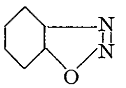
171. *Some Derivatives of Benz-*1*-thia-*2 : 3*-diazole, the Nature of the Thiadiazole Ring, and a Note on the Thiolation of* 2*-Chloro-*5*-nitroaniline.*

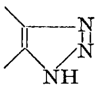
By Herbert H. Hodgson and Douglas P. Dodgson.

2-Chloro-5-nitroaniline reacts with sodium monosulphide and sodium hydrogen carbonate in aqueous ethanolic solution to give 4-nitro-2-aminobenzenethiol in 97% yield, which on diazotisation becomes 5-nitrobenz-1-thia-2 : 3-diazole. This is reduced by iron and sulphuric acid to 5-aminobenz-1-thia-2 : 3-diazole, and thence converted by usual methods into 5-hydroxy- and the 5-*halogeno-benz*-1-*thia*-2 : 3-*diazoles* and also *benz*-1-*thia*-2 : 3-*diazole*-5-*azo*-β-*naphthol*. A cyclic structure is preferred for the thiadiazole ring in contrast to the quinonoid resonance structures of the analogous diazo-oxides. In the mono-reduction of 1-chloro-2 : 4-dinitrobenzene by stannous chloride in glacial acetic acid solution, 2-chloro-5-nitro- and 4-chloro-3-nitro-anilines are formed in about equal amounts.

Just as the *o*-aminophenols when diazotised give rise to diazo-oxides, so in like manner do *o*-aminothiophenols afford the somewhat analogous thiadiazoles. The diazo-oxides used to be regarded as having the ring structure (I), and Morgan and Porter (*J.*, 1915, **107**, 645) claimed to have established this formulation beyond doubt by the existence of naphthalene-1 : 8-diazo-oxide, whose colour could not be explained by an orthodox quinonoid structure but had to be attributed to a so-called " chromogenic complex ", $^{-}O{-}N{=}N^{-}$. Later, however, a quinonoid structure for the diazo-oxides in general was advocated by Sidgwick (cf. " The Organic Chemistry of Nitrogen ", Oxford, 1937, p. 422), and with the advent of the resonance theory (Pauling, " Nature of the Chemical Bond ", 1940, p. 152) all the apparent exceptions such as the above *peri*-diazonaphthol could be interpreted by means of ionic quinonoid structures (Hodgson and Marsden, *J. Soc. Dyers and Col.*, 1943, **59**, 271). Still later, Anderson and Roedel (*J. Amer. Chem. Soc.*, 1945, **67**, 955) have attempted to show by means of absorption spectra, whether the predominant structure of the 1 : 2- and 1 : 4-diazophenols in non-polar solvents is cyclic or quinonoid by comparing the absorption spectra of the diazophenols with those of compounds of known cyclic and of known quinonoid structure. The only previous work on absorption spectra in this field had been carried out by Hantzsch and Lifschitz (*Ber.*, 1912, **45**, 3011) who qualitatively compared the absorption spectra of diazoacetic ester and *p*-diazophenol, and concluded that the structure of the latter was quinonoid. Anderson and Roedel (*loc. cit.*) also



(I.)



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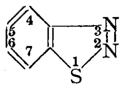
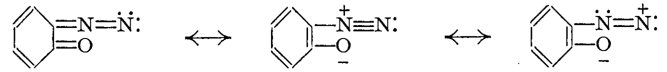


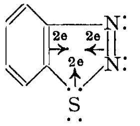
(III.)

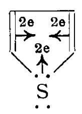
concluded that the *p*-diazophenol possessed a quinonoid structure, and that the *o*-compounds were not cyclic but probably quinonoid. When an attempt was made by Leigh and Anderson (*loc. cit.*) to obtain the above *peri*-diazonaphthol cited by Morgan and Porter (*loc. cit.*), they could not find any mention of its preparation, and failed to prepare it. The resonance system may



thus give an interpretation of the colour as well as of the other properties which the diazo-oxides exhibit, and in particular of the ready coupling ability which indicates the feeble nature of the N–O bond, if it really exists.

