

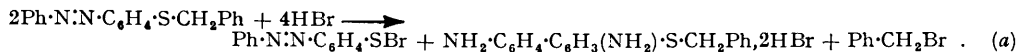
18. *o*-Mercapto-azo-compounds. Part VIII.\* Preparation and Debenzylation of 2-Benzylthio-2'- and -4'-nitroazobenzene.

By A. BURAWOY, A. CHAUDHURI, and C. E. VELLINS.

The action of hydrobromic acid and of bromine in glacial acetic acid on 2-benzylthio-2'- and -4'-nitroazobenzene, prepared by condensation in acetic acid of *o*-benzylthioaniline with *o*- and *p*-nitronitrosobenzene respectively, is investigated. The preparation and the reactions of various 2- and 4-nitroazobenzene-2'-sulphenyl derivatives and of the corresponding 2'-sulphinic acids and disulphides are reported.

DEBENZYLATION of 2-benzylthioazobenzene and of 2:2'-dibenzylthioazobenzene with bromine and of the former with hydrobromic acid, as well as the properties and reactions of the various compounds formed, have recently been discussed (Parts V, VI, VII \*). We have extended this investigation to 2-benzylthio-2'- and -4'-nitroazobenzene (I; X = S·CH<sub>2</sub>Ph) which are obtained by the condensation in acetic acid of *o*-benzylthioaniline with *o*- and *p*-nitronitrosobenzene respectively.

As shown in Part V, 2-benzylthioazobenzene is converted quantitatively by 48% hydrobromic acid in hot acetic acid into azobenzene-2-sulphenyl bromide (~50%) and 3-benzylthiobenzidine dihydrobromide (~50%) according to the general equation (a). The reaction is initiated by debenylation with formation of benzyl bromide and *o*-mercaptoazobenzene which is quickly dehydrogenated to di-(*o*-phenylazophenyl) disulphide, unchanged starting material serving as hydrogen acceptor and being reduced to 2-benzylthiohydrazobenzene. Fission of the disulphide linkage by hydrobromic acid yields azobenzene-2-sulphenyl bromide and *o*-mercaptoazobenzene which re-enters the reaction cycle, whereas 2-benzylthiohydrazobenzene undergoes the benzidine rearrangement. In the presence of azobenzene, the yield of azobenzene-2-sulphenyl bromide is increased, since the starting material is replaced by azobenzene as hydrogen acceptor.



2-Benzylthio-4'-nitroazobenzene behaves similarly, but, in addition to 4-nitroazobenzene-2'-sulphenyl bromide (I; X = SBr), *p*-nitroaniline is isolated in 30% yield, *i.e.*, the 2-benzylthio-4'-nitrohydrazobenzene formed is split by hydrobromic acid in preference to being rearranged (for references to the general tendency of *para*-substituted hydrazobenzenes, under the influence of acids, to undergo disproportionation to aniline derivatives rather than rearrangement see Jacobsen, *Annalen*, 1922, 428, 76). Again, in the presence of azobenzene the yield of the sulphenyl bromide is considerably increased and *p*-nitroaniline is not detected.

In contrast, heating 2-benzylthio-2'-nitroazobenzene with hydrobromic acid gives only 2-nitroazobenzene-2'-sulphenyl bromide (I; X = SBr). This indicates either that the starting material is unable to serve as a hydrogen acceptor or that its debenylation is faster than the dehydrogenation of the thiol (I; X = SH) and that the latter is oxidised to di-[*o*-(*o*-nitrophenylazo)phenyl] disulphide (II) which is split by hydrobromic acid as discussed. We have established by independent experiments that both di-[*o*-(*o*-nitrophenylazo)phenyl] disulphide and di-[*o*-(*p*-nitrophenylazo)phenyl] disulphide are quantitatively converted by boiling hydrobromic acid into the corresponding sulphenyl bromides (I; X = SBr).

