94. o-*Mercapto-azo-compounds. Part I. The Coupling of Tetrazotised 2 : 2′-Diaminodiphenyl Disulphide with β-Naphthol.*

By A. Burawoy and C. Turner.

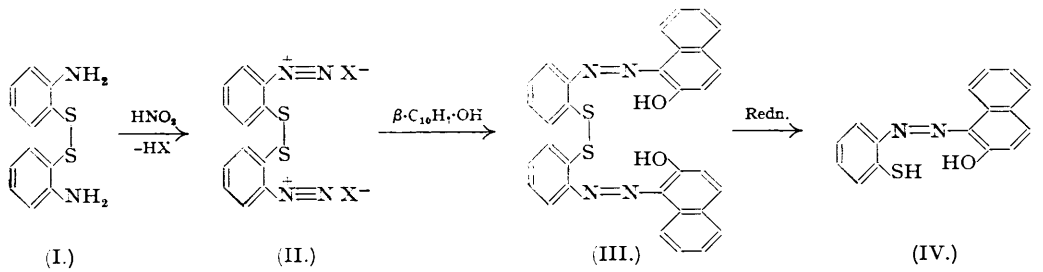
A general method for the preparation of the hitherto unknown *o*-mercapto-azo-compounds is developed.

Only monodiazotisation of 2 : 2′-diaminodiphenyl disulphide occurs in dilute acid, the product decomposing spontaneously to yield benz-1-thia-2 : 3-diazole (V). The tetrazonium salt (II) is formed and is stable in concentrated sulphuric acid, but is also decomposed by water with the formation of benzthiadiazole.

Coupling takes place when the concentrated sulphuric acid solution is added directly to solutions or suspensions of β-naphthol in aqueous sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, sodium acetate, or pyridine. Three different reactions are encountered. In all cases an intermediate product (XXX), formed by coupling with one mole of β-naphthol, is first formed. In sodium hydroxide and carbonate solution this decomposes to benzthiadiazole and unstable *o*-(2-hydroxynaphthalene-1-azo)benzenesulphenic acid (XXXI), which undergoes spontaneous disproportionation in sodium hydroxide solution, to yield di-*o*-(2-hydroxynaphthalene-1-azo)phenyl disulphide (III) and *o*-(2-hydroxynaphthalene-1-azo)benzenesulphinic acid (IX), whereas in sodium carbonate solution condensation with a second mole of β-naphthol to *o*-(2-hydroxynaphthalene-1-azo)phenyl 2-hydroxy-1-naphthyl sulphide (X) takes place. On the other hand, the intermediate (XXX) is sufficiently stable in sodium hydrogen carbonate or acetate solution or in pyridine to allow coupling with a second mole of β-naphthol in preference to degradation, the disulphide (III) being formed in good yield.

The mechanisms of these reactions are confirmed by independent experiments, and the structures of the products are established by unambiguous methods.

Owing to their technical and theoretical importance, *o*-hydroxy-azo-compounds have been the subject of numerous investigations. A study of the properties of the corresponding *o*-mercapto-azo-compounds should also be of interest. Such substances are as yet unknown, partly because the methods normally used in the preparation of the *o*-hydroxy-azo-compounds (reaction of a diazo-compound with a phenol coupling in the *o*-position, and reaction of a diazotised *o*-aminophenol with a suitable coupling component) are not applicable in this series. Thus, thiophenols are unable to couple, forming instead the corresponding diazothio-ethers Ar·N:N·SAr′ which apparently cannot be rearranged to yield azo-compounds (Ziegler, *Ber.*, 1890, **23**, 2471; Stadler, *Ber.*, 1884, **17**, 2076; Hantzsch and Freese, *Ber.*, 1895, **28**, 3237; Dunn and Fletcher, *Trans*



(I.) (II.) (III.) (IV.)

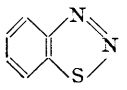
Kansas Acad. Sci., 1934, **37**, 123), and *o*-aminothiophenols yield on diazotisation the non-coupling benz-1-thia-2 : 3-diazoles (cf. Bernthsen, *Annalen*, 1889, **251**, 30; Jacobson *et al.*, *ibid.*, 1893, **277**, 209, 237, 257).

A few *o*-alkylthio-azo-compounds have been prepared, but only 2 : 2′-di(methylthio)azobenzene (Brand, *Ber.*, 1909, **42**, 3463) and 5-nitro-2-methylthiobenzeneazo-β-naphthol (Hodgson and Dodgson, *J.*, 1948, 870) appear to have been obtained in a pure state.

We first considered the possibility of tetrazotising 2 : 2′-diaminodiphenyl disulphide (I), coupling the tetrazonium salt (II) with β-naphthol, and finally reducing the di-*o*-(2-hydroxy-

naphthalene-1-azo)phenyl disulphide (III) formed to 1-(*o*-mercaptobenzeneazo)-2-naphthol (IV). Although we have succeeded in our aim, the reactions proved to be very complex.*

Previous attempts to prepare the tetrazonium salt of 2 : 2′-diaminodiphenyl disulphide or to couple it have been unsuccessful. Jacobson (*Ber.*, 1887, **20**, 1902) mentioned that boiling diazotised 2 : 2′-diaminodiphenyl disulphide with water yields the steam-volatile benz-1-thia-2 : 3-diazole (V). Hodgson (*J. Soc. Dyers and Col.*, 1924, **40**, 330) obtained a 50% yield of (V) on diazotising the diamine in dilute mineral acids, no coupling with β-naphthol being observed. Guha and Ghosh (*J. Indian Inst. Sci.*, 1929, **12**, *A*, 31) claimed the isolation of the tetrazonium salt (II), describing it as insoluble in water and unable to react with aniline or potassium ethyl xanthate; they also stated that it decomposed when stored at $> 20°$ or on subjection to the action of reducing agents or of coupling components, with the formation of a brown tar which, on steam-distillation, yielded (VII) by dehydration of di-*o*-hydroxyphenyl disulphide (VI). Not only does this contrast with Jacobson's and Hodgson's earlier observations, but (VI) has already been described by Haitinger (*Monatsh.*, 1883, **4**, 165) as stable up to 200°.



