232. *o-Mercapto-azo-compounds. Part II.* 1-(1-Mercapto-2-naphthylazo)-2-naphthol.*

By A. Burawoy and C. Turner.

The tetrazonium salt from di-(2-amino-1-naphthyl) disulphide (VII) reacts with water much faster than its benzene analogue, forming naphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazole (VIII). Coupling takes place when its concentrated sulphuric acid solution is added directly to alkaline β-naphthol, yielding only the sulphide (XI) and the naphthothiadiazole under all conditions. The disulphide (XV) is not obtained here. It is formed by treatment with sodium hydroxide of 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene (XIV) obtained by coupling diazotised 1-thiocyanato-2-naphthylamine (XIII) with β-naphthol. Reduction yields 1-(1-mercapto-2-naphthylazo)-2-naphthol (XVI). The oxidation and complex salt formation of the *o*-mercapto-azo-compounds are discussed.

A representative of the hitherto unknown *o*-mercapto-azo-compounds, 1-*o*-mercaptophenylazo-2-naphthol (V), was prepared from di-*o*-aminophenyl disulphide (I) by Burawoy and Turner (Part I *). This and reactions of the intermediates are represented in the first scheme on p. 1287.

We have now attempted to prepare 1-(1-mercapto-2-naphthylazo)-2-naphthol (XVI) by the same method. In contrast to its analogue in the benzene series, however, the tetrazonium salt (VII) formed in concentrated sulphuric acid, *rapidly* decomposes on addition to water, yielding naphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazole (VIII) in 50—60% yield. It does not couple with β-naphthol in sodium acetate, whereas in sodium hydroxide, sodium carbonate, or sodium hydrogen carbonate the red sulphide (XI) is isolated in good yield in addition to the naphthothiadiazole; however, the violet colour of the solutions of the crude product in organic solvents may indicate the formation of negligible amounts of the desired di-2-(2-hydroxy-1-naphthylazo)-1-naphthyl disulphide (XV).

These results indicate that the tetrazonium salt (VII), being less stable than its benzene analogue in presence of water, is hydrolysed in sodium acetate solution in preference to coupling with β-naphthol. In aqueous sodium hydroxide, sodium carbonate, or sodium hydrogen carbonate, one of the diazonium groups couples with one molecule of β-naphthol with sufficient rapidity, although the yields of naphthothiadiazole indicate partial decomposition of the tetrazonium salt. Coupling is followed by rapid decomposition of

