274. *The Reactions of Sodium Mono- and Di-sulphides with* 1-*Chloro*-2-*nitro*-, 2-*Chloro*-1-*nitro*-, *and* 1-*Chloro*-4-*nitro-naphthalene.*

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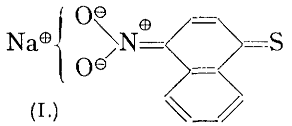
The object of this work was the preparation of various dinaphthyl disulphides, but when the three chloronitronaphthalenes (1 : 2-, 2 : 1-, and 1 : 4-) reacted with sodium disulphide in a molecular ratio of 2 : 1 in boiling alcoholic solution as for the corresponding benzene analogues (Hodgson and Wilson, J., 1925, **127**, 440), mixtures of dinitrodinaphthyl mono- and di-sulphides were obtained in each case, in the proportions of about 1 : 13, 1 : 12, and 1 : 12 respectively; in contrast, the benzene compounds gave almost exclusively the disulphide. It appeared of interest, therefore, to examine the reaction with sodium monosulphide alone, and, under identical experimental conditions, the above proportions became about 1 : 1·2, 1 : 0·8, and 1 : 1·5 respectively, the disulphide being subsequently formed from the thiol which results initially in this reaction.

The three monosulphides were synthesised from the sodium salts of the thiols and the corresponding chloronitronaphthalenes, excellent yields being thus obtained. The sodium salts of the nitronaphthyl thiols formed red solutions in aqueous-alcoholic sodium hydroxide, a probable indication of thioquinonoid formation (I).



(I.)

4 : 4′-Dinitro-1 : 1′-dinaphthyl disulphide has only one melting point, thereby differing from the analogous 4 : 4′-dinitrodiphenyl disulphide (Blanksma, *Rec. trav. chim.*, 1901, **20**, 141).

Hoogeveen (*ibid.*, 1931, **50**, 37) reported that 1-chloro-2-nitronaphthalene reacted with sodium disulphide to form 2 : 2′-*dinitro*-1 : 1′-*dinaphthyl disulphide*, m. p. 204°, but no analyses were given. As stated previously, this reaction afforded a mixture of monosulphide (m. p. 204°) and disulphide (m. p. 176—177°), and Hoogeveen had obviously obtained the former product by fractional crystallisation from alcohol in which the mono- is less soluble than the di-sulphide and from which it therefore separated first.

Experimental.

1-Chloro-2-nitronaphthalene was prepared by Hodgson and Walker's method (J., 1933, 824); yield 19·9 g. from 18·8 g. of 2-nitro-1-naphthylamine. It was purified by distillation in steam (volatility *ca.* 0·75 g. per l. of distillate) or in a vacuum, then crystallised twice from alcohol and once from light petroleum, being obtained in pale yellow needles, m. p. 80·5—81° (Hodgson and Kilner, J., 1926, 7, gave m. p. 76°) (Found : N, 6·9; Cl, 16·8. Calc. : N, 6·7; Cl, 17·1%).

2-Chloro-1-nitronaphthalene, prepared (yield 19·3 g. from 18·8 g. of 1-nitro-2-naphthylamine) and purified in like manner (steam volatility *ca.* 2 g. per l.), was obtained in long, almost colourless needles, m. p. 99—100° (Vésely, *Ber.*, 1905, **38**, 137, gave m. p. 95·5°; Contardi and Mor, *Rend. Ist. Lombardo*, 1924, **57**, 646, gave m. p. 98·7°) (Found : N, 6·9; Cl, 16·8%).

1-Chloro-4-nitronaphthalene, prepared (yield 19·8 g. from 18·8 g. of 4-nitro-1-naphthylamine) and purified as above (volatility in steam *ca.* 1 g. per l.), afforded fan-shaped clusters of cream, silky needles, m. p. 87—87·5° (Atterberg, *Ber.*, 1876, **9**, 927, reported bright yellow needles from alcohol, m. p. 85°) (Found : N, 6·8; Cl, 17·0%).

1-*Chloro*-2-*bromonaphthalene*, prepared from 1-chloro-2-naphthylamine by the ordinary Sandmeyer procedure, crystallised from alcohol in pale yellow needles and from light petroleum (b. p. 40—60°) or ligroin (b. p. 80—100°) in large, thin, pale yellow parallelepipeds, m. p. 57° (Found : Cl + Br, 48·0. $C_{10}H_6ClBr$ requires Cl + Br, 47·8%).

Reactions with Sodium Disulphide.—General procedure. Crystallised sodium sulphide (12·6 g.) and powdered sulphur (1·6 g.), dissolved in boiling alcohol (200 c.c.), were added to a boiling solution of the chloronitronaphthalene (21·3 g.) in alcohol (300 c.c.). The resulting deep red solution was heated on the water-bath for the minimum period necessary to secure complete deposition of the mixture of mono- and di-sulphide formed (*ca.* 20 mins.), cooled, filtered, and the precipitate (16·8 g. from the 1 : 2-, 14·9 g. from the 2 : 1-, and 19·5 g. from the 1 : 4-isomeride) was washed first with alcohol, then with water, and finally steam-distilled to remove traces of unchanged chloronitronaphthalene; the filtrate above was poured into water to precipitate the remainder of the unchanged initial material, *viz.*, 2·6 g. of 1 : 2-, 3·6 g. of 2 : 1-, and 1·2 g. of 1 : 4-isomeride. It would appear from these data that the 1-chloro-4-nitro- is the most, and the 2-chloro-1-nitro-naphthalene the least reactive under the above conditions.