In contrast to the diazo-oxides, the thiadiazoles or diazosulphides only exist as *o*-compounds, and they are usually colourless, resembling in this respect the analogous azoimides (II), obtained by the action of nitrous acid on the *o*-diamines; they crystallise well, are feebly basic, as shown by their solubility in concentrated mineral acids, and are usually volatile in steam. The great stability of the parent substance, benz-1-thia-2 : 3-diazole (III), towards most chemical reagents has been indicated by Jacobson (*Annalen*, 1893, **277**, 209), but he mentions that, whereas oxidising agents have little effect on them under ordinary conditions, yet tin and hydrochloric acid reduce the thiadiazoles to the corresponding thiols, while heat causes elimination of nitrogen with formation of thianthren derivatives at 200—250°. In no case has the coupling property which diazo-oxides exhibit with alkaline β-naphthol been found in the diazo-sulphides. The thiadiazole ring thus resembles thiophen in its stability, and the same electronic configuration may be operative in both cases, *viz.*, the existence of the aromatic sextet [cf. Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions", Institute of Chemistry, 1932, p. 10]:

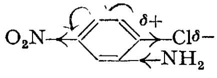




The thiadiazoles will thus bear considerable resemblance to naphthalene compounds.

In spite of the relative ease of formation of these compounds, the literature contains but few references to them, and these are mainly due to Jacobson (*Ber.*, 1888, **21**, 3106; *Annalen*, *loc. cit.*) and Fries (Fries and Engelbert, *Annalen*, 1915, **407**, 208; Fries, Vorbrodt, and Siebert, *ibid.*, 1927, **454**, 172; Fries, Koch, and Stukenbrock, *ibid.*, 1929, **468**, 162; Fries and Reitz, *ibid.*, 1936, **527**, 38).

In the present paper various thiadiazoles are described which are prepared from 2-chloro-5-nitroaniline. It is somewhat unexpected that whereas the chlorine in 1-chloro-2 : 4-dinitrobenzene is exceedingly reactive, nevertheless, after the conversion of the kationoid 2-nitro- into the anionoid 2-amino-group, the kationoid effect of the 4-nitro-group remains sufficiently powerful to render the chlorine still reactive towards some anionoid reagents such as the sodium sulphides despite the electron-releasing effect of the adjacent amino-group (see IV); also by reaction with aqueous sodium sulphide in presence of sodium hydrogen carbonate (cf. Hodgson and Birtwell, *J.*, 1944, 75) sodium 5-nitroaniline-2-mercaptide was formed, as shown by methylation to 4-nitro-2-aminothioanisole, and also by diazotisation, whereby 5-nitrobenz-1-thia-2 : 3-diazole was obtained. 4-Nitro-2-aminothioanisole has a sweet taste resembling that of saccharin (cf. Blanksma and Van der Weyden, *Rec. Trav. chim.*, 1940, **59**, 629, who have reported the sweetness of the corresponding oxygen compounds). It is noteworthy that the derivatives no longer possessed the sweetness of the parent substance, again on analogy with Blanksma's observations for the oxygen compounds. The 4 : 4′-dinitro-2 : 2′-diaminodiphenyl mono- and di-sulphides are also not sweet. The sweetness would appear to depend very much on the group in the 1-position in the 4-nitro-2-aminoaryl configuration, since it is associated with the groups OMe (OAlk.), SMe, Cl (Halogens), CO_2Me (CO_2Alk.), and CN, but not with other groups.



(IV.)

That the reactivity of the chlorine in 2-chloro-5-nitroaniline is very much reduced, however, follows from its inertness towards sodium thiosulphate (see Experimental), whereas 1-chloro-2 : 4-dinitrobenzene readily reacts with sodium thiosulphate to give ultimately a mixture of 2 : 4 : 2′ : 4′-tetranitrodiphenyl mono- and di-sulphides (Twiss, *J.*, 1914, **105**, 1678). It is of interest that 2-bromo-5-nitroaniline failed to give any monosulphide on being heated with sodium monosulphide for 90 minutes in ethanol, whereas with a sodium polysulphide the monosulphide was formed (Fries, *Annalen*, 1929, **468**, 162).