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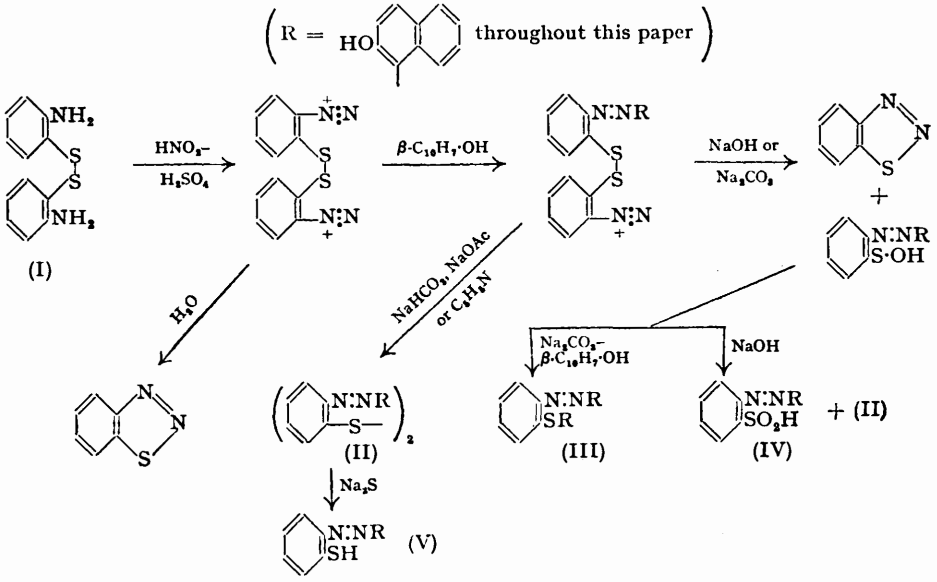
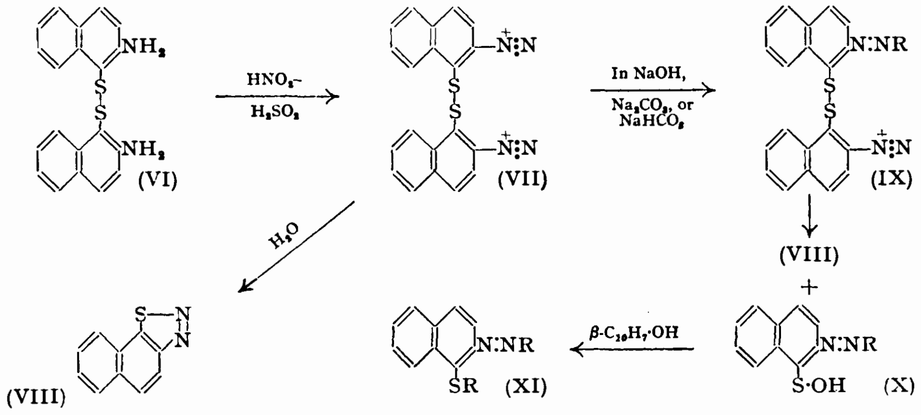
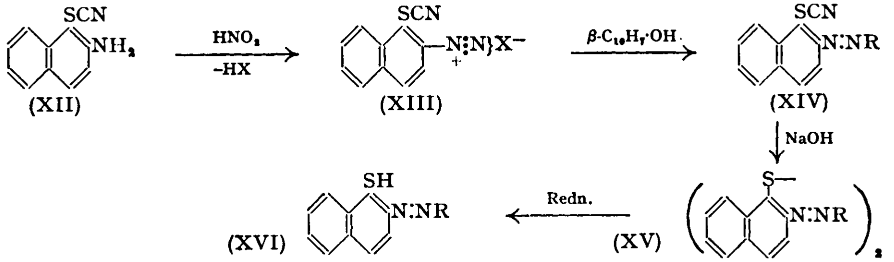
* Part I, *J.*, 1950, 469.



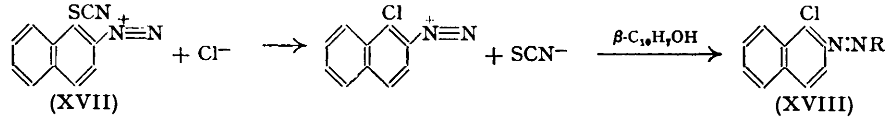
the monodiazonium intermediate (IX) to naphthothiadiazole and 2-(2-hydroxy-1-naphthylazo)-1-naphthalenesulphenic acid (X) which then reacts with another molecule of β-naphthol, a normal reaction of sulphenic acids, to yield 2-hydroxy-1-naphthyl 2-(2-hydroxy-1-naphthylazo)-1-naphthyl sulphide (XI). It is noteworthy that, in contrast to its analogue in the benzene series, the sulphenic acid (X), in sodium hydroxide, reacts with another molecule of β-naphthol in preference to disproportionating to the disulphide and sulphinic acid.



