o-*Mercapto-azo-compounds. Part IV.* Preparation and Debenzylation of* 1-(2-*Benzylthiophenylazo*)-2-*naphthol and* 1-(1-*Benzylthio*-2-*naphthylazo*)-2-*naphthol.*

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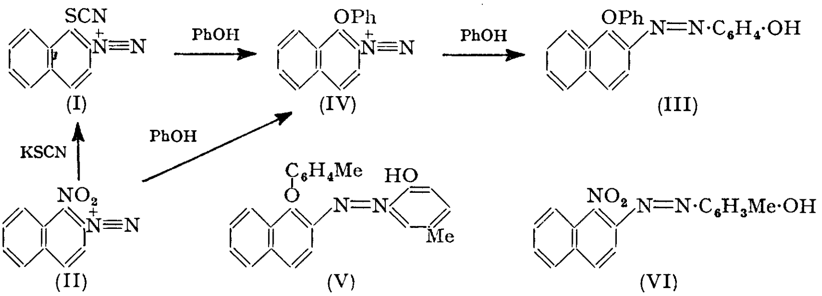
The coupling of diazotised 1-thiocyanato- and 1-nitro-2-naphthylamine with phenol, *p*-cresol, and 1-naphthol is investigated and the anomalous course of these reactions discussed.

Diazonium salts from *o*-aminophenyl benzyl sulphide and 2-amino-1-naphthyl benzyl sulphide are stable only in concentrated sulphuric acid solutions, which on direct addition to alkaline solutions of 2-naphthol yield 1-(2-benzylthiophenylazo)- and 1-(1-benzylthio-2-naphthylazo)-2-naphthol (XIV and XXIX) respectively. The latter are debenzylated smoothly by aluminium bromide in benzene, to yield almost quantitatively the corresponding *o*-mercapto-azo-compounds.

The preparation of *o*-mercapto-azo-compounds, starting from diazotised 2 : 2′-diaminodiphenyl disulphide (Part I *), 1-thiocyanato-2-naphthylamine (Part II *), or *o*-nitronaphthylamines (Part III *) has recently been described. In all cases, 2-naphthol was used as coupling component. Attempts to replace this by other phenols did not lead to *o*-mercapto-azo-compounds, the reactions taking an unexpected course.

The diazonium salt (I) obtained either by diazotisation of 1-thiocyanato-2-naphthylamine or by the addition of potassium thiocyanate to diazotised 1-nitro-2-naphthylamine (II), couples with phenol in aqueous sodium carbonate, but the product, obtained in very good yields (84%), is 2-*p*-hydroxyphenylazo-1-phenoxynaphthalene (III), probably because coupling with phenol is slower than with 2-naphthol: displacement of the thiocyanato-group in the diazonium salt (I) by the phenoxide ion, *i.e.*, the formation of the 1-phenoxynaphthalene-2-diazonium ion (IV), is faster than coupling and precedes it. This type of replacement reaction is apparently novel. Diazotised 1-nitronaphthylamine (II), when coupled directly with phenol, similarly yields the same azophenol (III), the nitro-group, in this case, being replaced by the phenoxide ion. The identity of the products confirms the suggested structure. However, it is worth noting that diazotised 1-chloro-2-naphthylamine, when coupled with phenol, yields only the expected 1-chloro-2-*p*-hydroxyphenylazonaphthalene.

p-Cresol, like phenol, with diazotised 1-thiocyanato- and 1-nitro-2-naphthylamine yields 2-(2-hydroxy-5-methylphenylazo)-1-*p*-tolyloxynaphthalene (V). From the latter diazonium salt, however, the normal coupling product, 2-(2-hydroxy-5-methylphenylazo)-1-nitronaphthalene (VI) is also isolated.