Separation of the mono- and di-sulphides. The mixture (5 g.) was added to a hot solution of crystalline sodium sulphide (1·75 g.) and sodium hydroxide (1·0 g.) in alcohol (150 c.c.) and water (30 c.c.), boiled for 5 minutes under reflux, and the insoluble monosulphide filtered off; the crude amounts were: 0·4 g. (m. p. 180—188°), 0·35 g. (m. p. 191—194°), and 0·4 g. (m. p. 232—235°) respectively from the 1 : 2-, 2 : 1-, and 1 : 4-isomerides. The hot, deep red filtrate above could be oxidised by air or by hydrogen peroxide, but better by addition of a hot saturated solution of potassium ferricyanide until the red colour disappeared. The crude yields of disulphide obtained were: 1·75 g. (m. p. 152—161°) from the 1 : 2-, 3·4 g. (m. p. 165—172°) from the 2 : 1-, and 4·25 g. (m. p. 178—182°) from the 1 : 4-isomeride.

Synthesis of the dinitrodinaphthyl monosulphides. The mixture of sulphide and disulphide (1·0 g.) prepared as above was added to a boiling solution of crystallised sodium sulphide (0·35 g.) and sodium hydroxide (0·2 g.) in alcohol (40 c.c.) and water (10 c.c.), refluxed for 5 minutes, filtered, and the appropriate chloronitronaphthalene (1·0 g.) dissolved in alcohol (20 c.c.) added to the filtrate. The mixture was refluxed until the red colour had disappeared (15—45 mins.) and the yellow reaction product had separated. The latter was filtered off, steam-distilled to remove unchanged chloronitronaphthalene, and crystallised from glacial acetic acid. All the three sulphides so obtained were insoluble in ether, slightly soluble in boiling alcohol but more soluble in boiling benzene, and moderately soluble in boiling glacial acetic acid and acetic anhydride. In each case the monosulphide was less soluble than the corresponding disulphide, and the 1 : 4- less soluble than the 1 : 2- and the 2 : 1-isomerides.

Action of alcoholic sodium sulphide on the chloronitronaphthalenes. Crystallised sodium sulphide (3 g.), dissolved in alcohol (25 c.c.) and water (5 c.c.), was boiled and added to a boiling solution of the chloronitronaphthalene (5·2 g.) in alcohol (50 c.c.). The resulting deep red mixture was refluxed for 10 minutes although the solid precipitate of dinitrodinaphthyl mono- and di-sulphides (as thiol) mostly separated out in about 3 minutes while the intensity of the red colour greatly diminished. After cooling, the solid matter was filtered off, washed first with hot alcohol then with water, and finally steam-distilled to remove unchanged chloronitronaphthalene. The separation of the mono- and di-sulphides was effected as above, and their ratios are reported on p. 1352.

The Individual Products.—General. The colours which each product gives with cold concentrated sulphuric acid, chlorosulphonic acid, and 26% oleum severally are placed in this order after the m. p.

1 : 1′-*Dinitro*-2 : 2′-*dinaphthyl sulphide* crystallised from hot glacial acetic acid in glistening, pale yellow, rectangular plates, m. p. and mixed m. p. with the synthetic product, 203—204° (colourless but pale violet to blue on heating; violet; violet) (Found: N, 7·5; S, 8·5 $C_{20}H_{12}O_4N_2S$ requires N, 7·4; S, 8·5%).

2 : 2′-*Dinitro*-1 : 1′-*dinaphthyl sulphide* formed pale yellow parallelepipeds, m. p. and mixed m. p. with synthetic product, 204—205° (pale yellow turning to green and then to dark blue on heating; dark greenish-brown; light brown) (Found: N, 7·5; S, 8·6%); and 4 : 4′-*dinitro*-1 : 1′-*dinaphthyl sulphide*, long golden yellow needles, m. p. and mixed m. p. with synthetic product, 239—240° (pink changing to reddish-brown; reddish-brown; dark mauve) (Found: N, 7·6; S, 8·4%).

1 : 1′-*Dinitro*-2 : 2′-*dinaphthyl disulphide* crystallised from hot glacial acetic acid (charcoal) in long, yellow parallelepipeds, m. p. 189—190° (very pale yellow which deepens on heating; deep golden-yellow; reddish-orange) (Found: N, 7·2; S, 16·0. $C_{20}H_{12}O_4N_2S_2$ requires N, 6·9; S, 15·7%).

2 : 2′-*Dinitro*-1 : 1′-*dinaphthyl disulphide* formed stout, hexagonal, yellow plates or parallelepipeds, m. p. 176—177° (yellowish-brown; brown; light brown) (Found: N, 7·1; S, 16·0%); and 4 : 4′-dinitro-1 : 1′-dinaphthyl disulphide, pale yellow needles, m. p. 188—189° (Cleve, *Ber.*, 1890, **23**, 960, gives m. p. 186°) (claret; reddish-brown; dark brown) (Found: N, 7·1; S, 15·5%).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group), for various gifts.

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[*Received, June 8th*, 1937.]