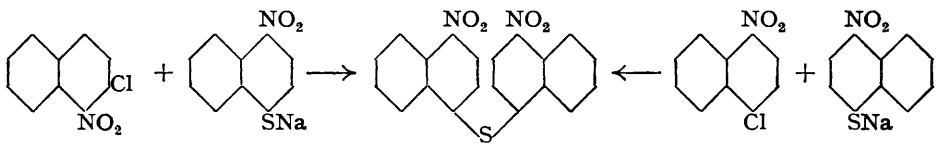
196. *Anomalous Reactions of the Sodium Salt of 4-Nitronaphthalene-1-thiol with 2-Chloro-1-nitronaphthalene and with 2-Chloro-1-nitrobenzene.*

By Herbert H. Hodgson and Eric Leigh.

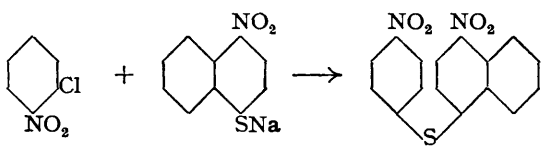
The reactions of 1 : 2-, 2 : 1-, and 4 : 1-chloronitronaphthalenes with the sodium salts of 1 : 2-, 2 : 1-, and 4 : 1-nitronaphthalenethiols have been investigated and in most cases the product is the expected dinitrodinaphthyl sulphide :

$$C_{10}H_6Cl{\cdot}NO_2 + NO_2{\cdot}C_{10}H_6{\cdot}SNa \longrightarrow (C_{10}H_6{\cdot}NO_2)_2S$$

The reaction between the sodium salt of 4-nitronaphthalene-1-thiol and 2-chloro-1-nitronaphthalene, however, gives, not the expected 1 : 4′-*dinitro*-2 : 1′-*dinaphthyl sulphide* (which was prepared in another way), but 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide, which is also obtained by the normal reaction between the same sodium salt and 1-chloro-4-nitronaphthalene :



An abnormal result is also obtained in the reaction between the same sodium salt and 2-chloro-1-nitrobenzene, the product being 4-*nitrophenyl* 4-*nitro*-1-*naphthyl sulphide* :



An explanation of these abnormal results is suggested.

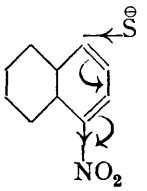
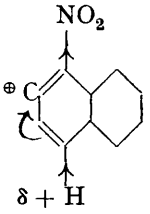
During the preparation of a number of dinitrodinaphthyl sulphides it was found that, whereas the sodium salt of 4-nitronaphthalene-1-thiol reacted as anticipated with 1-chloro-2-nitronaphthalene to form 2 : 4′-*dinitro*-1 : 1′-*dinaphthyl sulphide*, there unexpectedly resulted 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide (previously prepared by Hodgson and Leigh, J., 1937, 1352) when the isomeric 2-chloro-1-nitronaphthalene was used. On the other hand, the sodium salt of 1-nitronaphthalene-2-thiol reacted normally with

1-chloro-4-nitronaphthalene to form 1 : 4′-*dinitro*-2 : 1′-*dinaphthyl sulphide* and also with 1-chloro-2-nitro- and 2-chloro-1-nitro-naphthalene to give the respective sulphides.

Naturally it became of interest to ascertain how 2-chloro-1-nitrobenzene would react with the sodium salt of 4-nitronaphthalene-1-thiol: the same anomaly was found, *viz.*, the formation of 4-*nitrophenyl* 4-*nitro*-1-*naphthyl sulphide*, which was also formed normally when 4-chloronitrobenzene was used instead of its *o*-isomeride. The sodium salt of 2-nitrobenzene-1-thiol, however, reacted normally with 4-chloro-1-nitronaphthalene to give 2-*nitrophenyl* 4-*nitro*-1-*naphthyl sulphide*, and all the reactions appeared to be normal in the benzene series. It was found, however, that, whereas 2-chloro- and 4-chloro-nitrobenzenes failed to react with the sodium salts of 2-nitronaphthalene-1-thiol and 1-nitronaphthalene-2-thiol, the corresponding reactions of the sodium salts of 2-nitro- and 4-nitrobenzene-1-thiol readily took place. This result is in conformity with the property that the chlorine atoms in the 2-chloro- and 4-chloro-nitrobenzenes are much less easily displaced by alkali than those in the corresponding chloronitronaphthalenes, a circumstance probably due to the electron-attracting effect of the second nucleus (cf. Hodgson and Elliott, J., 1935, 1850).