In order to ascertain the optimum reaction conditions, sodium mono- and di-sulphides, a sodium polysulphide of composition used by Fries (*loc. cit.*), and a mixture of sodium sulphide and sodium hydrogen carbonate (Hodgson and Birtwell, *loc. cit.*) were caused to react with 2-chloro-5-nitroaniline in different mixtures of ethanol and water with varying periods of heating, the results being recorded in the table below. Inspection of these results shows that the reaction appears to proceed in two stages, *viz.*, (*a*) the ultimate formation of the sodium mercaptide where no sodium hydrogen carbonate is employed, and (*b*) further reaction with 2-chloro-5-nitroaniline to give the monosulphide. Since the conditions appear to be most favourable for the formation of the sodium mercaptide in the cases of the polysulphides, the yields of monosulphide are greater than in the experiments with sodium sulphide alone. When sodium hydrogen carbonate is present and therefore the reagent is practically pure sodium hydrogen sulphide, then the thiol is formed in 97% yield; but when a saturated solution of 2-chloro-5-nitroaniline containing this compound in suspension [Expt. 5(*a*), p. 874] is boiled for 5 hours, the thiol is slowly converted into monosulphide by condensation with the chloro-compound. No sulphide dye was formed in any of the reactions.

Since tin and hydrochloric acid might be expected to attack the thiadiazole ring in 5-nitrobenz-1-thia-2 : 3-diazole (cf. Jacobson, *loc. cit.*; although Fries does not refer to any such behaviour), its reduction was conveniently and rapidly effected either by alkaline sodium dithionite (hydrosulphite) or still more efficiently with iron powder and dilute aqueous-alcoholic sulphuric acid. The 5-aminobenz-1-thia-2 : 3-diazole thus formed was readily converted by the usual methods (diazotisation, etc.) into the 5-hydroxy- and the 5-halogeno-benz-1-thia-2 : 3-diazoles, and also *benzthiadiazole*-5-*azo*-β-*naphthol*.

The preparation of 2-chloro-5-nitroaniline by the stannous chloride mono-reduction of 1-chloro-2 : 4-dinitrobenzene in glacial acetic acid solution, and its subsequent removal by steam distillation in *ca.* 50% yield, has confirmed Blanksma's observation (*Rec. Trav. chim.*, 1946, **65**, 329) that mono-reduction involved each nitro-group to about the same extent, whereas Anschütz (*Ber.*, 1886, **19**, 2161) had claimed that only the 2-nitro-group was attacked. The 4-chloro-3-nitroaniline, which is non-volatile in steam, can be isolated from the flask liquor.

EXPERIMENTAL.

Preparation of 2-*Chloro*-5-*nitroaniline by a Modification of Blanksma's Method* (loc. cit.).—A solution of 1-chloro-2 : 4-dinitrobenzene (20·25 g., 0·1 g.-mol.) in boiling glacial acetic acid (40 c.c.) was treated with powdered stannous chloride (57 g., 0·3 g.-mol), added at such a rate as to maintain ebullition. When the addition was completed (2—3 mins.) the solution was boiled, with shaking, for a further 5 minutes, then diluted with water (100 c.c.) and made alkaline by the stirred addition (to avoid coagulation) of 20% aqueous sodium hydroxide (300 c.c., 1·5 g.-mols.). The mixture was then steam-distilled; 2-chloro-5-nitroaniline passed over (7·8 g.; yield *ca.* 45%) and was filtered off after the distillate (*ca.* 7 l.) had been kept at 0° for *ca.* 30 mins.; it crystallised from 80% aqueous ethanol in long yellow needles, m. p. 118° (Beilstein and Kurbatov, *Annalen*, 1876, **182**, 100, give m. p. 117—118°).