Both nitro-derivatives (like 2-benzylthioazobenzene and 2:2'-dibenzylthioazobenzene) yield almost quantitatively the corresponding stable sulphenyl bromides (I; X = SBr) and the sulphenyl tribromides (I; X = SBr<sub>3</sub>) when heated with 1 mol. and with an excess of bromine respectively in acetic acid. 2-Nitroazobenzene-2'-sulphenyl tribromide is rather

\* Parts I, V, VI, and VII, *J.*, 1950, 469; 1954, 90, 4481; 1955, 3798.

unstable and cannot be isolated in a pure state, since it quickly dissociates into the sulphenyl bromide and bromine.

Both nitroazobenzene-2'-sulphenyl bromides show many of the reactions characteristic of other known sulphenyl halides. Thus, with dimethylaniline they yield *p*-dimethylamino-phenyl *o*-(*o*- and *p*-nitrophenylazo)phenyl sulphide respectively (I; X = S·C<sub>6</sub>H<sub>4</sub>·NMe<sub>2</sub>-*p*).

Again, on addition of an excess of sodium hydroxide to the suspensions of the bromides in water or aqueous ethanol, deep blue solutions are formed immediately, the colour being due to the presence of the sodium 2- and 4-nitroazobenzene-2'-sulphenate respectively (I; X = SONa). Although the salts could not be isolated, their existence has been established by immediate treatment of the blue alkaline solutions with methyl sulphate, whereupon methyl *o*-(*o*- and *p*-nitrophenylazo)phenyl sulphoxide respectively (I; X = SMeO) are formed in good yield. [This is similar to the conversion of the blue sodium salts of anthraquinone- and 4-aminoanthraquinone-1-sulphenic acid by methyl sulphate into the corresponding methyl sulphoxides (Fries, *Ber.*, 1912, **45**, 2365; Fries and Schürman, *Ber.*, 1919, **52**, 2170, 2182).] The blue colour disappears slowly, disproportionation taking place with formation of the insoluble di-[*o*-(*o*-nitrophenylazo)phenyl] disulphide and its *p*-nitro-isomer respectively (III) and the soluble sodium 2- and 4-nitroazobenzene-2'-sulphinates respectively (I; X = SO<sub>2</sub>Na) which give on acidification the free sulphinic acids.

The *p*-nitro-isomer disproportionates more rapidly. If the stirring of the reaction mixture is continued after the disappearance of the blue colour, the amount of the 4-nitroazobenzene-2'-sulphinic acid increases at the expense of the disulphide and the acid is finally the only product present. The disulphide linkage is split by sodium hydroxide to yield (i) 2-mercapto-4'-nitroazobenzene (I; X = SH) which is quickly reoxidised to the disulphide and (ii) the sulphenic acid (I; X = S·OH) which, again, disproportionates to disulphide and more sulphinic acid (for the similar behaviour of 2-benzylthioazobenzene-2'-sulphenyl bromide towards aqueous sodium hydroxide see Part VII).

The identity of the disulphides has been confirmed by their formation from the corresponding sulphenyl bromides by the action of zinc in boiling benzene solution. The sulphinic acids are also obtained by the treatment of the corresponding sulphenyl tribromides with aqueous sodium hydroxide. Their exclusive formation and the non-appearance of the intermediate blue colour characteristic of the sodium sulphenates confirm the quadrivalency of the sulphur atom in the tribromides. The sulphinic acids have been characterised as nitrobenzyl sulphones (I; X = SO<sub>2</sub>·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>-*p*) and their structures are confirmed by conversion by hydrobromic acid in acetic acid into the corresponding sulphenyl bromides (for this characteristic reaction of sulphinic acids and references, cf. Parts I, V, and VII).

Both nitroazobenzene-2'-sulphenyl bromides, like azobenzene-2-sulphenyl bromide and 2-benzylthioazobenzene-2'-sulphenyl bromide, but unlike other known sulphenyl bromides, are very stable and water-soluble and are easily converted by double decomposition in water into the cyanide, thiocyanate, chloride, iodide, and perchlorate respectively (I; X = SCN, S·SCN, SCl, SI, S·ClO<sub>4</sub>).