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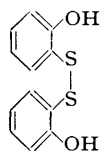

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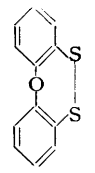
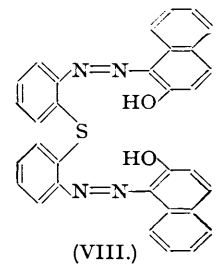


(VII.)



(VIII.)

Re-investigating the action of nitrous acid on 2 : 2′-diaminodiphenyl disulphide, we found, in agreement with Hodgson, that in dilute hydrochloric or sulphuric acid benzthiadiazole contaminated with varying amounts of resinous material separates immediately on addition of sodium nitrite, and that it can be isolated in 45—60% yield by ether-extraction. We do not confirm Guha and Ghosh's claims. The supposed tetrazonium salt decomposing above 20° is undoubtedly impure benzthiadiazole which melts at about 24° and solidifies again on cooling. Steam-distillation yields pure benzthiadiazole, but no (VII).

The tetrazonium *salt* (II) is formed when diazotisation is carried out in concentrated sulphuric acid with nitrosylsulphuric acid. It is stable in this medium, but is slowly decomposed by water with the formation of benzthiadiazole. When the sulphuric acid solution is poured into ice-water and the resultant clear solution immediately extracted with ether, only traces of benzthiadiazole are obtained. However, it soon begins to separate and after about three hours can be extracted in about 75% yield. This, incidentally, compares favourably with other known methods of preparation.

The slow degradation of the tetrazonium salt (II) in water is also indicated by coupling samples of the solution with β-naphthol in aqueous sodium hydroxide. The amount of the violet-red disulphide (III) formed (cf. below) slowly decreases with time when the tetrazonium solution is set aside (at 0°) before coupling, and after a few hours' storage none is obtained. In its place a small amount ($< 5\%$) of an orange-brown azo-compound is formed which has been identified as *di*-o-(2-*hydroxynaphthalene*-1-*azo*)*phenyl sulphide* (VIII) by unambiguous synthesis from tetrazotised 2 : 2′-diaminodiphenyl sulphide and β-naphthol.

Treatment of the sulphuric acid solution of the tetrazonium salt with aqueous cuprous chloride gives, not 2 : 2′-dichlorodiphenyl disulphide, but an orange-brown *complex* of benzthiadiazole and cuprous chloride, the yield of benzthiadiazole obtained by ether-extraction after addition of sodium hydroxide being about 84%.

Since the tetrazonium salt is decomposed by the action of water, coupling was carried out by direct addition of the concentrated sulphuric acid solution to alkaline solutions (or suspensions) of β-naphthol. The resultant products varied considerably with the nature of the alkali used. Three distinct reactions may occur which, fortunately, can be realised separately by coupling in aqueous solutions of (i) sodium hydroxide, (ii) sodium carbonate, and (iii) sodium hydrogen carbonate, sodium acetate, or pyridine.

In the first case, benzthiadiazole (V), the *disulphide* (III) (which dissolves in organic solvents

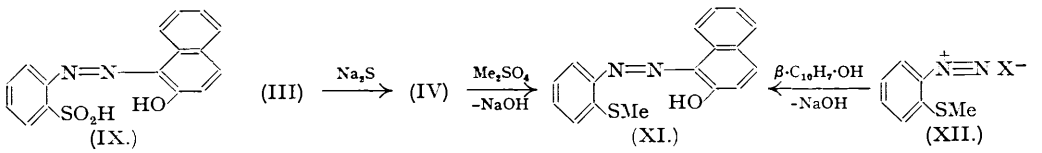
* *o*-Hydroxyazo-compounds are formulated in this paper for convenience as azo-compounds, although they may actually be phenylhydrazones (cf. Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180).

with a characteristic violet colour), and bright red sodium *o*-(2-hydroxynaphthalene-1-azo)-benzenesulphinate (as IX) are formed.

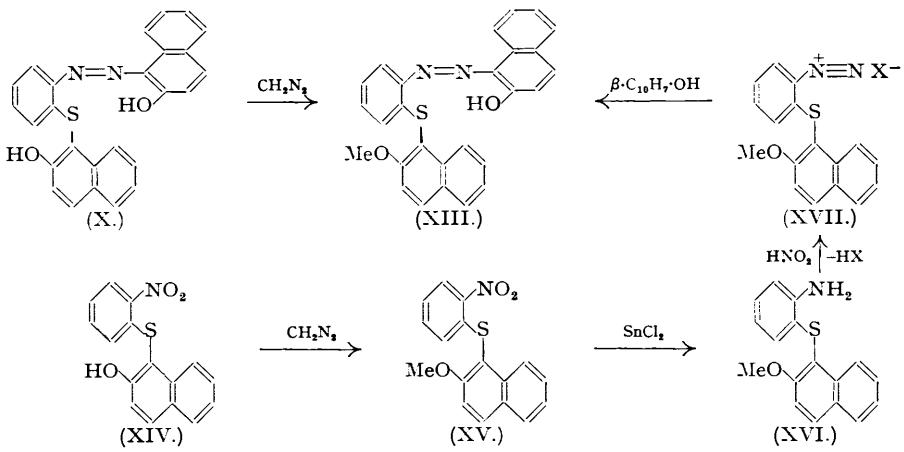
Coupling with the sodium salt of β-naphthol in excess of sodium carbonate yields benzthiadiazole and the reddish-brown o-(2-*hydroxynaphthalene*-1-*azo*)*phenyl* 2-*hydroxy*-1-*naphthyl sulphide* (X). No disulphide (III) or sulphinic acid (IX) can be isolated.

Finally, in excess of sodium hydrogen carbonate, sodium acetate, or pyridine, the disulphide (III) is obtained alone and in good yield.