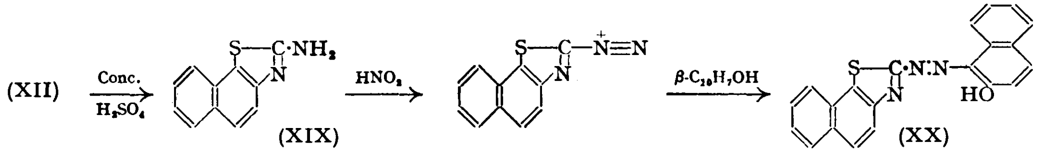
We therefore attempted an alternative method: the preparation of 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene (XIV) from 1-thiocyanato-2-naphthylamine (XII) by diazotisation and coupling with β-naphthol, and its conversion by sodium hydroxide into the desired disulphide (XV). Although we succeeded, the reactions proved rather complicated. 1-Thiocyanato-2-naphthylamine, after diazotisation in the usual manner in aqueous hydrochloric acid solution, coupled with β-naphthol to yield 1-chloro-2-(2-hydroxy-1-naphthylazo)naphthalene (XVIII) previously obtained by Morgan (*J.*, 1902, **81**, 1381) by the diazotisation of 1-nitro-2-naphthylamine in aqueous hydrochloric acid and coupling with β-naphthol. Exchange between the nuclear thiocyanato-group and the chlorine ion of 1-thiocyanatonaphthalene 2-diazonium chloride (XVII) had occurred. This is similar to the reverse rearrangement of *p*-chlorobenzenediazonium thiocyanate to *p*-thiocyanatobenzenediazonium chloride observed by Hantzsch and Hirsch (*Ber.*, 1896, **29**, 947).



The diazonium salt (XIII) is obtained by diazotising 1-thiocyanato-2-naphthylamine (XII) in aqueous thiocyanic, dilute sulphuric, or concentrated sulphuric acid, coupling with β-naphthol giving the desired azo-compound (XIV). However, in concentrated sulphuric acid, some conversion into 2-aminonaphtho(2′ : 1′-4 : 5)-1 : 3-thiazole (XIX) could not be avoided. The diazonium salt of the latter substance yielded subsequently with β-naphthol

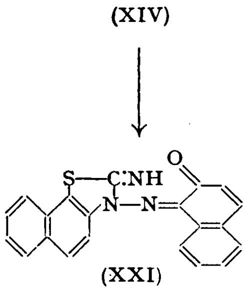


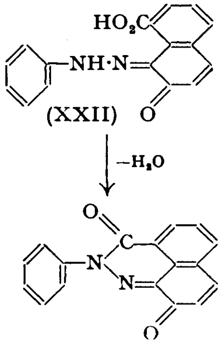
the azothiazole (XX), which was difficult to separate. When heated, the thiocyanato-compound (XIV) isomerises to a product which may be (XXI); and this on further heating decomposes to a high-melting substance of unknown constitution. This ring closure is similar to those observed by Willstätter, Ulbrich, Pogány, and Maimeri (*Annalen*, 1930,

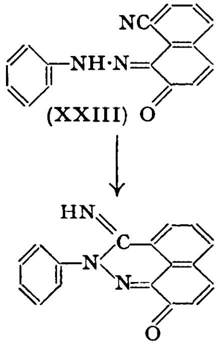


477, 161) and by Burawoy and Markowitsch (*ibid.*, 1933, **504**, 71) for 1-phenylazo-2-naphthol-8-carboxylic acid (XXII) and its nitrile (XXIII) respectively.

Finally, 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene (XIV) was obtained pure as dark red prisms of m. p. 151° by rapid recrystallisation from a small amount of hot

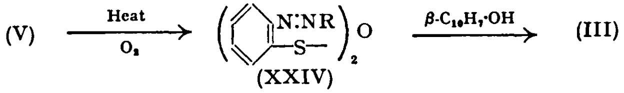






benzene, immediate filtration being essential. Quick treatment of its benzene solution with hot aqueous sodium hydroxide yields di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide (XV) which dissolves in organic solvents with a characteristic violet colour and is reduced by hot alcoholic sodium sulphide to the violet-blue salt of 1-(1-mercapto-2-naphthylazo)-2-naphthol (XVI). The free red thiol is obtained by acidification of the aqueous-alcoholic solution of this salt. It was characterised by the formation of the red *S*-methyl derivative.