As has been established for the corresponding azobenzene-2-sulphenyl derivatives, these compounds, except for the water-insoluble cyanides, are able to exist as true salts of structure (III). The effect of substituents on the structure and equilibria in different solvents of the azobenzene-2-sulphenyl derivatives is being further investigated by physical methods.

2-Nitroazobenzene-2'-sulphenyl iodide is much less stable to heat than azobenzene-2-sulphenyl iodide and its 4-nitro-derivative. Attempts to crystallise it were unsuccessful, since it dissociates quickly into the disulphide and iodine. 4-Nitroazobenzene-2'-sulphenyl thiocyanate, a reddish-brown crystalline compound after drying in a vacuum, becomes orange-yellow in air with the uptake of 1 mol. of water; the change is reversible and is apparently unaccompanied by a change of the crystal form. The possibility that these two states correspond to the non-ionic and the ionic structure respectively cannot be excluded.

Attempts to reduce the disulphides to the corresponding thiols by ethanolic sodium

sulphide were only partly successful, the reaction being complicated by the presence of the reducible nitro-group. Di-[*o*-(*o*-nitrophenylazo)phenyl] disulphide yields a crude yellow product which could not be purified, but consists mainly of 2-mercapto-2'-nitroazobenzene, since when freshly prepared it is soluble in ethanolic sodium hydroxide and on treatment with methyl sulphate and with benzyl chloride is converted in good yields into 2-methylthio- and 2-benzylthio-2'-nitroazobenzene respectively.

On the other hand, no indication of the formation of 2-mercapto-4'-nitroazobenzene has been obtained on reduction of di-[*o*-(*p*-nitrophenylazo)phenyl] disulphide. Instead, di-[*o*-(*p*-aminophenylazo)phenyl] disulphide (IV) could be isolated, purified through its violet crystalline dihydroperchlorate and further characterised as its *NN'*-dibenzoyl derivative.



### EXPERIMENTAL

**2-Benzylthio-2'-nitroazobenzene.**—*o*-Nitronitrosobenzene (18 g.) in hot acetic acid (250 c.c.) was added to *o*-benzylthioaniline (25 g.) in acetic acid (100 c.c.). The mixture was kept at 50° for 15 min. and at room temperature overnight. The precipitate of almost pure 2-benzylthio-2'-nitroazobenzene (27 g.) was filtered off and washed with light petroleum. Addition of water to the filtrate yielded a further amount of less pure product (5.5 g.; total yield, 80%). Crystallisation from light petroleum (b. p. 60—80°) or benzene gave orange needles, m. p. 115—116° (Found: C, 65.6; H, 4.4; N, 11.8. C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>N<sub>3</sub>S requires C, 65.3; H, 4.3; N, 12.0%).

**2-Benzylthio-4'-nitroazobenzene**, similarly prepared, formed orange-red needles, m. p. 167—168°, from benzene (Found: C, 65.2; H, 4.0; N, 11.6%).

**2-Nitroazobenzene-2'-sulphenyl Bromide.**—2-Benzylthio-2'-nitroazobenzene (10 g.), bromine (4.6 g.), and acetic acid (250 c.c.) were refluxed for 5 min. On cooling, almost pure 2-nitroazobenzene-2'-sulphenyl bromide separated (9.4 g., 97%). Crystallisation from acetic acid gave yellow needles, m. p. 257—258° (Found: C, 42.1; H, 2.2; N, 12.1. C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>N<sub>3</sub>SBr requires C, 42.6; H, 2.3; N, 12.4%).

**4-Nitroazobenzene-2'-sulphenyl bromide** was similarly obtained as yellow needles, m. p. 279—280° (Found: C, 42.8; H, 2.6; N, 12.6%).

