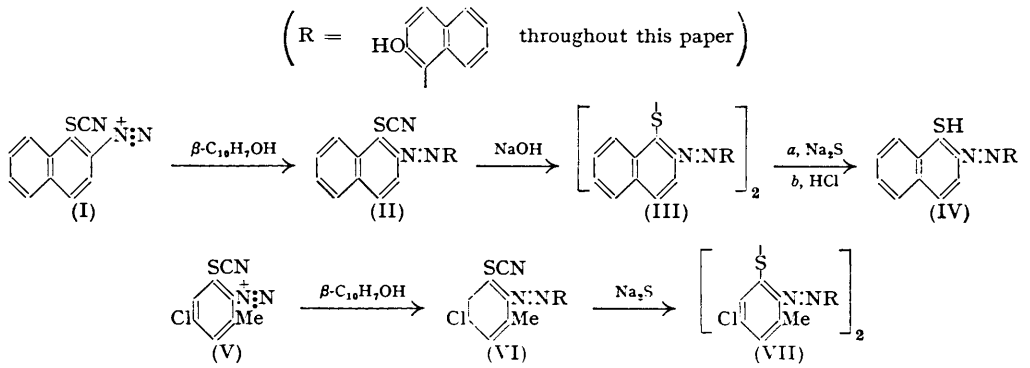
200. o-*Mercapto-azo-compounds. Part III.* Action of Thiocyanic Acid on Diazotised* o-*Nitroarylamines.*

By A. Burawoy and C. Turner.

The nitro-group in the diazonium salts from 1-nitro-2-naphthylamine and 2-nitro-1-naphthylamine is replaced by a thiocyanato-group in presence of thiocyanic acid. The thiocyanato-diazonium salts formed couple with β-naphthol to yield 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene (II) and its isomer (XIV) respectively. These substances are converted by alkali into disulphides (III and XVI respectively) which on reduction with sodium sulphide yield 1-(1-mercapto-2-naphthylazo)- (IV) and 1-(2-mercapto-1-naphthylazo)-2-naphthol (XVII).

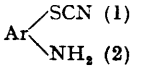
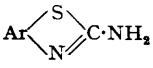
Preparation of 1-(1-mercapto-2-naphthylazo)-2-naphthol (IV) by the reactions (I) ⟶ (II) ⟶ (III) ⟶ (IV) has been described recently.* Specklin and Meybeck (*Bull. Soc. chim.*, 1951, **18**, 627), during unsuccessful attempts to prepare *o*-mercaptoazo-compounds, isolated the disulphide (VII) by coupling diazotised 2-amino-5-chloro-3-methylphenyl thiocyanate (V) with β-naphthol and treating the resultant (VI) with sodium sulphide.



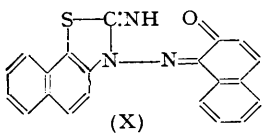
The utility of this method of preparation of *o*-mercaptoazo-compounds is limited by the generally difficult accessibility of *o*-thiocyanato-arylamines (VIII) and further by their

* Part II, *J.*, 1952, 1286; cf. also *J. Oil Colour Chem. Assoc.*, 1952, 907.

easy and often spontaneous conversion into the corresponding thiazoles (IX), particularly in the presence of acids or on heating.

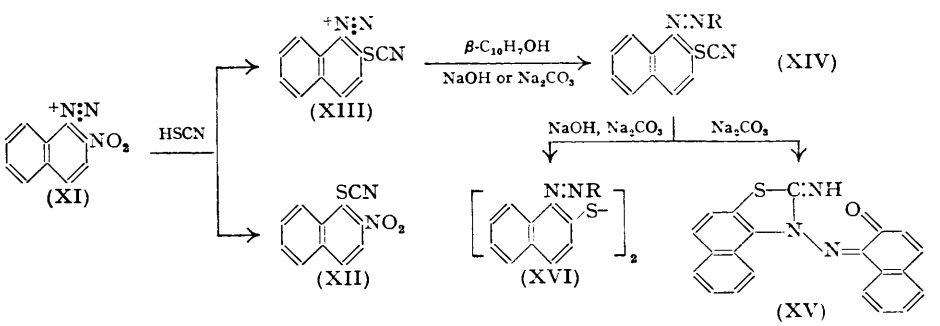
(VIII)  (IX) 