The different behaviour of the *o*-mercapto-azo-compounds of the benzene and naphthalene series is noteworthy. As already reported in Part I (*loc. cit.*), 1-*o*-mercaptophenylazo-2-naphthol (V) is very sensitive to heat, being easily converted into a brown, alkali-insoluble product, which is obtained pure from hot xylene as bright red prisms. We have now established that this substance is *o*-(2-hydroxy-1-naphthylazo)benzenesulphenic anhydride (XXIV), by analysis and by conversion into the sulphide (III) when melted with β-naphthol. The fact that oxidation of this thiol gives the sulphenic anhydride rather than, as usually, the disulphide explains earlier failures to convert di-*o*-(2-hydroxy-1-naphthylazo)phenyl disulphide (II) into the thiol (V) by boiling it with alkaline alcoholic glucose or with alcoholic sodium hydroxide alone. At this high temperature, the thiol formed is easily oxidised to the sulphenic anhydride (XXIV); this spontaneously disproportionates in the presence of alkali to the sulphinic acid (IV) and the original disulphide which again reacts in the same manner until an almost quantitative yield of the sulphinic acid is obtained, as already reported.



In contrast, the thiol (XVI) shows the usual behaviour, since it is very readily oxidised in air, particularly when dissolved in organic solvents or in alkaline conditions, yielding the disulphide (XV).

We have also prepared the copper, nickel, and cobalt complex salts of 1-*o*-mercaptophenylazo-2-naphthol and the copper and nickel salts of 1-(1-mercapto-2-naphthylazo)-2-naphthol. They possess the empirical formulæ $(C_{16}H_{11}ON_2S)_2M$ and $(C_{20}H_{13}ON_2S)_2M$ respectively. They are insoluble in water but slightly soluble in organic solvents such as benzene and chloroform. Their structures will be discussed elsewhere.

EXPERIMENTAL

Action of Water on Tetrazotised Di-(2-amino-1-naphthyl) Disulphide.—Di-(2-amino-1-naphthyl) disulphide (2 g.), dissolved in concentrated sulphuric acid (12 c.c.), was cooled to −5° and slowly added with stirring to nitrosylsulphuric acid (1 g. of sodium nitrite in 6 c.c. of concentrated sulphuric acid) in ice–salt. After 30 minutes, the solution was poured into ice water (500 c.c.). The yellow precipitate was filtered off and washed with water. Extraction with light petroleum (b. p. 60—80°) left an insoluble brown resin, m. p. 77—94° (0·6 g.). Evaporation of the solvent yields naphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazole, m. p. 88—89° (1·2 g., 56%) (Jacobson and Schwartz, *Annalen*, 1893, **277**, 260, give 89°).

Coupling of Tetrazotised Di-(2-amino-1-naphthyl) Disulphide with β-Naphthol.—The disulphide (4 g.) in concentrated sulphuric acid (25 c.c.) was tetrazotised with nitrosylsulphuric acid (2 g. of sodium nitrite in 12 c.c. of concentrated sulphuric acid). The tetrazonium solution was added to a stirred solution of β-naphthol (20 g.), sodium hydroxide (6 g.), and sodium carbonate (150 g.) in ice and water (2500 g.). The precipitate was filtered off; after removal of the excess of β-naphthol with 3% aqueous sodium hydroxide (500 c.c.), the product was washed with water and finally digested with methyl alcohol (100 c.c.). The residue of *2-hydroxy-1-naphthyl 2-(2-hydroxy-1-naphthylazo)-1-naphthyl sulphide* (3·6 g., 66%) crystallised from xylene or glacial acetic acid as red prisms, m. p. 232—233° (Found: C, 75·0; H, 4·4; N, 6·2; residue, 1·8. $C_{30}H_{20}O_2N_2S$ requires C, 76·3; H, 4·3; N, 5·9%). It dissolves in organic solvents with an orange colour and in concentrated sulphuric acid with a dark violet colour rapidly changing to light brown. Evaporation of the methyl alcohol washings yielded the naphthothiadiazole, which was purified by dissolution in ether, removal of β-naphthol with 3% sodium hydroxide, and evaporation, giving material of m. p. 88—89° (2·3 g., 108%). Similar results were obtained by using sodium hydrogen carbonate or sodium hydroxide instead of sodium carbonate [Yields, in presence of sodium hydroxide : (XI), 2·3 g., 42% ; naphthothiadiazole, 2·7 g., 1·26%]. No coupling took place in presence of sodium acetate.