When the diazonium salt (I) is coupled with 1-naphthol in the presence of sodium carbonate or acetate, there is, as with 2-naphthol, no replacement of the thiocyanato-group. An orange precipitate is first formed, rapidly becoming brown. Although

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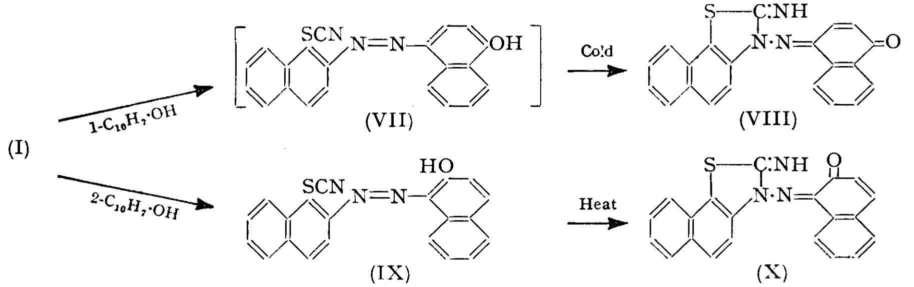
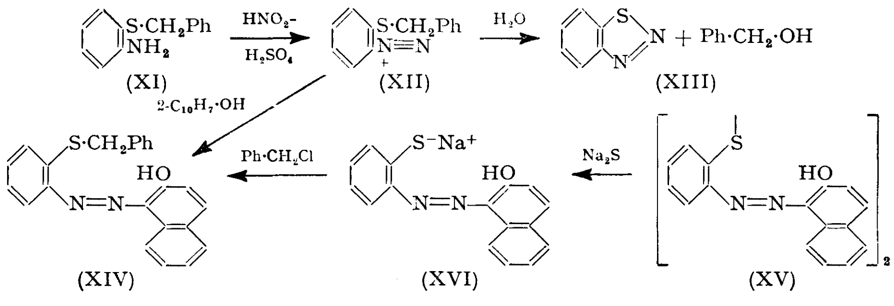
* Parts I—III, *J.*, 1950, 469; 1952, 1286; 1953, 959.

analysis of the recrystallised product corresponds to that of the desired 4-(1-thiocyanato-2-naphthylazo)-1-naphthol (VII), it does not show any of the expected properties. It is insoluble in, and is not affected by, aqueous or alcoholic sodium hydroxide, indicating the absence of a hydroxyl and of a thiocyanato-group. It should therefore be the cyclic isomer (VIII). After the coupling with 2-naphthol described earlier (Part II), 1-(1-thiocyanato-2-naphthylazo)-2-naphthol (IX) could be isolated, since it is not affected by sodium carbonate and is converted into the cyclic isomer (X) only on heating. Ring closure of 4-(1-thiocyanato-2-naphthylazo)-1-naphthol (VII) occurs much more readily, even in the presence of cold sodium carbonate or acetate, and its isolation is impossible. This ease of cyclisation should be due to its greater acidity, characteristic of *p*-hydroxyazo-compounds, facilitating the migration of the proton and the resulting isomerisation. This and the high yield (60—70%) should exclude the possibility that coupling has taken place in the *ortho*-position, although no rigorous proof of structure (VIII) has been obtained.