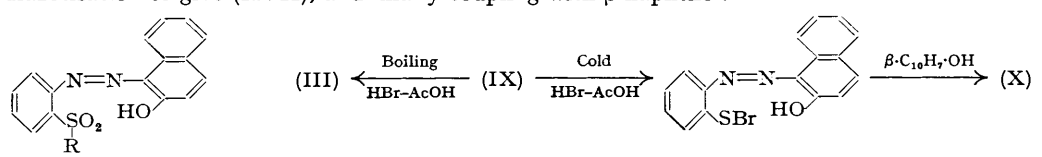
The structures of the various azo-compounds isolated were determined as follows. The disulphide (III) was reduced with sodium sulphide at room temperature and subsequently methylated with methyl sulphate to give 1-(o-*methylthiobenzeneazo*)-2-*naphthol* (XI), identical with a product synthesised unambiguously by coupling diazotised *o*-methylthioaniline (XII) with β-naphthol.



Acidification of an aqueous or alcoholic suspension of the sparingly soluble bluish-violet sodium salt of 1-(*o*-mercaptobenzeneazo)-2-naphthol with hydrochloric or acetic acid at room temperature yields the orange-red thiol itself, the first *o*-mercapto-azo-compound to be isolated. It is very sensitive to heat. In solution or in the solid state it is easily converted into a brown alkali-insoluble product. Its structure and the properties of *o*-mercapto-azo-compounds will be discussed elsewhere.



The sulphide (X) yields with diazomethane the 2′-*methyl ether* (XIII), the hydroxyl group in 1-benzeneazo-2-naphthol being unreactive under these conditions (cf. Kuhn and Bär, *Annalen*, **1935**, **516**, 143). The structure of this ether was established by unambiguous synthesis from *o*-nitrophenyl 2-hydroxy-1-naphthyl sulphide (XIV) (Zincke and Farr, *ibid.*,1912, **391**, 55) by methylation with diazomethane to (XV), reduction with stannous chloride to the *amine* (XVI), diazotisation to give (XVII), and finally coupling with β-naphthol.



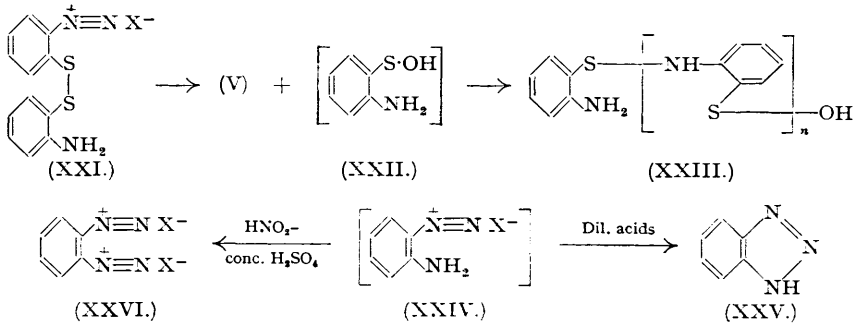
The sulphinic acid (IX) obtained from its water-soluble sodium salt by the addition of hydrochloric acid was characterised as o-(2-*hydroxynaphthalene*-1-*azo*)*phenyl methyl sulphone* (XVIII) and the corresponding p-*nitrobenzyl sulphone* (XIX). Its structure, besides being

suggested by general properties characteristic of sulphinic acids, was established by conversion (i) by hydrogen bromide in boiling glacial acetic acid into the disulphide (III), and (ii) by hydrogen bromide in cold glacial acetic acid into o-(2-*hydroxynaphthalene*-1-*azo*)*benzenesulphenyl bromide* (XX), and condensation of the latter with β-naphthol in quantitative yield to the sulphide (X).

Aromatic sulphinic acids $ArSO_2H$ are known to yield, with hydrogen bromide in glacial acetic acid, either the corresponding sulphenyl bromides ArSBr or the disulphides ArS·SAr depending on the reaction temperature and the nature of the sulphinic acid (Fries and Schürmann, *Ber.*, 1914, **47**, 1195); and aromatic sulphenyl halides are known to react with β-naphthol in suitable conditions to form 1-arylthio-2-naphthols (Zincke and Farr, *loc. cit.*; Fries, *Ber.*, 1912, **45**, 2965).

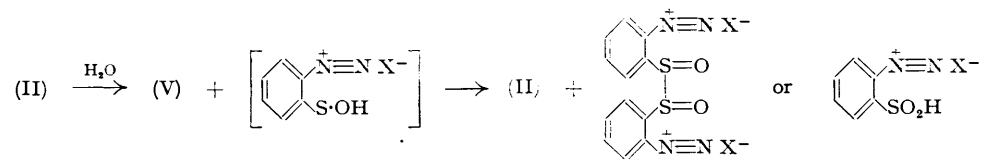
Discussion.

The spontaneous separation of benzthiadiazole on addition of sodium nitrite in dilute hydrochloric and sulphuric acids shows that the diazotisation of 2 : 2′-diaminodiphenyl disulphide proceeds, in the main, only as far as the monodiazonium salt (XXI). This spontaneously splits into benzthiadiazole (V) and probably aniline-2-sulphenic acid (XXII) which may undergo condensation to (XXIII) or other more complicated changes, yielding some unidentified resinous products. Any tetrazonium salt formed would decompose only slowly, with the formation of benzthiadiazole (cf. above). This is similar to the behaviour of *o*-phenylenediamine which cannot be tetrazotised in dilute acids, the monodiazonium salt (XXIV) spontaneously condensing internally with the formation of benztriazole (XXV) (Ladenburg, *Ber.*, 1876, **9**, 219), whereas in concentrated sulphuric acid the reaction proceeds to the stable tetrazonium salt (XXVI) (Hodgson and Walker, *J.*, 1935, 530).



(XXI.) (XXII.) (XXIII.) (XXVI.) (XXIV.) (XXV.)