Diazotisation of 1-Thiocyanato-2-naphthylamine in Hydrochloric Acid and Coupling with β-Naphthol.—1-Thiocyanato-2-naphthylamine (2 g.) in ethyl alcohol (200 c.c.) was poured into ice and water (100 g.) and concentrated hydrochloric acid (20 c.c.). Sodium nitrite (1·0 g.) in a small amount of water was added. The orange diazonium solution was poured into an ice-cold aqueous solution (200 c.c.) of β-naphthol (3 g.) and sodium hydroxide (10 g.). The red precipitate formed was filtered off, washed with water, and crystallised from benzene and, finally, from glacial acetic acid. It was obtained as dark red prisms (3·2 g., 96%), m. p. 232—234°, alone or mixed with a sample of 1-(1-chloro-2-naphthylazo)-2-naphthol prepared as below (Found: C, 72·5; H, 4·1; N, 8·5; Cl, 10·1. Calc. for $C_{20}H_{13}ON_2Cl$: C, 72·3; H, 4·0; N, 8·4; Cl, 10·7%).

A solution of 1-chloro-2-naphthylamine hydrochloride (21·4 g.) in hot water (300 c.c.) and concentrated hydrochloric acid (35 c.c.) was cooled and, after addition of ice (200 g.), diazotised with sodium nitrite (7·5 g.) in a small amount of water. On addition to an aqueous ice-cold solution of β-naphthol (20 g.) and sodium hydroxide (25 g,) in water (600 c.c.), a red precipitate of the azo-compound (XVIII) separated. It was filtered off, washed with water, and recrystallised from glacial acetic acid, forming dark red prisms with a bronze lustre, m. p. 233—234°, in almost quantitative yield.

Diazotisation of 1-*Thiocyanato*-2-*naphthylamine in Concentrated Sulphuric Acid and Coupling with* β-*Naphthol.*—Finely powdered 1-thiocyanato-2-naphthylamine (10 g.) was slowly added to nitrosylsulphuric acid (8 g. of sodium nitrite in 80 c.c. of concentrated sulphuric acid) at −5°. After 1 hour's stirring the solution was poured into β-naphthol (30 g.), sodium hydroxide (10 g.), and sodium carbonate (240 g.) in ice and water (4000 g.). The precipitate formed was filtered off, washed with water, and finally digested with methyl alcohol (500 c.c.). The yield was 14·2 g. (80%). By rapid crystallisation from hot benzene, or concentration of a cold benzene solution under a vacuum, 2-(2-*hydroxy*-1-*naphthylazo*)-1-*thiocyanatonaphthalene* (XIV) was obtained as dark red prisms, m. p. 149·5—151° (Found: C, 71·2; H, 3·9; N, 12·1. $C_{21}H_{13}ON_3S$ requires C, 71·0; H, 3·7; N, 11·8%). It dissolves with a violet colour in concentrated sulphuric acid. By repeated crystallisations of the crude product from xylene, and removal of the insoluble decomposition products of 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene pure 2-(2-*hydroxy*-1-*naphthylazo*)*naphtho*(2′ : 1′-4 : 5)*thiazole* (XX) was obtained as aggregates of dark green needles, m. p. 240—242°, not depressed when the specimen was mixed with a pure sample prepared as below.