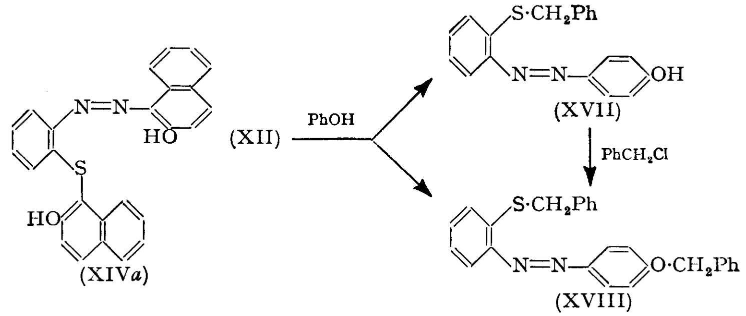
The limitations of the methods developed previously led us to investigate a possibly more general method of preparing *o*-mercaptoazo-compounds. Harnish and Tarbell (*J. Amer. Chem. Soc.*, 1948, **70**, 4123) have shown that aryl benzyl sulphides can be debenzylated easily and in good yield by aluminium bromide in cold benzene. Heating with hydrobromic acid in glacial acetic acid causes only partial scission of the benzyl-group. In agreement with the observations reported by Specklin and Meybeck whilst this work was in progress (*Bull. Soc. chim.*, 1951, **18**, 621), diazotisation of *o*-aminophenyl benzyl sulphide (XI) in presence of water yields only benzo-1-thia-2 : 3-diazole (XIII). However, we have found that the diazonium salt (XII) can be prepared by diazotisation with nitrosylsulphuric acid in concentrated sulphuric acid, in which it is stable. On addition to water, it undergoes rapid degradation to the benzothiadiazole and benzyl alcohol. Although some coupling with 2-naphthol can be observed immediately after dilution, it no longer takes place after a few minutes. This behaviour is similar to the degradation of the tetrazonium salt of 2 : 2′-diaminodiphenyl disulphide reported in Part I. On direct addition in concentrated sulphuric acid to 2-naphthol in aqueous alkali, diazotised *o*-aminophenyl benzyl sulphide (XII) couples to yield 1-*o*-benzylthiophenylazo-2-naphthol (XIV), but there is some degradation to benzothiadiazole. The best yield of the azo-compound is obtained by coupling in the presence of sodium carbonate. In addition to (XIV), a very small amount (<2%) of 2-hydroxy-1-naphthyl *o*-(2-hydroxy-1-naphthylazo)phenyl sulphide (XIV*a*) is formed; this was obtained by coupling tetr-



azotised 2 : 2′-diaminodiphenyl disulphide with 2-naphthol in aqueous sodium carbonate (Part I). The side-reaction is not due to the presence of traces of the disulphide in the starting material, but probably to hydrolysis and oxidation of *o*-aminophenyl benzyl sulphide by concentrated sulphuric acid.

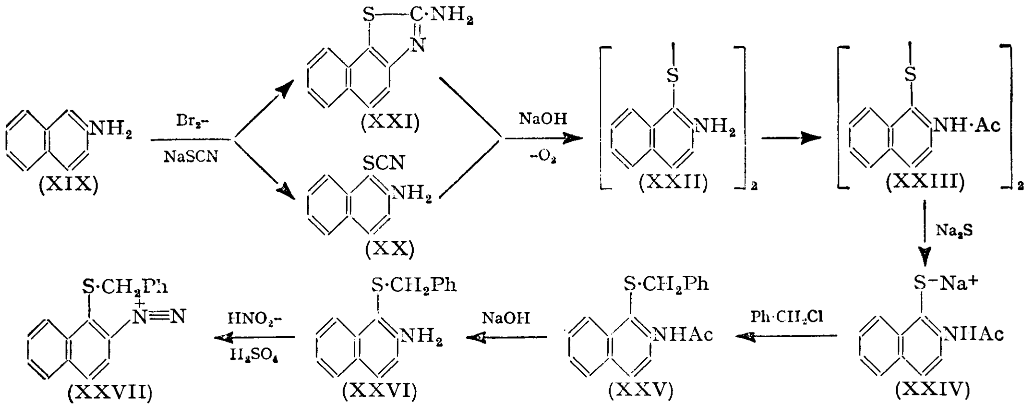
The azo-compound (XIV) was also prepared from di-*o*-(2-hydroxy-1-naphthylazo)-phenyl disulphide (XV) by reduction to the sodium salt (XVI) of the corresponding thiol, followed by benzylation, thus proving its structure.