In both these series of dinaphthyl and phenyl naphthyl sulphides, the 4-nitro-compounds are much less soluble in benzene, glacial acetic acid, and acetic anhydride than the corresponding 2-nitro-isomerides, a fact which probably indicates co-ordination between the 2-nitro-group and the sulphur atom.

A tentative explanation of the above anomalies is submitted: After the initial separation of the sodium and chlorine as ions, the residual thio (I) and 1-nitronaphthyl (likewise nitrophenyl) (II) ions might undergo a sequence of internal changes, *viz.*, (*a*) a restraint

(I.)  (II.) 

imposed on the reactivity of the negatively charged sulphur atom in (I) by the electromeric effect of the 4-nitro-group, (*b*) rapid ionisation of the 4-hydrogen atom in (II) by the combined electron-attracting effects of the nitro-group and the positive 2-carbon pole, whereby the seat of the positive charge is transferred to the 4-carbon atom, and (*c*) combination of (I) and (II) at the respective ionic centres. Change (*b*) cannot occur in the ion from 1-chloro-2-nitronaphthalene, its reactivity therefore being as expected, but in the case of the sodium salt of 2-nitronaphthalene-1-thiol and 2-chloro-1-nitronaphthalene, where anomaly might have been anticipated, the much more readily ionised thiol apparently reacts with much greater velocity than its 4-nitro-isomeride and so combination occurs at the 2-carbon of (II) before change (*b*) can take place.

Experimental.

General Procedure.—The solid mixture (1 g.) of dinitrodinaphthyl mono- and di-sulphides obtained by treatment of a chloronitronaphthalene with alcoholic sodium disulphide is boiled for 5 minutes under reflux with a solution of crystallised sodium sulphide (0·35 g.) and sodium hydroxide (0·2 g.) in alcohol (40 c.c.) and water (6 c.c.), the insoluble monosulphide filtered off, and the filtrate (F) used for the various condensations described below.

The colours which each sulphide gives with cold concentrated sulphuric acid, chlorosulphonic acid, and 26% oleum are placed in this order immediately after the m. p.

2 : 4′-*Dinitro*-1 : 1′-*dinaphthyl Sulphide.*—(*a*) A mixture of 1-chloro-2-nitronaphthalene (1·0 g.), alcohol (20 c.c.), and solution F (prepared from 1-chloro-4-nitronaphthalene) was boiled under reflux for 30 minutes, and the precipitate filtered off and treated with steam to remove any excess of 1-chloro-2-nitronaphthalene. 2 : 4′-*Dinitro*-1 : 1′-*dinaphthyl sulphide* (1·5 g.), so obtained, crystallised from glacial acetic acid in long yellow needles, m. p. 162—163° (deep bright red, changing to brown on heating; russet-brown; deep reddish-brown) (Found:

N, 7·6; S, 8·5. $C_{20}H_{12}O_4N_2S$ requires N, 7·4; S, 8·5%), slightly soluble in ether, rather more soluble in boiling alcohol, and readily soluble in cold benzene and acetic anhydride.

(*b*) This compound was prepared alternatively (as above) from 1-chloro-4-nitronaphthalene and solution F (from 1-chloro-2-nitronaphthalene).

1 : 2′-*Dinitro*-2 : 1′-*dinaphthyl Sulphide*.—Solution F (from 2-chloro-1-nitronaphthalene) was treated with 1-chloro-2-nitronaphthalene as described above, and, alternatively, solution F (from 1-chloro-2-nitronaphthalene) with 2-chloro-1-nitronaphthalene. The 1 : 2′-*dinitro*-2 : 1′-*dinaphthyl sulphide* obtained in both cases crystallised from glacial acetic acid (charcoal) in slender golden-yellow needles or parallelepipeds, m. p. 172—173° (cherry-red; violet; bluish-violet) (Found: N, 7·5; S, 8·6%), slightly soluble in ether, more soluble in boiling alcohol, and readily soluble in hot benzene or acetic anhydride.