Diazotisation of 1-*Thiocyanato*-2-*naphthylamine in Thiocyanic Acid and Coupling with* β-*Naphthol.*—A solution of ammonium thiocyanate (100 g.) in an equivalent amount of 40% sulphuric acid at 0° was extracted with amyl alcohol (100 c.c.), and the alcoholic layer then extracted with ice-cold water (2 × 100 c.c.). The aqueous thiocyanic acid obtained was added at 0° to a solution of 1-thiocyanato-2-naphthylamine (5 g.) in ethyl alcohol (200 c.c.). This was treated with sodium nitrite (25 g.) in a small amount of water. The filtered orange diazonium solution was poured into an ice cold aqueous solution (1000 c.c.) of β-naphthol (15 g.), sodium hydroxide (5 g.), and sodium carbonate (80 g.). The precipitate was filtered off, washed with water, and digested with methyl alcohol (200 c.c.) (yield, 2·1 g., 24%). One crystallisation from benzene gave a product of m. p. 148—150°, identical with 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene described above.

Diazotisation of 1-*Thiocyanato*-2-*naphthylamine in Dilute Sulphuric Acid and Coupling with* β-*Naphthol.*—To a solution of 1-thiocyanato-2-naphthylamine (5 g.) in acetone (250 c.c.) and 10% sulphuric acid (200 c.c.) was added sodium nitrite (5 g.) in a small amount of water. The diazonium solution obtained was quickly poured into water and ice (1500 g.) containing β-naphthol (12 g.), sodium hydroxide (4 g.), and sodium carbonate (100 g.). The red precipitate was filtered off, washed with water, and digested with methyl alcohol (yield, 7·7 g., 87%). One crystallisation from benzene gave a product of m. p. 149—151°, alone or mixed with the foregoing product.

Action of Heat on 2-(2-*Hydroxy*-1-*naphthylazo*)-1-*thiocyanatonaphthalene.*—The compound was heated in toluene under reflux for 30 minutes. After cooling and filtration from a small amount of black insoluble matter, light petroleum was added, a *product* of m. p. 186—188° being precipitated, probably (XXI) (Found: C 70·9; H, 3·5; N, 12·0. $C_{21}H_{13}ON_3S$ requires C, 71·0; H, 3·7; N, 11·8%). It dissolves in concentrated sulphuric acid with a carmine colour. It has none of the properties of 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene; in particular, it cannot be converted by sodium hydroxide into di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide. It could not be recrystallised, as further heating, such as boiling for 10 minutes in xylene, produced a black precipitate of m. p. about 340°, which only dissolved in hot glacial acetic acid containing some concentrated hydrochloric acid. By adding a larger amount of the latter acid a red *hydrochloride* with a green lustre crystallised (Found: C, 59·7;

H, 4·1; N, 6·9; Cl, 9·0. $C_{20}H_{14}O_3N_2S,HCl$ requires C, 60·2; H, 3·8; N, 7·0; Cl, 8·9%). Aqueous sodium hydroxide regenerates the original black compound, which dissolves in concentrated sulphuric acid with a violet colour which slowly fades with the formation of a red precipitate.

2-(2-Hydroxy-1-naphthylazo)naphtho(2′ : 1′-4 : 5)thiazole.—Well-powdered 2-aminonaphthothiazole (2 g.) was added to nitrosylsulphuric acid (1 g. of sodium nitrite in 25 c.c. of concentrated sulphuric acid). After 30 minutes at 0°, the solution was dropped into β-naphthol (10 g.), sodium hydroxide (3 g.), and sodium carbonate (100 g.) in ice and water (2000 g.). The precipitated *azo*-compound was filtered off, washed with water, and finally digested with methyl alcohol (200 c.c.) (yield, 1·1 g., 31%). Recrystallisation from glacial acetic acid gave aggregates of dark green needles containing one mol. of acetic acid of crystallisation, of m. p. 240—242°, which dissolved in organic solvents with a red-brown colour and in concentrated sulphuric acid with a pure blue colour (Found : C, 65·9; H, 4·4; loss on drying, 14·2. $C_{21}H_{13}ON_3S,CH_3{\cdot}CO_2H$ requires C, 66·3; H, 4·1; loss on drying, 14·5. Found, after drying : C, 70·9; H, 3·9; N, 12·1. $C_{21}H_{13}ON_3S$ requires C, 71·0; H, 3·7; N, 11·8%).