**Action of Hydrobromic Acid on 2-Benzylthio-4'-nitroazobenzene.**—(a) 2-Benzylthio-4'-nitroazobenzene (4 g.), acetic acid (120 c.c.), and 48% hydrobromic acid (100 c.c.) were refluxed for 5 min. On cooling, 4-nitroazobenzene-2'-sulphenyl bromide separated (0.8 g.). The filtrate was reduced to a small volume under a vacuum, water was added, and the solution extracted with chloroform from which an additional amount of the sulphenyl bromide was obtained (1.9 g.; total yield, 49%). Crystallisation from acetic acid gave yellow needles, m. p. 279—280° not depressed on admixture with the product described above. The aqueous mother-liquor was made alkaline and extracted with ether, which on concentration yielded *p*-nitroaniline, m. p. and mixed m. p. 146° (0.5 g., 30%).

(b) A mixture of 2-benzylthio-4'-nitroazobenzene (2.5 g.), azobenzene (3 g.), acetic acid (80 c.c.), and 48% hydrobromic acid (45 c.c.) was refluxed for 5 min. and poured into water (300 c.c.). The precipitate of almost pure 4-nitroazobenzene-2'-sulphenyl bromide, m. p. 279—280°, was collected (1 g.). Extraction of the filtrate with chloroform yielded an additional amount of the bromide (0.85 g.; total yield, 78%). No *p*-nitroaniline could be isolated.

**Action of Hydrobromic Acid on 2-Benzylthio-2'-nitroazobenzene.**—This isomer (2 g.), acetic acid (40 c.c.), and 48% hydrobromic acid (60 c.c.) similarly yielded 2-nitroazobenzene-2'-sulphenyl bromide (total yield, 82%). Crystallisation from acetic acid gave yellow needles, m. p. 257—258°, not depressed by the product obtained by the action of bromine. No *o*-nitroaniline was formed.

**Action of Zinc on 2-Nitroazobenzene-2'-sulphenyl Bromide.**—A solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in benzene (30 c.c.) was refluxed with zinc dust (3 g.) for 15 min. The solution was filtered hot and concentrated. The precipitate of di-[*o*-(*o*-nitrophenylazo)-*p*henyl] disulphide was collected (0.25 g., 67%). Crystallisation from benzene gave orange-yellow needles, m. p. 172—173° (Found: C, 56.2; H, 3.6; N, 15.9. C<sub>24</sub>H<sub>16</sub>O<sub>4</sub>N<sub>8</sub>S<sub>2</sub> requires C, 55.8; H, 3.1; N, 16.3%).

*Action of Zinc on 4-Nitroazobenzene-2'-sulphenyl Bromide.*—4-Nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in benzene (200 c.c.) was refluxed with zinc dust (3 g.) for 30 min. After hot filtration and concentration to a small volume, the precipitate of *disulphide* was collected (0.25 g., 67%). It crystallised from benzene as orange needles, m. p. 228—229° (Found : C, 56.1; H, 3.3; S, 12.6.  $C_{24}H_{16}O_4N_6S_2$  requires C, 55.8; H, 3.1; S, 12.4%).

*Action of Hydrobromic Acid on Di-[o-(o-nitrophenylazo)phenyl] Disulphide.*—The disulphide (0.2 g.), acetic acid (15 c.c.), and 48% hydrobromic acid (5 c.c.) were refluxed for 3 min. After cooling and addition of water, the solution was extracted with chloroform from which, on addition of light petroleum, 2-nitroazobenzene-2'-sulphenyl bromide was obtained (0.2 g., 76%). Crystallisation from acetic acid gave yellow needles, m. p. 258°.

The *p*-isomer similarly gave 4-nitroazobenzene-2'-sulphenyl bromide (0.2 g., 76%), crystallising from acetic acid as yellow needles, m. p. 279—280°.