Similarly, coupling of the diazonium salt (XII) with phenol in sodium carbonate solution yields the alkali-soluble 2-benzylthio-4′-hydroxyazobenzene (XVII), and also,



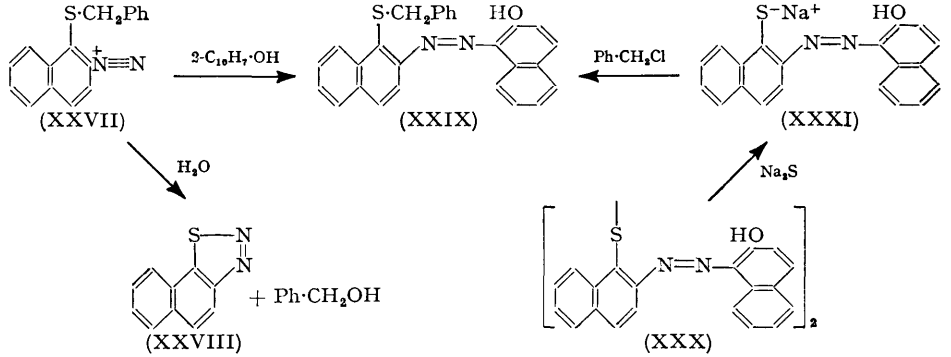
unexpectedly, some 4-benzyloxy-2′-benzylthioazobenzene (XVIII). The latter is also obtained by treatment of the azophenol (XVII) with benzyl chloride in aqueous sodium hydroxide. Its formation in this reaction is due to benzylation of the azophenol, either by the benzyl alcohol produced by the accompanying degradation of some of the diazo-compound, or, more probably, by attack of the azophenoxide ion from (XVII) on the diazonium salt (XII), followed by degradation. Coupling in presence of aqueous sodium hydroxide yields a smaller amount of the azophenol (XVII), degradation being faster than in sodium carbonate solution, as also shown by our experiments with 2-naphthol.

2-Amino-1-naphthyl benzyl sulphide (XXVI) has been prepared as follows: 2-Naphthylamine (XIX), on treatment with bromine and sodium thiocyanate in glacial acetic acid, yields a mixture of 1-thiocyanato-2-naphthylamine (XX) and 2-aminonaphtho-(2′ : 1′-4 : 5-thiazole (XXI), which, on fusion with alkali and aerial oxidation, is converted into crude di-(2-amino-1-naphthyl) disulphide (XXII). The latter is acetylated, then reduced with sodium sulphide, the sodium salt of 2-acetamido-1-mercaptonaphthalene (XXIV) formed is directly benzylated with benzyl chloride, and, finally, the 2-acetamido-1-naphthyl benzyl sulphide (XXV) is hydrolysed to (XXVI).



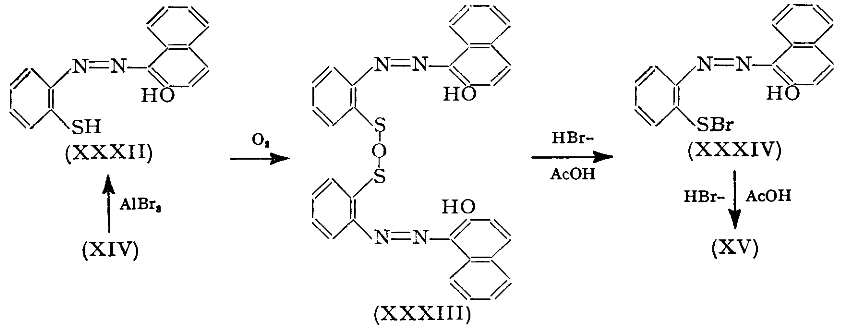
On diazotisation, this amine behaves qualitatively like its benzene analogue. The diazonium salt (XXVII) is stable in concentrated sulphuric acid, but undergoes degradation to naphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazole (XXVIII) on addition to water. This proceeds much faster than in the benzene series, no coupling being observed immediately after dilution with water. This quantitative difference is similar to that observed for the degradation by water of the tetrazonium salt of 2 : 2′-diaminodiphenyl disulphide and di-(2-amino-1-naphthyl) disulphide (Part II).

Addition of the solution of the diazonium salt (XXVII) in concentrated sulphuric acid to a solution of sodium 2-naphthoxide in sodium carbonate yields the desired 1-(1-benzylthio-2-naphthylazo)-2-naphthol (XXIX) in moderate yield, in addition to some naphthothiadiazole. The structure of the azo-compound has been confirmed by its preparation from di-2-(2-hydroxy-1-naphthylazo)-1-naphthyl disulphide (XXX), by reduction to the sodium salt of 1-(1-mercapto-2-naphthylazo)-2-naphthol (XXXI) and subsequent treatment with benzyl chloride.