The slow decomposition of the tetrazonium salt (II) on addition of its solution in concentrated sulphuric acid to ice-water should yield benzthiadiazole (V) and diazobenzene-2-sulphenic acid (XXVII) (or its anhydride) in equimolecular proportions. Since at least 70% of benzthiadiazole is recovered, the sulphenic acid must have undergone further changes which have not yet been fully elucidated.



(XXVII.) (XXVIII.) (XXIX.)

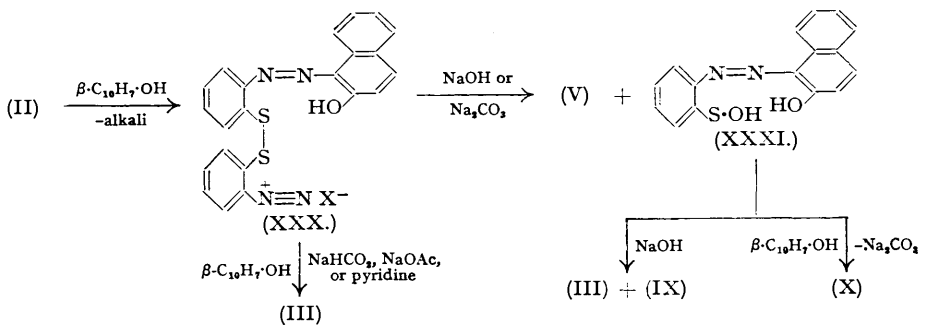
Substances forming the unstable sulphenic acids ArS·OH (such as the sulphenyl halides ArSX) are known to undergo easy disproportionation to the corresponding disulphides ArS·SAr and either disulphoxides ArSO–SOAr or sulphinic acids $ArSO_2H$ (Zincke and Farr, *loc. cit.*). Therefore it would be reasonable to assume that diazobenzene-*o*-sulphenic acid (XXVII) would behave similarly and would form the tetrazonium salt (II), which would again decompose yielding an additional amount of benzthiadiazole, and either the tetrazonium salt of 2 : 2′-diaminodiphenyl disulphoxide (XXVIII) or diazobenzene-*o*-sulphinic acid (XXIX). However, coupling with alkaline β-naphthol yields, rather surprisingly, instead of the corresponding azo-compounds, the monosulphide (VIII). Our experiments do not afford any evidence for the

mechanism of the formation of tetrazotised 2 : 2′-diaminodiphenyl sulphide, but we have ascertained that it is not due to the presence of a small amount of 2 : 2′-diaminodiphenyl sulphide in the starting material.

The almost spontaneous formation of benzthiadiazole by the action of cuprous chloride on the tetrazonium salt (II) indicates either (i) its direct reduction, or (ii) its degradation to benzthiadiazole and diazobenzene-*o*-sulphenic acid (cf. above) followed by reduction of the latter. Since the degradation in absence of cuprous chloride is only slow, the former interpretation is more likely.

The reaction of the tetrazonium salt (II) with β-naphthol in sodium hydroxide solution is initiated by coupling with one mole of β-naphthol which is followed by degradation of the intermediate (XXX) to benzthiadiazole (V) and the salt of *o*-(2-hydroxynaphthalene-1-azo)-benzenesulphenic acid (XXXI). The latter, like all known substances forming sulphenic acids as intermediate with sodium hydroxide (such as the sulphenyl halides), will quickly undergo disproportionation to equimolecular quantities of the disulphide (III) and the sodium sulphinate (IX). This interpretation is supported (i) by the yields of disulphide and sulphinic acid obtained, which would correspond to about 90% of theory, and (ii) by the analogous disproportionation of the sulphenyl bromide (XX) with sodium hydroxide at room temperature, which is also initiated by the formation of the sodium sulphenate (XXXI).

For various reasons, it is unlikely that the degradation of the tetrazonium salt (II) to benzthiadiazole and sodium diazobenzene-*o*-sulphenate takes place first and is followed by the coupling of this diazo-compound with β-naphthol and, finally, disproportionation. Thus, the disulphide (III) is not formed if the tetrazonium solution in concentrated sulphuric acid is first added to sodium hydroxide, sodium carbonate, or sodium hydrogen carbonate alone and then quickly treated with β-naphthol. The separation of benzthiadiazole, *i.e.*, degradation, is spontaneous in these conditions.



Coupling of tetrazotised 2 : 2′-diaminodiphenyl disulphide with β-naphthol.

The disulphide (III) is certainly not produced by direct coupling of the tetrazonium salt with 2 moles of β-naphthol, as might superficially appear. This would not account (i) for the simultaneous formation of benzthiadiazole and *o*-(2-hydroxynaphthalene-1-azo)benzene-sulphinic acid, or (ii) for the results of the coupling in sodium carbonate solution. In these more weakly alkaline conditions, the rate of degradation of the tetrazonium salt (II) would, if different, be slower than in aqueous sodium hydroxide. The formation of the disulphide would, therefore, be expected to be more complete, whereas, at most, traces are formed.

The reaction in sodium carbonate solution will proceed first as in sodium hydroxide, but the sulphenic acid (XXXI), being comparatively stable under these more weakly alkaline conditions, reacts with β-naphthol in preference to undergoing disproportionation and so yields the sulphide (X).

There is no report in the literature of the behaviour of sulphenic acids, their anhydrides or halides towards cold sodium carbonate solution as compared with sodium hydroxide, but we have established (i) that when the sulphenyl bromide (XX) in benzene is shaken with a 2% sodium hydroxide solution disproportionation occurs at once, whereas with a 2% sodium carbonate solution this is comparatively slow, and (ii) that in presence of β-naphthol only a very small amount (< 5%) of the sulphide (X) is formed in the former case and an almost quantitative yield in the latter.

Coupling in aqueous pyridine, sodium hydrogen carbonate, or sodium acetate is also initiated by the formation of the intermediate (XXX). However, in these weakly alkaline or acid

conditions this product is sufficiently stable to allow coupling with a second mole of β-naphthol to take preference over degradation. Thus, only the disulphide (III) is formed. Although this is the most economical method for the preparation of this substance, the yields obtained (40—65%) and the isolation of small amounts of benzthiadiazole indicate that coupling is accompanied by a partial degradation of the tetrazonium salt.