*Action of Sodium Hydroxide on 2-Nitroazobenzene-2'-sulphenyl Bromide.*—10% Aqueous sodium hydroxide (60 c.c.) was added to a suspension of 2-nitroazobenzene-2'-sulphenyl bromide (3 g.) in water (350 c.c.) and ethanol (100 c.c.). A deep blue solution was formed immediately. After 24 hours' stirring the colour had disappeared and a precipitate of almost pure di-[o-(o-nitrophenylazo)phenyl] disulphide was collected (1.4 g., 92%; m. p. and mixed m. p. 171—173°). On acidification of the filtrate with hydrochloric acid 2-nitroazobenzene-2'-sulphinic acid separated (0.85 g., 94%). Crystallisation from aqueous ethanol at 50° gave yellow prisms, m. p. 144—145° (Found : C, 49.3; H, 3.4; N, 14.5.  $C_{12}H_9O_4N_3S$  requires C, 49.5; H, 3.1; N, 14.4%).

*Methyl o-(o-Nitrophenylazo)phenyl Sulphoxide.*—40% Aqueous sodium hydroxide (5 c.c.) was added to a solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in methanol (100 c.c.). The blue solution was shaken immediately with methyl sulphate (3 c.c.) for 30 min.; the blue colour disappeared. After addition of water, the precipitate of *methyl o-(o-nitrophenylazo)phenyl sulphoxide* was filtered off (0.3 g., 70%). It crystallised from aqueous methanol as orange needles, m. p. 128—129° (Found : C, 54.7; H, 3.8; N, 14.6.  $C_{13}H_{11}O_3N_3S$  requires C, 54.0; H, 3.8; N, 14.5%).

*Action of Sodium Hydroxide on 4-Nitroazobenzene-2'-sulphenyl Bromide.*—10% Aqueous sodium hydroxide (40 c.c.) was added to a suspension of 4-nitroazobenzene-2'-sulphenyl bromide (2 g.) in water (900 c.c.). After 30 minutes' stirring the blue colour, which developed immediately, disappeared and the precipitate of di-[o-(*p*-nitrophenylazo)phenyl] disulphide was filtered off (0.8 g., 78%). It crystallised from benzene as orange needles, m. p. and mixed m. p. 228—229°. On acidification of the filtrate with hydrochloric acid 4-nitroazobenzene-2'-sulphinic acid separated (0.6 g., 104%). Crystallisation from methanol gave brown-yellow needles, m. p. 133—134° (Found : C, 49.6; H, 3.3; N, 14.3%). The experiment was repeated, but the reaction allowed to proceed for 3 hr. : disulphide (0.55 g., 54%) and sulphinic acid (0.8 g., 137%) were obtained. After 24 hr. only the sulphinic acid could be obtained.

*Methyl o-(p-Nitrophenylazo)phenyl Sulphoxide.*—40% Aqueous sodium hydroxide (5 c.c.) was shaken with a solution of 4-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in methanol (100 c.c.) and methyl sulphate (3 c.c.) for 30 min. After filtration to remove a small amount of disulphide, water was added and the precipitate of almost pure *sulphoxide* collected (0.25 g., 58%). It crystallised from aqueous methanol as orange needles, m. p. 175—176° (Found : C, 54.3; H, 3.7; N, 14.2%).

*p-Dimethylaminophenyl o-(p-Nitrophenylazo)phenyl Sulphide.*—A solution of 4-nitroazobenzene-2'-sulphenyl bromide (0.6 g.) and dimethylaniline (2 c.c.) in acetic acid (200 c.c.) was refluxed for 1 hr. and subsequently concentrated to a small volume. On addition of water, *p-dimethylaminophenyl o-(p-nitrophenylazo)phenyl sulphide* separated (0.5 g., 75%). Crystallisation from light petroleum (b. p. 80—100°) gave orange needles, m. p. 187—189° (Found : C, 63.3; H, 4.8; N, 14.7.  $C_{20}H_{18}O_2N_4S$  requires C, 63.5; H, 4.8; N, 14.8%).

*p-Dimethylaminophenyl o-(o-nitrophenylazo)phenyl sulphide*, similarly prepared, crystallised from light petroleum as dark orange needles, m. p. 186—187° (Found : C, 63.6; H, 4.7; N, 15.2%).