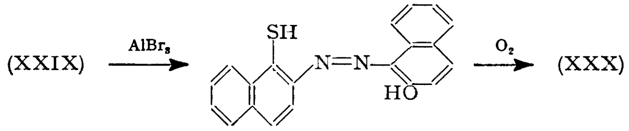


Both 1-(2-benzylthiophenylazo)-2-naphthol and 1-(1-benzylthio-2-naphthylazo)-2-naphthol are stable to a boiling mixture of concentrated hydrobromic acid and glacial acetic acid.

1-(2-Benzylthiophenylazo)-2-naphthol (XIV) is debenzylated by means of aluminium bromide in benzene almost quantitatively to 1-*o*-mercaptophenylazo-2-naphthol (XXXII), identical with the product obtained by coupling tetrazotised 2 : 2′-diaminodiphenyl disulphide with 2-naphthol, followed by reduction of the disulphide (XV) formed with sodium sulphide (Part I). This has been established by the melting points, colour reactions of the thiol, and formation of its *S*-methyl ether and the sulphenic anhydride (XXXIII). The structure of the anhydride has been confirmed by conversion into di-*o*-(2-hydroxy-1-naphthylazo)phenyl disulphide (XV) by hydrobromic acid in boiling acetic acid, the sulphenyl bromide (XXXIV), which is unstable under these conditions, being undoubtedly an intermediate.



The action of aluminium bromide on 1-(1-benzylthio-2-naphthylazo)-2-naphthol (XXIX) is similar, 1-(1-mercaptonaphthylazo)-2-naphthol (XXXV) being obtained quantitatively. The latter is identical with the product obtained in the series of reactions starting with the coupling of 1-thiocyanatonaphthalene-2-diazonium salt with 2-naphthol (Parts II and III). This, again, was established by melting points and colour reactions of the thiol, as well as by the formation of its *S*-methyl ether and of the corresponding disulphide (XXX).



(XXXV)

Debenzylation of the azonaphthols (XIV) and (XXIX) by the action of bromine has also been investigated under various conditions (in cold chloroform or boiling glacial acetic acid, with varying quantities of bromine). However, this reaction is not very fast and is always preceded or accompanied by nuclear bromination, resulting in the formation of mixtures which are not easily separated. As an example, the preparation of a dibromodi-*o*-(2-hydroxy-1-naphthylazo)phenyl disulphide from (XIV) is described in the Experimental section.

EXPERIMENTAL

Coupling of 1-*Thiocyanatonaphthalene*-2-*diazonium Salts with Phenol.*—A solution of a 1-thiocyanatonaphthalene-2-diazonium salt was prepared from 1-thiocyanato-2-naphthylamine (2 g.) or from 1-nitro-2-naphthylamine (2 g.) (for details, see Parts II and III) and added to phenol (5 g.) and sodium carbonate (20 g.) in water and ice (500 g.). The light brown precipitate formed (3·0 g., 84%) was filtered off and washed with water. Recrystallisation from dilute alcohol gave yellow plates of 2-p-*hydroxyphenylazo*-1-*phenoxynaphthalene* (III), m. p. 163—165° (Found: C, 77·3; H, 4·8; N, 8·2. $C_{22}H_{16}O_2N_2$ requires C, 77·6; H, 4·7; N, 8·2%).

Coupling of 1-*Thiocyanatonaphthalene*-2-*diazonium Salts with* p-*Cresol.*—A solution of a 1-thiocyanatonaphthalene-2-diazonium salt prepared by either of the above methods was coupled with *p*-cresol (5 g.) in presence of sodium carbonate (20 g.) in ethyl alcohol (100 c.c.) and water and ice (500 g.). The brown precipitate formed (3·0 g., 77%) was filtered off and washed with water. Recrystallisation from ethyl alcohol yielded small brown needles of 2-(2-*hydroxy*-5-*methylphenylazo*)-1-p-*tolyloxynaphthalene* (V), m. p. 153—154° (Found: C, 77·9; H, 5·4; N, 7·8. $C_{24}H_{20}O_2N_2$ requires C, 78·3; H, 5·5; N, 7·6%).