Preparation of 5-*Nitrobenz*-1-*thia*-2 : 3-*diazole*.—(i) A boiling solution of 2-chloro-5-nitroaniline (17·25 g., 0·1 g.-mol.) in ethanol (250 c.c.) was treated gradually with a solution of crystallised sodium sulphide (36 g., 0·15 g.-mol.) and sodium hydrogen carbonate (12·6 g., 0·15 g.-mol.) in water (100 c.c.), and the mixture heated on the boiling water-bath for one hour before the addition of 20% aqueous sodium hydroxide (20 c.c., 0·1 g.-mol.); it was then poured on a mixture of ice and water (750 c.c.) and filtered. Sodium nitrite (7 g., 0·1 g.-mol.) was dissolved in the filtrate, which was then stirred into a mixture of sulphuric acid (25 c.c., *d* 1·84) and ice (250 g.). After being kept for one hour, the brown precipitate of crude 5-nitrobenz-1-thia-2 : 3-diazole (17·5 g., 97%), m. p. 135—145°, was removed and purified by steam-distillation, being obtained in pale yellow needles, m. p. 145°; the crude thiadiazole also crystallised from ethanol (charcoal) in almost colourless needles, m. p. 143—145° (Found : N, 23·4. Calc. for $C_6H_3O_2N_3S$: N, 23·2%), which sublime readily at 80—100° under atm. pressure. The steam volatility was *ca.* 1 g. per l., and a boiling saturated solution on cooling to 0° afforded a crystalline precipitate of *ca.* 2 g. per l. The compound was readily soluble in hot 20% aqueous hydrochloric acid from which it could be precipitated by ammonia, or from which it crystallised in colourless needles, m. p. and mixed m. p. with initial substance, 145°, and although readily soluble in the usual organic solvents it was only sparingly soluble in hot ligroin. It was also readily soluble in concentrated sulphuric acid, but the strong yellow colour reported by Fries (*loc. cit.*) was not observed. An acetone solution treated with a drop of aqueous sodium hydroxide gave a violet colour which was discharged by acid and restored by alkali; on keeping, the violet colour slowly turned brown.

(ii) A solution of 2-chloro-5-nitroaniline (1·725 g.) in boiling ethanol (6 c.c.) was treated according to Fries's procedure (*loc. cit.*) for the bromo-analogue with a solution of crystallised sodium sulphide (1·8 g., 0·0075 g.-mol.) and sulphur (0·36 g., 0·011 g.-mol.) in water (2 c.c.). Reaction was vigorous, and the solution became dark red; after 1 hrs.' heating on the water-bath, the mixture was cooled in ice, the red crystalline separation filtered off, suspended in water (50 c.c.) containing sodium nitrite (0·7 g.;

0·01 g.-mol.), and then poured into a mixture of sulphuric acid (4 c.c., *d* 1·84), ethanol (30 c.c.), and ice (120 g.). The precipitate of crude 5-nitrobenz-1-thia-2 : 3-diazole (1·3 g.) was purified as above; it contained 4 : 4′-dinitro-2 : 2′-diaminodiphenyl monosulphide as impurity.

Preparation of 4-*Nitro-*2-*aminothioanisole.*—The alkaline solution above, before the addition of sodium nitrite, was shaken with 20% aqueous sodium hydroxide (4 c.c.) and methyl sulphate (0·95 c.c.) for 5 minutes; it became almost colourless, and on cooling a precipitate of 4-nitro-2-aminothioanisole separated, which crystallised from water (charcoal) in orange needles, m. p. 105° (Fries, Vorbrodt, and Siebert, *Annalen*, 1927, **454**, 172, give m. p. 105°) (Found : N, 15·3. Calc. for $C_7H_8O_2N_2S$: N, 15·2%). The *acetyl* derivative was prepared by dissolution of the amine (0·3 g.) in a mixture of acetic anhydride (2 c.c.) and dimethylaniline (4 c.c.), heating on the water-bath for 30 mins., and stirring into 4% aqueous hydrochloric acid (100 c.c.); the precipitated solid (0·35 g.) was washed with the dilute acid, and crystallised from methanol in pale lemon-yellow needles, m. p. 157° (Found : N, 12·6. $C_9H_{10}O_3N_2S$ requires N, 12·9%).