*4-Nitrobenzyl o-(o-Nitrophenylazo)phenyl Sulphone.*—A solution of 4-nitrobenzyl bromide (0.5 g.), 2-nitroazobenzene-2'-sulphinic acid (0.4 g.), and sodium hydroxide (0.08 g.) in ethanol (30 c.c.) was refluxed for 3 hr. On cooling, the *sulphone* separated (0.4 g., 70%). Crystallisation from benzene gave orange needles, m. p. 230—232° (Found : C, 53.0; H, 3.2; N, 13.4.  $C_{19}H_{14}O_6N_4S$  requires C, 53.5; H, 3.3; N, 13.2%).

*4-Nitrobenzyl o-(p-nitrophenylazo)phenyl sulphone* similarly formed an orange-red powder, m. p. 249—250°, from benzene (Found : C, 53.8; H, 3.5; N, 13.3%).

*Action of Hydrobromic Acid on 2- and 4-Nitroazobenzene-2'-sulphinic Acid.*—(a) 2-Nitroazobenzene-2'-sulphinic acid (0.3 g.) in acetic acid (10 c.c.) was refluxed with 48% hydrobromic acid (2 c.c.) for 10 min. On cooling, 2-nitroazobenzene-2'-sulphenyl bromide separated [0.3 g., 86%; yellow needles (from acetic acid), m. p. 257—258°]. (b) 4-Nitroazobenzene-2'-sulphinic acid (0.85 g.) in acetic acid (20 c.c.) was refluxed with 48% hydrobromic acid (5 c.c.) for 3 min. Almost pure 4-nitroazobenzene-2'-sulphenyl bromide (0.65 g.) separated. Another 0.2 g. were obtained by extraction of the mother-liquor with chloroform (total yield, 86%). Crystallisation from acetic acid gave yellow needles, m. p. 279—280°.

*2-Nitroazobenzene-2'-sulphenyl Chloride.*—Concentrated hydrochloric acid (60 c.c.) was added to a solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.6 g.) in boiling water (500 c.c.). On saturation with salt and cooling in ice, the *chloride* separated (0.45 g., 86%). Crystallisation from toluene gave yellow needles, m. p. 237—239° (Found : C, 49.5; H, 2.7; N, 14.1.  $C_{12}H_8O_2N_3S$  requires C, 49.1; H, 2.7; N, 14.3%).

The 4-*nitro-isomer* crystallised from acetic acid as yellow plates, m. p. 258—259° (Found : C, 49.4; H, 2.8%).

*4-Nitroazobenzene-2'-sulphenyl Iodide.*—A solution of potassium iodide (1.5 g.) in water (10 c.c.) was added to 4-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in boiling water (200 c.c.). On cooling, 4-*nitroazobenzene-2'-sulphenyl iodide* (0.35 g., 62%) separated. Crystallisation from ethanol gave violet-brown needles, m. p. 200—202° (Found : C, 37.3; H, 2.1.  $C_{12}H_8O_2N_3SI$  requires C, 37.4; H, 2.1%).

The 2-*nitro-isomer*, formed in 87% yield as an immediate precipitate, m. p. 149—150° (Found : C, 37.9; H, 2.2; N, 10.7.  $C_{12}H_8O_2N_3SI$  requires C, 37.4; H, 2.1; N, 10.9%), could not be crystallised from ethanol or benzene, since it readily dissociated into iodine and pure di-[*o*-(*o*-nitrophenylazo)phenyl] disulphide.

*2-Nitroazobenzene-2'-sulphenyl Perchlorate.*—A solution of sodium perchlorate (3 g.) in water (100 c.c.) was added to a solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.7 g.) in water (500 c.c.) at 60°. On cooling, the *perchlorate* separated (0.5 g., 67%). Crystallisation from ethanol gave yellow needles, m. p. 176° (with detonation) (Found : C, 40.3; H, 2.4.  $C_{12}H_8O_6N_3S$  requires C, 40.3; H, 2.4%).