Coupling of 1-*Nitronaphthalene*-2-*diazonium Sulphate with Phenol.*—1-Nitro-2-naphthylamine (2 g.) was diazotised and added to phenol (5 g.) and sodium carbonate (20 g.) in water and ice (500 g.). The product obtained in 80% yield gave, on recrystallisation from dilute alcohol, 2-*p*-hydroxyphenylazo-1-phenoxynaphthalene, m. p. 163—165°, not depressed on admixture with the product prepared as above (Found: C, 77·4; H, 4·6; N, 8·2).

Coupling of 1-*Nitronaphthalene*-2-*diazonium Sulphate with* p-*Cresol.*—1-Nitro-2-naphthylamine (2 g.) was diazotised and added to a mixture of *p*-cresol (5 g.) in ethyl alcohol (50 c.c.) and sodium carbonate (20 g.) in water and ice (300 g.). The brown precipitate (2·6 g.), when recrystallised once from ethyl alcohol, gave a product of m. p. 130—133°. This was separated into several small fractions by extraction with light petroleum (b. p. 40—60°) (Soxhlet). On evaporation, the first fraction, m. p. 148—150°, consisted of nearly pure 2-(2-hydroxy-5-methylphenylazo)-1-*p*-tolyloxynaphthalene, small brown needles [from light petroleum (b. p. 60—80°)], m. p. 151—153°, not depressed on admixture with the product obtained as above. The other fractions melted at 133—135° and consisted of a mixture of this product and 2-(2-hydroxy-5-methylphenylazo)-1-nitronaphthalene (VI), which could be again partly separated by the same process. A residue of m. p. 176—177° consisting of 2-(2-*hydroxy*-5-*methylphenylazo*)-1-*nitronaphthalene* remained in the thimble, and on recrystallisation from ethyl alcohol yielded yellow needles, m. p. 181—182° (Found: C, 66·2; H, 4·4; N, 13·9. $C_{17}H_{13}O_3N_3$ requires C, 66·4; H, 4·2; N, 13·7%).

Coupling of 1-*Chloronaphthalene*-2-*diazonium Sulphate with Phenol.*—A solution of 1-chloro-2-naphthylamine hydrochloride (2 g.) in 10% sulphuric acid (50 c.c.), water and ice (200 g.) was diazotised with sodium nitrite (1 g.) in a small amount of water, and added to phenol (5 g.) and sodium carbonate (20 g.) in water and ice (300 g.). The precipitate formed (2·4 g., 91%), recrystallised from dilute alcohol, gave orange-yellow needles of 1-*chloro*-2-p-*hydroxyphenylazonaphthalene*, m. p. 160° (Found: C, 68·1; H, 4·1; N, 9·8. $C_{16}H_{11}ON_2Cl$ requires C, 68·0; H, 3·9; N, 9·9%).

Coupling of 1-*Thiocyanatonaphthalene*-2-*diazonium Salts with* 1-*Naphthol.*—A solution of a

1-thiocyanatonaphthalene-2-diazonium salt, prepared by either of the methods indicated above, was added to 1-naphthol (5 g.), sodium hydroxide (2 g.), and sodium carbonate (20 g.) in water and ice (500 g.). During coupling, the orange precipitate first formed gradually changed to a purple-brown one. It was digested with methyl alcohol (100 c.c.) (yield of residue, 2·6 g., 69%). Recrystallisation from glacial acetic acid gave very dark crystals of the cyclic *product* (VIII), m. p. 303—305°, which dissolve in organic solvents with a brownish-red colour and in concentrated sulphuric acid with a purplish-red colour (Found: C, 71·3; H, 3·8; N, 11·8. $C_{21}H_{13}ON_3S$ requires C, 71·0; H, 3·7; N, 11·8%). The product is insoluble in aqueous or alcoholic sodium hydroxide.