1 : 4′-*Dinitro*-2 : 1′-*dinaphthyl Sulphide*.—Solution F (from 2-chloro-1-nitronaphthalene) was treated with 1-chloro-4-nitronaphthalene as described above. The *product* crystallised from glacial acetic acid (charcoal) in small yellow needles, m. p. 125—126° (maroon; dark violet; mauve) (Found: N, 7·5; S, 8·4%), which were almost insoluble in ether, more soluble in boiling alcohol, and easily soluble in cold benzene or acetic anhydride.

4 : 4′-*Dinitro*-1 : 1′-*dinaphthyl Sulphide*.—When solution F (from 1-chloro-4-nitronaphthalene) was treated with 2-chloro-1-nitronaphthalene as described above, 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide (Hodgson and Leigh, *loc. cit.*) was unexpectedly formed. It crystallised from hot glacial acetic acid in golden-yellow needles, m. p. and mixed m. p., with the product obtained from solution F and 1-chloro-4-nitronaphthalene, 239—240° (Found: N, 7·5; S, 8·6%). The solubilities of the two products and their colour reactions with concentrated sulphuric acid, chlorosulphonic acid, and 26% oleum were identical.

A further experiment was made to check this anomalous result. Pure 4 : 4′-dinitro-1 : 1′-dinaphthyl disulphide (5·0 g.) was reduced to the thiol, which was treated with 2-chloro-1-nitronaphthalene (5·0 g.) as in the previous work. The precipitated product (9·0 g.) was separated from the hot liquor, submitted to steam-distillation to remove traces of unchanged chloronitronaphthalene, washed with hot alcoholic sodium sulphide to extract any unchanged thiol, and crystallised from boiling glacial acetic acid. The golden-yellow needles (*ca.* 8 g.) obtained had m. p. 239—240° (Found: N, 7·5; S, 8·6%), and the product was identical with the previous preparations of 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide.

4-*Nitrophenyl* 2-*Nitro*-1-*naphthyl Sulphide*.—4 : 4′-Dinitrodiphenyl disulphide (1·0 g.) (Hodgson and Wilson, J., 1925, **127**, 440) was reduced to the sodium salt of 4-nitrobenzene-1-thiol by refluxing it for 10 minutes with a solution of crystallised sodium sulphide (0·45 g.) and sodium hydroxide (0·25 g.) in alcohol (20 c.c.) and water (10 c.c.); the resulting solution was boiled for 30 minutes with a solution of 1-chloro-2-nitronaphthalene (1·5 g.) in alcohol (30 c.c.). 4-*Nitrophenyl* 2-*nitro*-1-*naphthyl sulphide* (1·7 g.), which separated on cooling, crystallised from boiling glacial acetic acid in clusters of long, pale yellow needles, m. p. 121—122° (orange; dark brown; olive-green) (Found: N, 8·6; S, 9·9. $C_{16}H_{10}O_4N_2S$ requires N, 8·6; S, 9·8%), which were fairly readily soluble in ether, more soluble in boiling alcohol, and readily soluble in hot benzene or acetic anhydride.

4-*Nitrophenyl* 1-*Nitro*-2-*naphthyl Sulphide*.—4 : 4′-Dinitrodiphenyl disulphide (1·0 g.) was reduced as above, and the solution refluxed for 45 minutes with 2-chloro-1-nitronaphthalene (1·5 g.) in alcohol (30 c.c.). 4-*Nitrophenyl* 1-*nitro*-2-*naphthyl sulphide* (1·1 g.), thus obtained, crystallised from boiling glacial acetic acid in almost colourless needles, m. p. 122—123° (mauve; deep olive-green; intense violet) (Found: N, 8·7; S, 9·6%), which were slightly soluble in ether, more soluble in boiling alcohol, and fairly readily soluble in hot benzene or acetic anhydride.