Hantzsch and Hirsch (*Ber.*, 1896, **29**, 947; 1898, **31**, 1253) observed that halogenobenzenediazonium thiocyanates rearrange to thiocyanatobenzenediazonium halides in cold alcohol. This led us to investigate the action of thiocyanates on diazotised *o*-nitroarylamines with the view to replacing the *o*-nitro-group by a thiocyanato-group. This would be an easy route to *o*-thiocyanatoaryldiazonium salts, with the advantage that ring closure of the *o*-thiocyanatoarylamines would be avoided. Korczynski, Kniatowna, and Kaminski (*Bull. Soc. chim.*, 1922, **31**, 1179) reported that diazonium groups can be replaced by thiocyanato-groups on addition of thiocyanic acid, in absence of a metal-salt catalyst and at room temperature. We have indeed found that diazotised *o*-nitroaniline and, more rapidly, diazotised 2 : 4-dinitroaniline yield under these conditions *o*-nitro- and 2 : 4-dinitro-thiocyanatobenzene respectively, without exchange between the nitro-group and the thiocyanate ion. However, reaction of 1-nitronaphthalene-2-diazonium sulphate with potassium thiocyanate leads to almost quantitative replacement of the nitro- by a thiocyanato-group without elimination of the diazonium group. Coupling the diazonium salt (I), formed in this manner, with β-naphthol results in an almost quantitative yield of (II), thus offering a much improved method for the preparation of the thiol (IV). The


(X)

thiocyanato-derivative (II) was originally obtained from benzene as dark red prisms of m. p. 149·5—151°. Later, when using either 1-nitro- or 1-thiocyanato-2-naphthylamine as starting material, only dark red needles could be isolated which contain one molecule of benzene of crystallisation and darken at 148°, sinter at *ca.* 215°, and finally melt at *ca.* 265°. At 100°, these needles lose benzene, but are converted into the isomeric compound of probable structure (X) reported earlier.

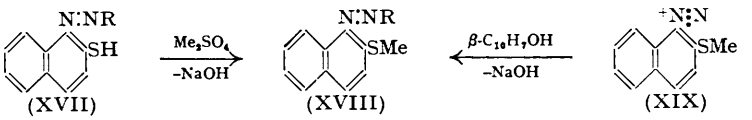
As 2-thiocyanato-1-naphthylamine is unknown and no simple method for its preparation can be devised, we investigated the action of potassium thiocyanate on diazotised 2-nitro-1-naphthylamine (XI) with a view to preparing 1-(2-mercapto-1-naphthylazo)-2-naphthol (XVII). Two reactions occurred simultaneously: (i) replacement of the diazonium group and formation of 1-thiocyanato-2-nitronaphthalene (XII) in 57% yield; (ii) exchange of the nitro-group and the thiocyanate ion, yielding the 2-thiocyanato-naphthalene-1-diazonium salt (XIII) which is stable under these conditions. A solution



of the latter couples with β-naphthol in aqueous sodium carbonate to yield mainly an isomer of the desired 1-(2-hydroxy-1-naphthylazo)-2-thiocyanatonaphthalene (XIV) with the probable structure (XV) and a small amount of di-1-(2-hydroxy-1-naphthylazo)-2-naphthyl disulphide (XVI). Both ring closure of the thiocyanato-compound (XIV), and its conversion into the disulphide, proceed much faster than in the case of the isomer (II)

which can be isolated and only undergoes these reactions at a high temperature. Formation of (XV) is avoided when coupling is carried out in aqueous sodium hydroxide. The disulphide (XVI) alone is obtained in good yield (34% calculated from 2-nitro-1-naphthylamine).

Alcoholic sodium sulphide reduces the disulphide to the blue sodium salt of 1-(2-mercapto-1-naphthylazo)-2-naphthol, which on acidification yields the free thiol (XVII), and on methylation with dimethyl sulphate gives the red 1-(2-methylthio-1-naphthylazo)-2-



naphthol (XVIII), also obtained by coupling diazotised 2-methylthio-1-naphthylamine (XIX) with β-naphthol. Like its isomer (III), 1-(2-mercapto-1-naphthylazo)-2-naphthol is readily reoxidised to the violet disulphide and forms complex salts with copper, cobalt, and nickel, which will be further investigated.

Experimental

Action of Potassium Thiocyanate on o-*Nitrobenzenediazonium Chloride.*—*o*-Nitroaniline (13·8 g.) in concentrated hydrochloric acid (100 c.c.) was diazotised with sodium nitrite (7 g.), and the ice-cooled diazonium solution added to potassium thiocyanate (50 g.) in water (100 c.c.). Precipitation of *o*-nitrothiocyanatobenzene set in immediately and was complete after 2 hours, when the filtrate ceased to couple with β-naphthol. Recrystallisation from carbon tetrachloride gave colourless plates, m. p. 132—133°. Müller (*Z. Farb. Text. Ind.*, 1906, **5**, 357) prepared this substance from the diazotised amine and potassium cuprous thiocyanate and gave m. p. 132·5°.