Di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] Disulphide.—2-(2-Hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene (5 g.) was quickly dissolved in hot benzene (200 c.c.) and added to vigorously stirred 3% aqueous sodium hydroxide (500 c.c.) at 100°. After 5 minutes, the benzene was evaporated and the precipitate of nearly pure *disulphide* (4·5 g., 97%) filtered off and washed free from alkali. Recrystallisation from toluene gave dark green needles, m. p. 242—244°, which dissolve with a dark violet colour in organic solvents and an orange colour in concentrated sulphuric acid (Found : C, 73·3; H, 4·0; N, 8·6. $C_{40}H_{26}O_2N_4S_2$ requires C, 73·0; H, 4·0; N, 8·5%).

1-(1-Mercapto-2-naphthylazo)-2-naphthol.—The foregoing disulphide (3 g.), suspended in ethyl alcohol (250 c.c.), was heated under reflux with sodium sulphide nonahydrate (6 g.) in water (30 c.c.) for 1 hour. After cooling and filtration, the dark blue-violet solution obtained was treated with water (300 c.c.) and hydrochloric acid in excess. The red precipitate of *1-(1-mercapto-2-naphthylazo)-2-naphthol* (2·85 g., 95%) was collected and washed with water. It crystallised from toluene (in absence of oxygen) and had m. p. 232—234° (Found : C, 72·4; H, 4·4; N, 8·4. $C_{20}H_{14}ON_2S$ requires C, 72·7; H, 4·3; N, 8·5%). It dissolves in organic solvents with an orange-red colour and in concentrated sulphuric acid with a violet-blue colour.

1-(1-Methylthio-2-naphthylazo)-2-naphthol.—The foregoing disulphide (1 g.), suspended in alcohol (80 c.c.), was heated under reflux with sodium sulphide nonahydrate (2 g.) in water (10 c.c.) for 1 hour and then cooled. Water (100 c.c.) was added, followed by three portions of 10% aqueous sodium hydroxide (5 c.c. each) and methyl sulphate (1·4 c.c. each), with vigorous shaking. The red precipitate of *1-(1-methylthio-2-naphthylazo)-2-naphthol* formed quantitatively was filtered off and washed with water. Recrystallisation from glacial acetic acid gave red needles with a green lustre, m. p. 174—175°, which dissolve in organic solvents with an orange colour and in concentrated sulphuric acid with a violet colour (Found : C, 73·3; H, 4·7; N, 8·1. $C_{21}H_{16}ON_2S$ requires C, 73·2; H, 4·7; N, 8·1%).

Oxidation of 1-o-Mercaptophenylazo-2-naphthol to o-(2-Hydroxy-1-naphthylazo)benzenesulphenic Anhydride.—Attempts to recrystallise 1-*o*-mercaptophenylazo-2-naphthol from organic solvents (acetone, benzene, toluene) yielded the sparingly soluble *o-(2-hydroxy-1-naphthylazo)benzenesulphenic anhydride* (XXIV) (cf. Part I of this series), bright red prisms, m. p. 241—243° (from xylene or chlorobenzene), giving orange solutions in organic solvents and a violet colour in concentrated sulphuric acid (Found: C, 66·8; H, 3·8; N, 10·0. $C_{32}H_{22}O_3N_4S_2$ requires C, 66·9; H, 3·9; N, 9·8%).