The 4-*nitro-salt* formed yellow-brown needles, m. p. 204° (with detonation), from ethanol (Found : C, 40.6; H, 2.5%).

*2-Nitroazobenzene-2'-sulphenyl Cyanide (2-Nitro-2'-thiocyanatoazobenzene).*—A solution of potassium cyanide (1 g.) in water (20 c.c.) was added to a solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in hot water (600 c.c.). The precipitate of *cyanide* was collected (0.4 g., 95%). Crystallisation from benzene gave yellow needles, m. p. 144° (Found : C, 55.3; H, 2.7; N, 20.1.  $C_{13}H_8O_2N_4S$  requires C, 54.9; H, 2.8; N, 19.7%).

The 4-*nitro-cyanide* crystallised from benzene as orange needles, m. p. 160° (Found : C, 55.3; H, 2.7; N, 19.9%).

*2-Nitroazobenzene-2'-sulphenyl Thiocyanate.*—A solution of 2-nitroazobenzene-2'-sulphenyl bromide (0.5 g.) in water (600 c.c.) was treated with potassium thiocyanate. The precipitated *thiocyanate* (0.4 g., 86%) crystallised from benzene as yellow-orange needles, m. p. 132° (Found : C, 50.0; H, 2.3; N, 17.8.  $C_{13}H_8O_2N_4S_2$  requires C, 49.4; H, 2.5; N, 17.7%).

The 4-*nitro-thiocyanate* (86%), formed at 60°, crystallised from benzene as reddish-brown needles or plates (after drying in a vacuum) which decompose at 200° (Found : C, 49.2; H, 2.6; N, 18.2%). In air, 1 mol. of water was quickly absorbed and the colour changed to orange-yellow (Found : C, 47.2; H, 3.1; N, 16.7.  $C_{13}H_8O_2N_4S_2 \cdot H_2O$  requires C, 46.7; H, 3.0; N, 16.7%).

*4-Nitroazobenzene-2'-sulphenyl Tribromide.*—2-Benzylthio-4'-nitroazobenzene (2 g.), bromine (2 g., 2.1 mols.), and acetic acid (80 c.c.) were refluxed for 3 min. On cooling, almost pure 4-*nitroazobenzene-2'-sulphenyl tribromide* separated (2.5 g., 89%). Crystallisation from acetic acid containing a small amount of bromine gave a yellow powder, m. p. 232° (decomp.) (Found : C, 29.1; H, 1.6; Br, 48.4.  $C_{15}H_8O_2N_3SBr_3$  requires C, 28.9; H, 1.6; Br, 48.2%).

*Action of Sodium Hydroxide on 4-Nitroazobenzene-2'-sulphenyl Tribromide.*—The tribromide (1 g.) was dissolved in water (40 c.c.) containing sodium hydroxide (0.5 g.). No intermediate blue colour developed. On addition of salt, sodium 4-nitroazobenzene-2-sulphinate separated (0.5 g., 80%). Acidification of its aqueous solution with hydrochloric acid precipitated almost quantitatively 4-nitroazobenzene-2'-sulphinic acid; it crystallised from methanol as brown-yellow needles, m. p. and mixed m. p. 133—134°.

*Action of Sodium Hydroxide on 2-Nitroazobenzene-2'-sulphenyl Tribromide.*—2-Benzylthio-2'-nitroazobenzene (1 g.), bromine (1 g.), and acetic acid (50 c.c.) were refluxed for 3 min. After

cooling, the dark, fuming precipitate of 2-nitroazobenzene-2'-sulphenyl tribromide was collected (1 g.). It quickly lost bromine, being converted into 2-nitroazobenzene-2'-sulphenyl bromide. The freshly filtered crude tribromide (1 g.) was quickly treated with aqueous sodium hydroxide (0.5 g. in 30 c.c.). No blue colour developed. The red solution was filtered and sodium 2-nitroazobenzene-2'-sulphinate was salted out (0.5 g., 80%). Acidification of its aqueous solution with hydrochloric acid yielded almost quantitatively the free sulphinic acid, which crystallised from aqueous methanol as light yellow prisms, m. p. and mixed m. p. 144—145°.