Action of Potassium Thiocyanate on 2 : 4-*Dinitrobenzenediazonium Sulphate.*—2 : 4-Dinitroaniline (16·7 g.) was slowly added to nitrosylsulphuric acid (from 7 g. of sodium nitrite in 150 c.c. of concentrated sulphuric acid) at 35°, stirred for 2 hours, and poured on ice (500 g.). On addition of this mixture to potassium thiocyanate (50 g.) in water (100 c.c.), 2 : 4-dinitrothiocyanatobenzene separated immediately in almost quantitative yield. It formed light yellow prisms (from chloroform), m. p. 138—139°, not depressed by an authentic specimen obtained from potassium thiocyanate and 1-chloro-2 : 4-dinitrobenzene in boiling ethyl alcohol (Austin and Smith, *Amer. Chem. J.*, 1886, **8**, 90, give m. p. 139°). The filtrate did not couple with β-naphthol.

Action of Ammonium Thiocyanate on 1-*Nitronaphthalene*-2-*diazonium Sulphate and Coupling with* β-*Naphthol.*—1-Nitro-2-naphthylamine (2 g.) in ethyl alcohol (100 c.c.) was added to 10% sulphuric acid (50 c.c.) and ice, and quickly diazotised with sodium nitrite (2 g.) in a small amount of water. After 5 minutes, urea (5 g.) was added and the diazonium solution poured into ammonium thiocyanate (15 g.) in water (50 c.c.), set aside for 5 minutes, filtered, and added to a solution of β-naphthol (5 g.), sodium hydroxide (2 g.), and sodium carbonate (25 g.) in water and ice (400 g.). The red precipitate of 2-(2-hydroxy-1-naphthylazo)-1-thiocyanatonaphthalene was washed with water and finally digested with methyl alcohol. Recrystallisation from benzene yielded the *solvate* as dark red needles with a green lustre, containing one molecule of benzene of crystallisation, which darken at 148°, sinter at *ca.* 215° and finally melt at *ca.* 265° (Found : C, 74·0; H, 4·4. $C_{21}H_{13}ON_3S.C_6H_6$ requires C, 74·6; H, 4·4%). It is identical with the product obtained directly from 1-thiocyanato-2-naphthylamine. At 100° it gives the cyclic product (X), m. p. 184—186°, described in Part II (Found, after drying : C, 71·1; H, 3·3; N, 11·8. Calc. for $C_{21}H_{13}ON_3S$: C, 71·0; H, 3·7; N, 11·8%).

Action of Potassium Thiocyanate on 2-*Nitronaphthalene*-1-*diazonium Sulphate and Coupling with* β-*Naphthol.*—Well-powdered 2-nitro-1-naphthylamine was slowly added with stirring to nitrosylsulphuric acid (from 1 g. of sodium nitrite in 40 c.c. of concentrated sulphuric acid) at room temperature. After 4 hours the solution obtained was dropped into ice-cooled water (1000 c.c.) containing potassium thiocyanate (20 g.). Evolution of nitrogen accompanied the almost immediate precipitation of 1-*thiocyanato*-2-*nitronaphthalene* (1·4 g., 57%). Recrystallisation from ethyl alcohol gave light yellow needles, m. p. 99—100° (Found : C, 56·9; H, 2·5; N, 11·9. $C_{11}H_6O_2N_2S$ requires C, 57·4; H, 2·6; N, 12·2%).

The filtrate was added to a solution of β-naphthol (10 g.), sodium hydroxide (4 g.), and

sodium carbonate (120 g.) in water and ice (2 kg.). The red precipitate was washed with water and digested with methyl alcohol (100 c.c.) (yield, 1·4 g.). It consists mainly of the cyclic isomer (XV) of 1-(2-hydroxy-1-naphthylazo)-2-thiocyanatonaphthalene, contaminated by a small quantity of di-1-(2-hydroxy-1-naphthylazo)-2-naphthyl disulphide (XVI). Recrystallisation from toluene yielded the *disulphide* as dark red-violet needles with a green lustre, m. p. 252—254°, which dissolve in organic solvents with a violet and in concentrated sulphuric acid with a yellow colour (Found: C, 73·0; H, 3·9; N, 8·7. $C_{40}H_{26}O_2N_4S_2$ requires C, 73·0; H, 4·0; N, 8·5%). Evaporation of the toluene mother-liquor yielded 1·2 g. of the *compound* (XV), which crystallised from glacial acetic acid as red needles with a green lustre, m. p. 161—162°. They dissolve in organic solvents with a brownish-red and in concentrated sulphuric acid with a blue colour (Found: C, 70·6; H, 3·3; N, 11·9. $C_{21}H_{13}ON_3S$ requires C, 71·0; H, 3·7; N, 11·8%).