4-*Nitrothioanisyl-*2-*azo-β-naphthol* was obtained when 4-nitro-2-aminothioanisole (0·25 g.) was diazotised and coupled with alkaline β-naphthol as usual; the crude, brick-red azo-compound (0·4 g., 90%) crystallised from glacial acetic acid in scarlet needles, m. p. 236° (Found : N, 12·6. $C_{17}H_{13}O_3N_3S$ requires N, 12·4%).

4-*Nitro-*2-*acetamido-*1-*thiophenyl acetate* was obtained when a solution of the sodium salt of 4-nitro-2-amino-1-thiophenol (containing *ca.* 0·4 g.) was shaken at room temperature with acetic anhydride (3 c.c.); an immediate yellow precipitate of the compound appeared, which crystallised from ethanol in pale cream needles, m. p. 161° (Found : N, 11·3. $C_{10}H_{10}O_4N_2S$ requires N, 11·0%). When kept at 150°, the compound suffers a reduction in m. p. and probably changes into 5-nitro-2-methylbenzthiazole, since the preparation of this type of compound is carried out by heating an *o*-aminothiophenol with acetic anhydride.

4 : 4′-Dinitro-2 : 2′-diaminodiphenyl disulphide was formed when the solution of the sodium mercaptide was aerated. Oxidation with potassium ferricyanide, however, caused immediate precipitation of a very impure material of m. p. <100° which was difficult to purify; the air-oxidised product crystallised from glacial acetic acid in yellow needles, m. p. 178° (Fries, *Annalen*, 1929, **468**, 162, gives m. p. 178°) (Found : N, 16·8. Calc. for $C_{12}H_{10}O_4N_4S_2$: N, 16·6%).

Preparation of 4 : 4′-*Dinitro-*2 : 2′-*diaminodiphenyl Sulphide.*—2-Chloro-5-nitroaniline (1·725 g., 0·01 g.-mol.) was dissolved in hot ethanol (96 c.c.), and a solution of sulphur (0·36 g.) and crystallised sodium sulphide (1·8 g.) in water (2 c.c.) added (equivalent to 0·0075 g.-mol. of $Na_2S_{2\cdot5}$). The mixture was then refluxed on the water-bath for 5 hours, after which it was poured on ice (100 g.) containing N-sodium hydroxide (10 c.c.). After filtration to remove the thiophenol, the red residue of the monosulphide was washed with hot water, and the compound purified by recrystallisation from ethanol (charcoal), being obtained in short red needles, m. p. 218° (Fries, *Annalen*, 1929, **468**, 162, gives m. p. 211°) (Found : N, 18·5. Calc. for $C_{12}H_{10}O_4N_4S$: N, 18·3%). The diacetyl derivative was prepared by boiling the amine (0·3 g.) in a mixture of acetic anhydride (3 c.c.) and fused sodium acetate (1 g.) for 2 hours; it separated on dilution with water, and crystallised from glacial acetic acid in colourless needles, m. p. 245° (Fries, *loc. cit.*, gives m. p. 245°) (Found : N, 14·5. Calc. for $C_{16}H_{14}O_6N_4S$: N, 14·3%).

Reduction of 5-*Nitrobenz-*1-*thia-*2 : 3-*diazole.*—(a) *By sodium dithionite* (" *hydros* "). The thiadiazole (0·45 g.), suspended in hot 20% aqueous sodium hydroxide (20 c.c.), was treated with sodium dithionite (2 g.) in small portions and the mixture boiled until dissolution was complete. On cooling, the 5-aminobenz-1-thia-2 : 3-diazole was extracted by ether, and then crystallised (0·15 g.) from water in yellow needles, m. p. 95° (Fries and Reitz, *Annalen*, 1936, **527**, 38, give m. p. 95°) (Found : N, 27·8. Calc. for $C_6H_5N_3S$: N, 27·8%), which were soluble in cold water to the extent of 7·5 g. per l., and very soluble in hot water.