Finally, it should be mentioned that the disulphide (III) is not stable to alkali, being converted, on prolonged contact at room temperature or on heating, into the sulphinic acid (IX). Undoubtedly this reaction is initiated by hydrolysis to the salts of 1-(*o*-mercaptobenzeneazo)-2-naphthol (IV) and the sulphenic acid (XXXI), which is a general reaction of disulphides (cf., *e.g.*, Schiller and Otto, *Ber.*, 1876, **9**, 1637; Fromm, *Annalen*, 1921, **426**, 313; Reissert and Manns, *Ber.*, 1928, **61**, 1308). Subsequently, (IV) is probably re-oxidised to the disulphide, and (XXXI) undergoes disproportionation to the disulphide and the sulphinic acid, which is, finally, the only product isolated.

The investigation is being continued in various directions.

Experimental.

Diazotisation of 2 : 2′-Diaminodiphenyl Disulphide in Dilute Mineral Acids.—The suspension of the amine hydrochloride obtained by intimate mixing of 2 : 2′-diaminodiphenyl disulphide (5 g.) and concentrated hydrochloric acid (20 c.c.) was poured into water (300 c.c.) at 0°. Sodium nitrite (4 g.) in a small amount of water was added. Benzthiadiazole and a brown resinous product, insoluble in water and ether, immediately separated. Extraction with ether yielded crude benzthiadiazole, m. p. 31—33° (m. p. when pure, 35°) (3·2 g., 58%). After filtration the aqueous layer was added to an alkaline solution of β-naphthol. 0·17 G. of an alkali-insoluble brown azo-compound separated. The experiment was repeated with sulphuric instead of hydrochloric acid and with increasing amounts of acid; the results were similar, yields of benzthiadiazole varying between 45 and 60%.

Diazotisation of 2 : 2′-Diaminodiphenyl Disulphide according to Guha and Ghosh (loc. cit.).—2 : 2′-Diaminodiphenyl disulphide (3 g.) and concentrated hydrochloric acid (7·5 c.c.) were mixed with mechanical stirring. The amine did not dissolve as claimed by Guha and Ghosh, but a suspension of the hydrochloride was obtained. This was cooled with ice, and a solution of sodium nitrite (1·8 g.) in water (15 c.c.) was added. An oil immediately separated, which soon solidified to a light-brown solid. When filtered off and washed with ice-cold water this melted at *ca.* 24°, solidifying again on cooling. No decomposition or evolution of nitrogen was observed. Steam-distillation of the precipitate yielded almost pure benzthiadiazole (m. p. 34—35°; 1·5 g., 46%).

Tetrazotisation of 2 : 2′-Diaminodiphenyl Disulphide in Concentrated Sulphuric Acid.—Sodium nitrite (3·6 g.) was slowly added with stirring to concentrated sulphuric acid (25 c.c.) at 0° and stirring continued for a further 10 minutes. The temperature was then raised to 70° during 20 minutes and the clear solution obtained was cooled to −10°. Powdered 2 : 2-diaminodiphenyl disulphide (5 g.) was dissolved in concentrated sulphuric acid (17 c.c.) at room temperature with vigorous stirring. After cooling to 0°, the solution was slowly added to the nitrosylsulphuric acid solution kept in a freezing mixture. The time allowed for diazotisation was varied between 10 minutes and 24 hours, with very little effect on the yields obtained in the following experiments. It was generally 30 minutes.

Action of Water on Tetrazotised 2 : 2′-Diaminodiphenyl Disulphide in Concentrated Sulphuric Acid.—The tetrazonium salt solution from the disulphide (5 g.) was poured into ice-water (800 c.c.). On extracting the solution immediately with ether, no benzthiadiazole was obtained. The solution with β-naphthol in aqueous sodium hydroxide gave the red precipitate of di-*o*-(2-hydroxynaphthalene-1-azo)-phenyl disulphide (III) recognised by its characteristic violet colour in benzene. After 30 minutes, crystalline benzthiadiazole began to separate and coupling as indicated above to decrease. After 4—6 hours, the solution ceased to yield any violet product with alkaline β-naphthol, indicating complete degradation of the tetrazonium salt. Extraction with ether yielded almost pure benzthiadiazole, m. p. 34—35° (4·0 g., 73%). The aqueous layer was poured into a solution of β-naphthol (3 g.) and sodium hydroxide (80 g.) in water (700 c.c.) at 0°. Alkali-insoluble, brown di-*o*-(2-hydroxynaphthalene-1-azo)phenyl sulphide (VIII) (0·5 g., 5%) was precipitated, which crystallised from xylene as reddish-orange needles, m. p. 284—286° (cf. below). The experiment was repeated, but the tetrazonium solution was kept at 0° up to 4 days before and after addition to water. The yields of benzthiadiazole and sulphide varied little.

Action of Aqueous Sodium Hydroxide, Sodium Carbonate, or Sodium Hydrogen Carbonate on Tetrazotised 2 : 2′-Diaminodiphenyl Disulphide.—A tetrazonium salt solution prepared from the disulphide (5 g.) was poured into ice-water (800 g.) containing sodium hydroxide (80 g.). Crude benzthiadiazole (2·7 g., 50%) separated immediately. The mother-liquor did not yield any azo-compound on subsequent quick addition of β-naphthol. Similar results were obtained when sodium hydroxide was replaced by sodium carbonate or sodium hydrogen carbonate.