Coupling of the filtered solution of 2-thiocyanatonaphthalene-1-diazonium sulphate obtained as above with a solution of β-naphthol (10 g.) and sodium hydroxide (120 g.) in water and ice (2 kg.) resulted in the formation of almost pure disulphide (1·2 g., 34%), which crystallised from benzene or toluene as dark violet-red needles, m. p. 252—254°, not depressed by mixing with the product obtained as above.

1-(2-*Mercapto*-1-*naphthylazo*)-2-*naphthol*.—Sodium sulphide nonahydrate (0·5 g.) in water (3 c.c.) was added to a suspension of di-1-(2-hydroxy-1-naphthylazo)-2-naphthyl disulphide (0·2 g.) in ethyl alcohol (25 c.c.). After 4 hours' shaking at room temperature the *sodium* salt of 1-(2-mercapto-1-naphthylazo)-2-naphthol was filtered off and washed with oxygen-free water (yield, 0·15 g., 70%). It was obtained as small dark crystals with a bronze lustre, insoluble in water, but slightly soluble in ethyl alcohol with a blue colour (Found: Na, 6·2. $C_{20}H_{13}ON_2SNa$ requires Na, 6·5%). Addition of a slight excess of dilute hydrochloric acid to its alcoholic suspension yields the free *thiol*. This crystallised from toluene under nitrogen as small red prisms with a golden lustre, m. p. 244—246° (Found: C, 71·8; H, 4·3; N, 8·3. $C_{20}H_{14}ON_2S$ requires C, 72·7; H, 4·3; N, 8·5%). It dissolves in organic solvents with an orange and in concentrated sulphuric acid with a blue colour, the latter rapidly becoming yellow, probably owing to oxidation to the corresponding disulphide. It is readily reoxidised to the disulphide, *e.g.*, by heating its toluene solution in a stream of air.

1-(2-*Methylthio*-1-*naphthylazo*)-2-*naphthol*.—Sodium sulphide nonahydrate (0·6 g.) in water (5 c.c.) was added to well-powdered di-1-(2-hydroxy-1-naphthylazo)-2-naphthyl disulphide (0·25 g.) suspended in ethyl alcohol (30 c.c.), and the mixture refluxed for 30 minutes. After dilution with water (30 c.c.), methyl sulphate (4 × 1·0 c.c.) and 10% aqueous sodium hydroxide (4 × 4 c.c.) were added. 1-(2-*Methylthio*-1-*naphthylazo*)-2-*naphthol* separated almost quantitatively. Recrystallisation from ethyl alcohol or light petroleum gave dark red needles with a green lustre, m. p. 158—159°, which dissolve in organic solvents with an orange-red and in concentrated sulphuric acid with a violet colour (Found: C, 73·5; H, 4·8; N, 8·2. $C_{21}H_{16}ON_2S$ requires C, 73·2; H, 4·7; N, 8·1%). This compound is identical with a specimen prepared by coupling diazotised 2-methylthio-1-naphthylamine with β-naphthol.

Metallic Complex Salts of 1-(2-*Mercapto*-1-*naphthylazo*)-2-*naphthol*.—To a filtered solution of 1-(2-mercapto-1-naphthylazo)-2-naphthol (0·3 g.) in acetone (300 c.c.) was added copper sulphate pentahydrate (0·5 g.) in water (300 c.c.). A violet *copper* compound, m. p. 225—228°, separated in 65% yield [Found: Cu, 14·5; S, as SO_4, 3·1. $(C_{20}H_{13}ON_2SCu)_2SO_4$ requires Cu, 14·4; S, as SO_4, 3·6%]. The *cobalt* salt, m. p. 204—207°, was similarly prepared, a solution of cobalt sulphate being added (yield, 60%) [Found: Co, 13·0; S, as SO_4, 4·3. $(C_{20}H_{13}ON_2SCo)_2SO_4$ requires Co, 13·5; S, as SO_4, 3·7%]. The *nickel* salt, prepared similarly by use of nickel sulphate (yield, 65%), had m. p. 158—162° [Found: Ni, 8·3. $(C_{20}H_{13}ON_2S)_2Ni$ requires Ni, 8·2%]. These salts dissolve in chloroform and to a lesser degree in benzene and acetone with a violet, reddish-brown, and wine-red colour respectively. They are insoluble in water, ethyl alcohol, and light petroleum.

COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, November 27th*, 1952.]