(b) *By iron powder.* The thiadiazole (3·62 g., 0·02 g.-mol.) was mixed with iron powder (pin dust) (0·24 g.-mol.), sulphuric acid (1 c.c.), water (30 c.c.), and ethanol (10 c.c.), and, when frothing had ceased, the mixture was refluxed for 3 hours with occasional stirring; charcoal and ethanol (60 c.c.) were then added, and the boiling continued for a further hour. The mixture was filtered hot, and the residue extracted with ethanol three times (3 × 40 c.c.); the combined extract was mixed with the filtrate to which hydrochloric acid (2 c.c., *d* 1·18) was then added and the whole evaporated with frequent additions of water until all the ethanol had been removed. The cooled aqueous solution (80 c.c.) was neutralised with ammonia, and the precipitated 5-aminobenz-1-thia-2 : 3-diazole (2·5 g., 82%) filtered off; it crystallised from water in yellow needles, m. p. 95°. The filtrate was acidified with hydrochloric acid, diazotised by addition of sodium nitrite, and the diazonium salt coupled with alkaline β-naphthol to give *benz-*1-*thia-*2 : 3-*diazole-*5-*azo-β-naphthol* (1 g., corresponding to a further addition to the yield of amine of 17%, *i.e.*, a total yield of 99%), which crystallised from 90% acetic acid (charcoal) in bright red micro-crystals, m. p. 209° (Found : N, 18·4. $C_{16}H_{10}ON_4S$ requires N, 18·3%); it gave a reddish-pink solution in concentrated sulphuric acid, changing to pale pink on dilution with water.

Preparation of 5-*Hydroxybenz-*1-*thia-*2 : 3-*diazole.*—The above amine (0·15 g.) in hydrochloric acid (1 c.c., *d* 1·18) and water (20 c.c.) was treated at 0° with sodium nitrite (0·07 g.), and the solution added gradually to 10% aqueous sulphuric acid at 80°. After frothing had ceased, the cooled mixture was extracted with ether, the extract shaken with 1% aqueous sodium hydroxide, the ether removed, and the alkaline solution acidified and again extracted with ether, the extract dried (Na_2SO_4), and allowed to evaporate gradually in the air; very pale yellow needles of 5-hydroxybenz-1-thia-2 : 3-diazole (0·05 g.) separated, m. p. 161° (Fries, Vorbrodt, and Siebert, *loc. cit.*, give m. p. 161°) (Found : N, 18·7. Calc. for $C_6H_4ON_2S$: N, 18·4%), which were volatile in steam.

5-Chlorobenz-1-thia-2 : 3-diazole was formed when a solution of 5-aminobenz-1-thia-2 : 3-diazole (1·5 g.) in hydrochloric acid (10 c.c., *d* 1·18) and water (40 c.c.) was diazotised at 0° by addition of sodium nitrite (0·07 g.) dissolved in the minimum amount of water, and the mixture poured into one of cuprous chloride (4 g.) in hydrochloric acid (10 c.c., *d* 1·18) at 60°. After frothing had ceased, the chloro-compound (0·05 g.) was removed by steam-distillation and obtained in colourless needles, m. p. 105° (Beilstein and Kurbatov, *Annalen*, 1879, **197**, 81, give m. p. 103·5°; Pollak, Riesz, and Kohane, *Monatsh.*, 1928, **49**, 213, give m. p. 107°) (Found: N, 16·7. Calc. for $C_6H_3N_2ClS$: N, 16·4%), which sublime readily above 70° at atmospheric pressure, are easily soluble in organic solvents and strong mineral acids, and are slightly soluble in hot water.