Di-o-(2-hydroxynaphthalene-1-azo)phenyl Sulphide (VIII).—2 : 2′-Diaminodiphenyl sulphide (1·3 g.) was dissolved in concentrated hydrochloric acid (6 c.c.), glacial acetic acid (20 c.c.), and boiling water (100 c.c.). Sodium nitrite (0·85 g.) in a small amount of water was added at 0° and the mixture stirred for 10 minutes. The tetrazonium salt solution was poured into a solution of β-naphthol (3·5 g.) and sodium hydroxide (30 g.) in water (300 c.c.). The precipitated *sulphide* (2·8 g., 88%) was filtered off. It was obtained from xylene as reddish-orange needles, m. p. 284—286° (Found: N, 10·7; S, 5·9. $C_{32}H_{22}O_2N_4S$ requires N, 10·6; S, 6·1%).

Action of Cuprous Chloride on Tetrazotised 2 : 2′-Diaminodiphenyl Disulphide in Concentrated Sulphuric Acid.—A tetrazonium salt solution prepared from 5 g. of the disulphide was poured into an

ice-cold solution of cuprous chloride (10 g.) in concentrated hydrochloric acid (90 c.c.), whereupon the brown *complex* (8·0 g.) of benzthiadiazole and cuprous chloride immediately separated (Found: Cu, 27·2. $2C_6H_4N_2S,Cu_2Cl_2$ requires Cu, 27·0%).

This experiment was repeated, but, without isolation of the complex, sodium hydroxide was added and the benzthiadiazole extracted with ether. The yield of almost pure product (m. p. 34—35°) was 4·6 g. (85%).

Coupling of Tetrazotised 2 : 2′-Diaminodiphenyl Disulphide with β-Naphthol.—(i) *Coupling in sodium hydroxide solution.* A solution of tetrazotised disulphide (5 g.) in concentrated sulphuric acid was slowly added to a solution of β-naphthol (6 g.) and sodium hydroxide (80 g.) in water (500 c.c.) and kept below 5° by the addition of ice (1·5 kg.). *Di-(o-2-hydroxynaphthalene-1-azo)phenyl disulphide* (III), contaminated by some benzthiadiazole and sodium sulphate separated. After 2 hours, the precipitate (3·3 g., 89%) was filtered off, washed with warm water and digested with methyl alcohol (100 c.c.). Crystallisation from benzene gives dark red needles (with a green lustre), m. p. 233—234°, containing one mole of benzene which is slowly lost at room temperature and quickly at 100° (in a vacuum) (Found: N, 10·3; S, 11·4. $C_{32}H_{22}O_2N_4S_2$ requires N, 10·0; S, 11·5%). This disulphide dissolves in organic solvents with a violet, and in concentrated sulphuric acid with an orange, colour.

The filtrate was treated with carbon dioxide. A red precipitate of sodium *o*-(2-hydroxynaphthalene-1-azo)benzenesulphinate (IX) separated, contaminated by β-naphthol. After filtration, washing with a small amount of water, and drying, it was digested with chloroform (100 c.c.) and collected. Yield: 2·1 g. (91%). M. p. 296° (decomp.). Acidification of an aqueous solution of the salt with hydrochloric acid yielded the reddish-brown crystalline free *acid*, m. p. 165—166°, sparingly soluble in water and alcohol and dissolving in concentrated sulphuric acid with deep violet colour (Found: N, 9·3. $C_{16}H_{12}O_3N_2S$ requires 9·0%).

Steam-distillation of the mother-liquor from the main reaction yielded almost pure benzthiadiazole, m. p. 34—35° (1·9 g., 70%).

(ii) *Coupling in sodium carbonate solution.* A sulphuric acid solution of tetrazotised 2 : 2′-diaminodiphenyl disulphide (5 g.) was slowly added to a well-stirred solution of β-naphthol (20 g.) in 5% aqueous sodium hydroxide (120 c.c.) and sodium carbonate (100 g.) in water (800 c.c.). After 2 hours, the precipitate of o-(2-*hydroxynaphthalene*-1-*azo*)*phenyl* 2-*hydroxy*-1-*naphthyl sulphide* (X), contaminated with sodium sulphate, β-naphthol, and benzthiadiazole, was filtered off, washed with hot water and digested with methyl alcohol (100 c.c.). Yield: 5·6 g. (66%). Crystallisation from xylene gives brownish-red needles, m. p. 226—227° (Found: N, 6·8; S, 7·8. $C_{26}H_{18}O_2N_2S$ requires N, 6·6; S, 7·6%). This compound is sparingly soluble in cold organic solvents and in hot aqueous hydroxide with a brown colour. Concentrated sulphuric acid dissolves it with a violet colour which rapidly becomes brown.

Steam-distillation of the main mother-liquor yielded almost pure benzthiadiazole, m. p. 34—35° (1·3 g., 48%).

(iii) *Coupling in sodium hydrogen carbonate, sodium acetate, or pyridine.* A tetrazonium salt solution prepared from 2 : 2′-diaminodiphenyl disulphide (5 g.) was dropped into a well-stirred slution of urea (3 g.) and sodium hydrogen carbonate (160 g.) in water (2000 c.c.) to which β-naphthol (30 g.) in alcohol (200 c.c.) had been added. The temperature was kept below 5° by the addition of ice. The precipitate of the disulphide (III) and β-naphthol was filtered off and digested twice with 3% aqueous sodium hydroxide to remove β-naphthol. The yield of crude *disulphide* (III) was 6·8 g. (61%). On steam-distillation of the mother-liquor 0·25 g. of benzthiadiazole was recovered. No sulphide (X) or sulphinic acid (IX) could be isolated from the alkaline extracts.

Similar results were obtained when sodium hydrogen carbonate was replaced by sodium acetate or pyridine. The yields of disulphide varied between 40 and 65%.

1-(o-*Methylthiobenzeneazo*)-2-*naphthol* (XI).—(i) *Preparation from the disulphide* (III). A suspension of (III) (0·5 g.) in methyl alcohol (40 c.c.) was shaken for 2 hours at room temperature with a solution of sodium sulphide nonahydrate (1 g.) in water (10 c.c.). Some dark violet, sparingly soluble sodium salt of 1-(*o*-mercaptobenzeneazo)-2-naphthol (IV) separated. Water (100 c.c.) was added to the suspension, followed by 4 additions of 10% aqueous sodium hydroxide (10 c.c. each) and methyl sulphate (0·35 g. each), with vigorous shaking. 1-(o-*Methylthiobenzeneazo*)-2-*naphthol* (XI), which separated almost pure in quantitative yield, crystallised from ethyl alcohol in red needles, m. p. 163—164° (Found: N, 9·8. $C_{17}H_{14}ON_2S$ requires N, 9·6%).