Condensation of o-(2-Hydroxy-1-naphthylazo)benzenesulphenic Anhydride with β-Naphthol.—The anhydride (0·5 g.) and β-naphthol (1·0 g.) were heated together at 120° for 1 hour, the liquid mass becoming semi-solid. After cooling, it was digested with a little methyl alcohol, filtered off, and washed (0·65 g., 89%). One recrystallisation from xylene and a little charcoal gave brownish-red needles, m. p. 226—227°, not depressed by admixture of the compound with 2-hydroxy-1-naphthyl *o*-(2-hydroxy-1-naphthylazo)phenyl sulphide prepared by coupling tetrazotised di-*o*-aminophenyl disulphide and β-naphthol in aqueous sodium carbonate (cf. Part I of this series).

Oxidation of 1-(1-Mercapto-2-naphthylazo)-2-naphthol.—1-(1-Mercapto-2-naphthylazo)-2-naphthol (0·2 g.) in toluene (50 c.c.) was heated under reflux for 2 hours while a stream of oxygen passed through the solution. On concentration to a small volume, di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide (0·13 g.), m. p. 241—243°, crystallised. The m. p. was not depressed when the sample was mixed with one obtained directly by the action of sodium hydroxide on

2-(2-hydroxy-1-naphthylazo)thiocyanatonaphthalene, and the product gave an orange colour in concentrated sulphuric acid.

When a solution of 1-(1-mercapto-2-naphthylazo)-2-naphthol in alcoholic sodium hydroxide was shaken for a few minutes, di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide was quantitatively precipitated. One recrystallisation from toluene yielded a pure product of m. p. 242—244°.

Metallic Complex Salts of 1-(o-*Mercaptophenylazo*)-2-*naphthol.—Copper.* To a filtered solution of the sodium salt of 1-(*o*-mercaptophenylazo)-2-naphthol (0·5 g.) in ethyl alcohol (200 c.c.) were added water (300 c.c.), followed by an aqueous solution of copper sulphate pentahydrate (0·5 g.). The brown *salt* precipitated was filtered off and washed with water. It (0·35 g., 63%) had m. p. 306—308° (Found: Cu, 10·0. $C_{32}H_{22}O_2N_4S_2Cu$ requires Cu, 10·2%). The complex is slightly soluble in acetone, chloroform, and benzene, giving orange solutions, and insoluble in water, ethyl alcohol, and light petroleum.

Cobalt. This *salt* (0·40 g., 73%), m. p. 285—288°, was prepared similarly, a solution of cobalt sulphate being added (Found: Co, 9·2. $C_{32}H_{22}O_2N_4S_2Co$ requires Co, 9·6%). It is slightly soluble in acetone, chloroform, and benzene, giving dark brown solutions, and insoluble in water, ethyl alcohol, and light petroleum.

The *nickel* salt (yield, 55%) had m. p. 334—337° (Found: Ni, 9·5. $C_{32}H_{22}O_2N_4S_2Ni$ requires Ni, 9·6%). It is slightly soluble in chloroform and benzene, giving orange-brown solutions, and insoluble in water, ethyl alcohol, acetone, and light petroleum.

Metallic Complex Salts of 1-(1-*Mercapto*-2-*naphthylazo*)-2-*naphthol.—Copper.* To a filtered solution of 1-(1-mercapto-2-naphthylazo)-2-naphthol (0·3 g.) in acetone (200 c.c.) was added copper sulphate pentahydrate (0·3 g.) in water (300 c.c.). The brown salt (0·20 g., 61%), m. p. 256—258°, precipitated was filtered off and washed with water (Found: Cu, 9·1. $C_{40}H_{26}O_2N_4S_2Cu$ requires Cu, 8·8%). It is slightly soluble in acetone, chloroform, and benzene, giving purple solutions.

The *nickel* salt, prepared similarly in 73% yield, had m. p. 300—302° (Found: Ni, 8·1. $C_{40}H_{26}O_2N_4S_2Ni$ requires Ni, 8·2%) and was slightly soluble in acetone, chloroform, and benzene, giving red solutions.

Both salts are insoluble in water, ethyl alcohol, and light petroleum.

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