-1-*naphthylamine* (IX).—4-Nitro-1-naphthylamine was diazotised in hydrochloric acid as above, the excess of nitrous acid destroyed by urea, and the solution stirred into an equivalent amount of a fine suspension of 4-nitro-1-naphthylamine (made from a chilled solution in hot glacial acetic acid) to which an excess of sodium acetate over all the hydrochloric acid had been added. A slow reaction occurred, as indicated by the yellow suspension becoming red. After being kept overnight, the solid was filtered off and dissolved in boiling nitrobenzene, from which it separated in chocolate-brown prisms, m. p. 274°, depressed by admixture with the naphthol (II) (Found : N, 18·3. $C_{20}H_{13}O_4N_5$ requires N, 18·1%); it was sparingly soluble in acetone, giving a scarlet solution.

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