(ii) *Preparation from* o-*methylthioaniline.* To the aniline derivative (2 g.) in 10% hydrochloric acid (15 c.c.), sodium nitrite (1·1 g.) in a small amount of water was added at 0°. The diazonium solution was poured into a solution of β-naphthol (2·2 g.) in excess of aqueous sodium hydroxide. The red azo-compound formed was filtered off (Found: N, 9·7%) (2·2 g., 52%) and crystallised from ethyl alcohol in red needles, m. p. 163—164° undepressed by admixture with the product obtained as in (i).

1-(o-*Mercaptobenzeneazo*)-2-*naphthol* (IV).—A solution of sodium sulphide nonahydrate (2 g.) in water (10 c.c.) was added to a suspension of the disulphide (III) (1 g.) in ethyl alcohol (55 c.c.), and the mixture shaken for 4 hours at room temperature. Water (150 c.c.) was then added, and the sodium salt of 1-(*o*-mercaptobenzeneazo)-2-naphthol (0·75 g.) which separated in dark violet needles with a metallic bronze lustre was filtered off. By salting out the filtrate with sodium chloride a further 0·2 g. of less pure compound was obtained (total yield 0·95 g., 88%) (Found: N, 9·2; S, 10·2; Na, 7·5. $C_{16}H_{11}ON_2SNa$ requires N, 9·3; S, 10·6; Na, 7·6%).

On acidifying a suspension of the sodium compound (0·5 g.) in ethyl alcohol (50 c.c.) and water (200 c.c.) with concentrated hydrochloric acid (20 c.c.), 1-(o-*mercaptobenzeneazo*)-2-*naphthol* (IV) was obtained. When heated to 100° or crystallised from warm solvents, it was converted into a brown, alkali-insoluble product. Purified by concentration of its benzene solution at room temperature in a vacuum, it was obtained in red plates, sintering at about 115° and melting at 183—185° (Found: N, 10·1; S, 11·2. $C_{16}H_{12}ON_2S$ requires N, 10·0; S, 11·4%).

o-(2-*Hydroxynaphthalene*-1-*azo*)*phenyl* 2-*Methoxy*-1-*naphthyl Sulphide* (XIII).—(i) *Methylation of the* 2-*hydroxy*-1-*naphthyl sulphide* (X). Diazomethane (1·2 g.) in ether (200 c.c.) was added to the phenolic sulphide (2 g.) in dry benzene (400 c.c.). After 24 hours, the solvents were removed and the

residue of *methoxy-sulphide* was recrystallised from benzene, forming red, monohydrated needles, sintering at about 125° and melting at 174—175° (Found : loss at 100°/15 mm., 4·2. $C_{27}H_{20}O_2N_2S,H_2O$ requires H_2O, 4·0%). After drying, the substance melts at 174—175° without sintering (Found : N, 6·5; S, 7·4; OMe, 6·9. $C_{27}H_{20}O_2N_2S$ requires N, 6·4; S, 7·3; OMe, 7·1%).

(ii) o-*Nitrophenyl* 2-*methoxy*-1-*naphthyl sulphide* (XV). A solution of *o*-nitrophenyl 2-hydroxy-1-naphthyl sulphide (Zincke and Farr, *loc. cit.*) (10 g.) in dry benzene (400 c.c.) was treated with diazomethane (3·6 g.) in ether (350 c.c.). After 24 hours the solvents were removed, and the residue, of almost pure *methoxy-sulphide* (XV) crystallised from benzene. It was obtained as yellow prisms, m. p. 174—175° (Found : N, 4·5; OMe, 9·5. $C_{17}H_{13}O_3NS$ requires N, 4·5; OMe, 9·9%).

(iii) o-*Aminophenyl* 2-*methoxy*-1-*naphthyl sulphide* (XVI). Stannous chloride dihydrate (12 g.) in concentrated hydrochloric acid (20 c.c.) was added at 100° to a solution of the above nitro-ether (5 g.) in glacial acetic acid (60 c.c.). After being heated on the steam-bath for 3 hours, the mixture was cooled. The precipitate of amino-sulphide stannichloride formed was filtered off, washed, and decomposed with 5% aqueous sodium hydroxide (200 c.c.). The free *amine* was collected and washed (2·6 g., 58%). Crystallisation from ethyl alcohol gave almost colourless plates, m. p. 136—137° (Found : N, 5·1; S, 11·2. $C_{17}H_{15}ONS$ requires N, 5·0; S, 11·4%).

(iv) *Coupling of diazotised* o-*aminophenyl* 2-*methoxy*-1-*naphthyl sulphide with β-naphthol.* The amine (0·5 g.) was dissolved in glacial acetic acid (12 c.c.) and concentrated hydrochloric acid (2 c.c.). After dilution with water (200 c.c.), sodium nitrite (0·15 g.) in a small amount of water was added at 0°. The diazonium solution was poured into a solution of β-naphthol (0·7 g.) and sodium hydroxide (12 g.) in water (100 c.c.). The red precipitate of *o*-(2-hydroxynaphthalene-1-azo)phenyl 2-methoxy-1-naphthyl sulphide (XIII) formed was filtered off, washed, and dried (0·78 g., 96%). It crystallised from benzene in red, hydrated needles, which sinter at about 125° and melt at 174—175° (Found : loss at 100°/15 mm., 4·5%). After drying they melt at 174—175° without sintering (Found : N, 6·5; S, 7·0; OMe, 6·9%). A mixed melting point with the dried product obtained as above showed no depression.