4-*Nitrophenyl* 4-*Nitro*-1-*naphthyl Sulphide*.—4 : 4′-Dinitrodiphenyl disulphide (1·0 g.) was reduced, and the solution treated with 1-chloro-4-nitronaphthalene (1·5 g.) as above. 4-*Nitrophenyl* 4-*nitro*-1-*naphthyl sulphide* (1·8 g.), which separated, crystallised from boiling glacial acetic acid in yellow parallelepipeds, m. p. 236—238° (bright red; dark reddish-brown; dark mauve) (Found: N, 8·7; S, 9·7. $C_{16}H_{10}O_4N_2S$ requires N, 8·6; S, 9·8%), which depressed the m. p. of 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide (m. p. 239—240°) when mixed with it. The product was practically insoluble in ether and slightly soluble in boiling alcohol or glacial acetic acid, but more soluble in boiling benzene or acetic anhydride.

Alternatively, solution F (prepared from 1-chloro-4-nitronaphthalene) was treated with *o*-chloronitrobenzene (1·0 g.) as above; anomalous condensation occurred and 4-nitrophenyl 4-nitro-1-naphthyl sulphide (0·5 g.) separated. This crystallised from boiling glacial acetic acid in yellow parallelepipeds identical (m. p. and mixed m. p. 236—238°, and colour reactions) with the synthetic product above (Found: N, 8·7; S, 9·9%).

The latter experiment was repeated with pure 4 : 4′-dinitro-1 : 1′-dinaphthyl disulphide (12·0 g.), which was reduced to the thiol, and the solution treated with *o*-chloronitrobenzene (10·0 g.). The precipitated product (5·0 g.) was filtered off from the hot liquor, submitted to steam-distillation to remove unchanged *o*-chloronitrobenzene, and washed with hot alcoholic sodium sulphide. The residual 4-nitrophenyl 4-nitro-1-naphthyl sulphide crystallised from boiling glacial acetic acid (charcoal) in yellow parallelepipeds (*ca.* 4·5 g.), m. p. and mixed m. p. 236—238° (Found: N, 8·7; S, 9·8%), and was identical with the previous preparations. The initial mother-liquor contained only unchanged materials.

2-*Nitrophenyl* 2-*Nitro*-1-*naphthyl Sulphide.*—2 : 2′-Dinitrodiphenyl disulphide (1·0 g.) was reduced, and the solution treated with 1-chloro-2-nitronaphthalene (1·5 g.) as above. The precipitated 2-*nitrophenyl* 2-*nitro*-1-*naphthyl sulphide* (1·65 g.) crystallised from boiling glacial acetic acid in stout, yellow, hexagonal plates or parallelepipeds, m. p. 196—197° (pale yellow; dark violet; mauve) (Found: N, 8·7; S, 9·8%), which were slightly soluble in ether, more soluble in boiling alcohol, and readily soluble in hot benzene, glacial acetic acid, or acetic anhydride.

2-*Nitrophenyl* 1-*Nitro*-2-*naphthyl Sulphide.*—2 : 2′-Dinitrodiphenyl disulphide (1·0 g.) was reduced, and the solution treated with 2-chloro-1-nitronaphthalene as above. The 2-*nitrophenyl* 1-*nitro*-2-*naphthyl sulphide* formed crystallised from boiling glacial acid in stout, pale yellow parallelepipeds, m. p. 162—163° (yellowish-brown; violet; dark violet) (Found: N, 8·6; S, 9·8%), which were only very slightly soluble in ether, difficultly soluble in boiling alcohol, but readily soluble in hot benzene or acetic anhydride.

2-*Nitrophenyl* 4-*Nitro*-1-*naphthyl Sulphide.*—2 : 2′-Dinitrodiphenyl disulphide (1·0 g.) was reduced, and the solution treated with 1-chloro-4-nitronaphthalene (1·5 g.) as above. The precipitated 2-*nitrophenyl* 4-*nitro*-1-*naphthyl sulphide* (1·4 g.) crystallised from boiling glacial acetic acid in small, canary-yellow parallelepipeds, m. p. 157—158° (eosin-red; reddish-maroon; reddish-mauve) (Found: N, 8·8; S, 9·6%), which were fairly readily soluble in ether and more soluble in hot alcohol, benzene, and acetic anhydride.

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