*Action of Sodium Sulphide on Di-[o-(o-nitrophenylazo)phenyl] Disulphide.*—To a suspension of the disulphide (0.4 g.) in ethanol (50 c.c.) a solution of sodium sulphide nonahydrate (0.4 g.) in 5% aqueous sodium hydroxide (10 c.c.) was added, and the mixture refluxed for 5 min. The clear red solution was cooled, diluted with water, and acidified. A yellow precipitate consisting mainly of 2-mercapto-2'-nitroazobenzene was filtered off (0.25 g., 63%; m. p. 98—100°). On storage or on attempted crystallisation it became insoluble in ethanolic sodium hydroxide.

A solution of the freshly prepared crude thiol (0.15 g.) in 10% aqueous sodium hydroxide (3 c.c.) and ethanol (10 c.c.) was refluxed for 5 min. with benzyl chloride (0.2 c.c.). On concentration of the solution and cooling, 2-benzylthio-2'-nitroazobenzene crystallised (~0.1 g., 57%). Crystallisation from light petroleum gave orange needles, m. p. and mixed m. p. 115—116°.

The experiment was repeated, but benzyl chloride was replaced by methyl sulphate (0.2 c.c.). 2-Methylthio-2'-nitroazobenzene was obtained (~0.1 g., 64%). Crystallisation from ethanol gave orange needles, m. p. 114—115° (Found: C, 57.2; H, 3.8; N, 15.2.  $C_{13}H_{11}O_2N_3S$  requires C, 57.2; H, 4.0; N, 15.4%). The same product (0.2 g., 61%) was obtained on shaking the red solution, obtained on reduction of the disulphide (0.3 g.) with sodium sulphide, with 1% aqueous sodium hydroxide (100 c.c.) and methyl sulphate (2 c.c.).

*Action of Sodium Sulphide on Di-[o-(p-nitrophenylazo)phenyl] Disulphide.*—A solution of sodium sulphide nonahydrate (0.5 g.) in water (10 c.c.) and 10% aqueous sodium hydroxide (5 c.c.) was added to a suspension of the disulphide in boiling ethanol (30 c.c.), and the mixture was refluxed for 10 min. The resultant red solution was filtered hot and 70% perchloric acid (2 c.c.) was added. On addition of water and cooling, the violet di-[o-(p-aminophenylazo)phenyl] disulphide diperchlorate separated (0.35 g., 55%). Crystallisation from aqueous ethanol gave violet needles, m. p. 240° (with detonation) (Found: C, 44.3; H, 3.2; N, 13.0.  $C_{24}H_{20}N_6S_2 \cdot 2HClO_4$  requires C, 43.9; H, 3.3; N, 12.8%).

To a solution of the pure perchlorate (0.2 g.) in 50% aqueous ethanol (30 c.c.) 10% aqueous sodium hydrogen carbonate (10 c.c.) was added. The solution was extracted with benzene, from which light petroleum precipitated di-[o-(p-aminophenylazo)phenyl] disulphide (0.1 g., 72%). Crystallisation from benzene-light petroleum gave a yellow-brown powder, m. p. 124° (Found: C, 63.4; H, 4.4.  $C_{24}H_{20}N_6S_2$  requires C, 63.1; H, 4.4%).

Pure perchlorate (0.2 g.), ethanol (30 c.c.), 10% aqueous sodium hydroxide (10 c.c.), and benzoyl chloride (2 c.c.) were shaken for 30 min. On addition of water, di-[o-(p-benzamido-phenylazo)phenyl] disulphide separated (0.15 g., 74%). Crystallisation from ethanol gave a yellow powder, m. p. 190—192° (Found: C, 68.8; H, 3.9; N, 13.1.  $C_{38}H_{28}N_6O_2S_2$  requires C, 68.7; H, 4.2; N, 12.7%).

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