o-(2-*Hydroxynaphthalene*-1-*azo*)*phenyl Methyl Sulphone* (XVIII).—Sodium *o*-(2-hydroxynaphthalene-1-azo)phenylsulphinate (1 g.) was refluxed with methyl iodide (10 c.c.) for 6 hours. After cooling, the precipitate of *methyl sulphone* was filtered off, and washed repeatedly with 2% sodium hydroxide and finally with water. Crystallised from ethyl alcohol it formed brown needles, m. p. 184—185° (Found : N, 8·8. $C_{17}H_{14}O_3N_2S$ requires N, 8·6%).

p-*Nitrobenzyl* o-(2-*Hydroxynaphthalene*-1-*azo*)*phenyl Sulphone* (XIX).—The above-mentioned sodium sulphinate (2 g.) and *p*-nitrobenzyl bromide (2 g.) were refluxed in boiling ethyl alcohol (100 c.c.) for 30 hours. On dilution with water, a quantitative yield (2·7 g.) of p-*nitrobenzyl sulphone* was obtained. It crystallised from toluene in orange-red needles, m. p. 262—263° (Found : N, 9·6. $C_{23}H_{17}O_5N_3S$ requires N, 9·4%).

Conversion of the Sulphinic Acid (IX) *into the Disulphide* (III).—48% Hydrobromic acid (3 c.c.) was slowly added to a boiling suspension of the sulphinic acid (IX) (1 g.) in glacial acetic acid (25 c.c.). The solid went into solution. The cooled mixture was treated with water (400 c.c.). The disulphide (III) separated in quantitative yield (0·9 g.). Crystallisation from benzene gave a product, m. p. 233—234° alone or mixed with the product obtained by coupling tetrazotised 2 : 2′-diaminodiphenyl disulphide with β-naphthol.

Conversion of the Sulphinic Acid into o-(2-*Hydroxynaphthalene*-1-*azo*)*phenyl* 2-*Hydroxy*-1-*naphthyl Sulphide* (X).—(i) o-(2-*Hydroxynaphthalene*-1-*azo*)*phenylsulphenyl bromide* (XX). The sulphinic acid (IX) (2 g.), suspended in glacial acetic acid (50 c.c.) containing 48% hydrobromic acid (5 c.c.) and shaken for 48 hours at room temperature, slowly went into solution, and the *sulphenyl bromide* (XX) separated quantitatively as a fine dark-red crystalline powder. This was filtered off, washed with glacial acetic acid and finally with light petroleum. It melted at 184—186° (Found : N, 7·8; Br, 22·0. $C_{16}H_{11}ON_2BrS$ requires N, 7·8; Br. 22·3%).

(ii) *Condensation of the sulphenyl bromide with β-naphthol.* A mixture of the above sulphenyl bromide (0·5 g.) and β-naphthol (0·5 g.) was heated at 110—115°, hydrogen bromide being evolved and the liquid mass becoming gradually more viscous. After 15 minutes the reaction mixture was cooled and digested with methyl alcohol in order to remove the excess of β-naphthol. The insoluble residue consisted of almost pure *o*-(2-hydroxynaphthalene-1-azo)phenyl 2-hydroxy-1-naphthyl sulphide (0·55 g., 93%). Crystallisation from xylene yielded brownish-red needles, m. p. 226—227° alone or mixed with the product obtained by coupling tetrazotised 2 : 2′-diaminodiphenyl disulphide with β-naphthol in sodium carbonate solution.

Reaction of o-(2-*Hydroxynaphthalene*-1-*azo*)*benzenesulphenyl Bromide with β-Naphthol and Sodium Carbonate or Sodium Hydroxide Solution.*—(i) The sulphenyl bromide (0·5 g.) and β-naphthol (1·0 g.) in benzene (30 c.c.) were shaken with 2% aqueous sodium carbonate (40 c.c.) for 48 hours at room temperature. The aqueous layer contained only traces of coloured products. The benzene layer was washed with 3% aqueous sodium hydroxide and evaporated to dryness. The residue consisted of slightly impure sulphide (X) (0·46 g., 78%), which yielded a pure product m. p. 226—227°, after one crystallisation from xylene.

(ii) The experiment was repeated, but the sodium carbonate solution was replaced by 2% aqueous sodium hydroxide (30 c.c.). The benzene layer developed spontaneously the violet colour of the disulphide (III) which disappeared during the continued shaking. After 48 hours it contained only a small quantity (0·03 g.) of the crude sulphide (X). The aqueous layer was saturated with sodium chloride, whereupon sodium *o*-(2-hydroxynaphthalene-1-azo)benzene-2-sulphinate, m. p. 290° (decomp.), separated in almost quantitative yield.

Action of Sodium Hydroxide on the Disulphide (III).—The disulphide (0·5 g.) was refluxed for 3 hours with sodium hydroxide (2 g.) in aqueous ethyl alcohol (1 : 1; 40 c.c.). The solution obtained was diluted with water (50 c.c.) and extracted with benzene, from which a small amount of unchanged starting material (0·07 g.) was recovered. The aqueous layer was acidified with concentrated hydrochloric acid, and the precipitate of the sulphinic acid (IX), m. p. 164—166°, (0·44 g., 80%), collected.

Action of Sodium Hydroxide on o-(2-*Hydroxynaphthalene*-1-*azo*)*benzenesulphenyl Bromide.*—The

sulphenyl bromide (0·5 g.), benzene (100 c.c.), and 2% aqueous sodium hydroxide (50 c.c.) were shaken at room temperature for 1 hour. The benzene layer was washed with dilute sodium hydroxide solution in order to remove small amounts of the sulphinic acid (IX) and finally evaporated to dryness. The residue consisted of almost pure di-*o*-(2-hydroxynaphthalene-1-azo)phenyl disulphide, m. p. 230—233° (0·25 g., 96%). The alkaline aqueous layer was treated with concentrated hydrochloric acid, and the precipitated sulphinic acid (m. p. 164—165°; 0·10 g., 69%), collected.

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