5-*Bromobenz*-1-*thia*-2 : 3-*diazole* was obtained by diazotisation at 0° of a solution of the amino-compound (1·5 g.) in hydrobromic acid (2 c.c., *d* 1·7) and water (10 c.c.). The filtered solution was poured into one of cuprous bromide (4·5 g.) in hydrobromic acid (4 c.c., *d* 1·7), and the mixture steam-distilled; the bromo-compound separated from the steam distillate in colourless needles, m. p. 106° (Found: N, 13·2. $C_6H_3N_2BrS$ requires N, 13·0%), which were soluble in cold water to the extent of 0·1%.

5-*Iodobenz*-1-*thia*-2 : 3-*diazole* was formed when a solution of the above amine (1·5 g.) in sulphuric acid (2 c.c., *d* 1·84) and water (20 c.c.) was diazotised at 0°, and excess of nitrous acid removed by urea before the addition of potassium iodide (3·3 g.) in water (10 c.c.). The mixture was made just alkaline with sodium hydroxide and steam-distilled; the iodo-compound (1·1 g.) passed over and separated (0·8 g.) on cooling; it crystallised from 80% aqueous methanol in colourless cubes, m. p. 103° (Found: N, 11·0. $C_6H_3N_2IS$ requires N, 10·7%); by ether extraction of the steam-distillate (500 c.c.) a further 0·15 g. was obtained, indicating a solubility of 0·3 g. per l. at room temperature.

The Thiolation of 2-*Chloro*-5-*nitroaniline.—General analytical procedure.* A mixture of the aniline (1·725 g., 0·01 g.-mol.) and the reagent in the respective solvent (see table) was boiled for the period stated, then poured on ice (100 g.), and sodium hydroxide (0·04 g., 0·01 g.-mol.) added; the mixture was filtered, treated with sodium nitrite (0·7 g., 0·01 g.-mol.), and stirred into sulphuric acid (25 c.c., *d* 1·84) and ice (25 g.). After being kept for one hour, the 5-nitrobenz-1-thia-2 : 3-diazole was filtered off, dried, and weighed, whereby the amount of thiol formed was computed. The residue of the 4 : 4′-dinitro-2 : 2′-diaminodiphenyl monosulphide and unchanged 2-chloro-5-nitroaniline was extracted with hot water to remove the latter, and the residue dried and weighed as monosulphide; the aniline which separated from the cooled aqueous extract was then filtered off, dried, and weighed.

Expt.	Reactants and amounts (in g.).	Mol. ratio. Aniline/reagent.	Solvent: EtOH, c.c.	Solvent: H₂O, c.c.	Time of boiling, hrs.	Products, %. Unchanged material.	Products, %. Thiol.	Products, %. Monosulphide.
1	$Na_2S_2O_3,5H_2O$ (2·5)	2 : 1	15	10	6	100	—	—
2	$Na_2S,9H_2O$ (1·2)	2 : 1	6	2	5	45	10	45
3	$Na_2S,9H_2O$ (1·2) + S (0·16), equiv. to Na_2S_2	2 : 1	6	2	5	25	10	65
4	$Na_2S,9H_2O$ (1·8) + S (0·36), equiv. to $\frac{3}{2}$ $Na_2S_{2\cdot5}$	2 : 1·5	(*a*) 6	2	1	0	40	60
			(*b*) 6	2	5	0	35	65
5	NaSH obtained from: $Na_2S,9H_2O$. $NaHCO_3$.							
	(*a*) 2·4 0·84	1 : 1	6	2	5	33	8	33
	(*b*) 2·4 0·84	1 : 1	12·5	5	1	15	73	0
	(*c*) 3·6 1·26	1 : 1	25	10	1	0	88	0
	(*d*) 3·6 1·26	1 : 1	25	10	1	0	97	0

Note.—In Expt. 5 (*c*) the thiol formed was estimated as such, whereas in Expt. 5 (*d*) it was estimated as the much less soluble thiadiazole.

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