Coupling was also carried out in sodium acetate, yielding again only the cyclised compound (2·2 g., 62%).

o-*Aminophenyl Benzyl Sulphide* (XI).—This was prepared by an improved method of reducing benzyl *o*-nitrophenyl sulphide: this compound (18·2 g.), fine iron dust (24 g.), toluene (100 c.c.), and water (30 c.c.) were boiled under reflux with good stirring. Glacial acetic acid (3 c.c.) was then added and heating continued for 4 hr. The mixture was made alkaline with a little sodium hydroxide and steam-distilled. The toluene was discarded and the colourless, almost pure *o*-aminophenyl benzyl sulphide was collected (14·6 g., 91%). One crystallisation from light petroleum (b. p. below 40°) gave colourless plates, m. p. 43—44° (Sieglitz and Koch, *Ber.*, 1925, **58**, 78, give m. p. 45°).

Action of Water on Diazotised o-*Aminophenyl Benzyl Sulphide.*—Well-powdered *o*-aminophenyl benzyl sulphide (2 g.) was added with stirring to nitrosylsulphuric acid (1 g. of sodium nitrite in 15 c.c. of concentrated sulphuric acid) at −5°, and stirred for 10—15 min. Addition to ice and water (150 g.) gave an immediate precipitate. A few drops of the aqueous mixture were added to an alkaline solution of 2-naphthol, a red precipitate being formed. The amount of coupling gradually decreased with time until, after 6 min., only a red colour was observed. After 2 hr., the coupling power of the solution had disappeared entirely. Steam-distillation of the mixture yielded benzothiadiazole (0·6 g., 47%), m. p. 33—34°, also obtained directly by normal diazotisation in aqueous conditions of *o*-aminophenyl benzyl sulphide.

Coupling of Diazotised o-*Aminophenyl Benzyl Sulphide with* 2-*Naphthol.*—A diazonium solution prepared from *o*-aminophenyl benzyl sulphide (2 g.) and nitrosylsulphuric acid as above was slowly added to a well-stirred solution of 2-naphthol (3 g.), sodium hydroxide (2 g.), and sodium carbonate (70 g.) in water and ice (1500 g.). After 2 hr.' stirring the red precipitate was filtered off, washed with water, and digested with methyl alcohol (30 c.c.) in order to remove any benzothiadiazole (residue, 2·7 g., 77%). Recrystallisation from glacial acetic acid or ethyl alcohol gave dark red needles of 1-o-*benzylthiophenylazo*-2-*naphthol* (XIV), m. p. 161—162°, which dissolve in organic solvents with an orange colour and in concentrated sulphuric acid with a violet colour which slowly becomes brown (Found: C, 73·9; H, 4·9; N, 7·8. $C_{23}H_{18}ON_2S$ requires C, 74·6; H, 4·9; N, 7·6%). The methanolic mother-liquor gradually yielded 0·05 g. of 2-hydroxy-1-naphthyl *o*-(2-hydroxy-1-naphthylazo)phenyl sulphide, m. p. 226—227° after recrystallisation from xylene, not depressed in admixture with a pure sample obtained by coupling diazotised 2 : 2′-diaminodiphenyl disulphide with 2-naphthol in sodium carbonate solution (cf. Part I).

Coupling diazotised *o*-aminophenyl benzyl sulphide with 2-naphthol in aqueous sodium hydrogen carbonate instead of sodium carbonate gave similar results, the yield of 1-*o*-benzylthiophenylazo-2-naphthol being 1·4 g. (41%), and that of 2-hydroxy-1-naphthyl *o*-(2-hydroxy-1-naphthylazo)phenyl sulphide, 0·05 g. Coupling in aqueous sodium hydroxide did not yield any of the latter compound but 1·8 g. (52%) of the former.

1-*o*-Benzylthiophenylazo-2-naphthol was also obtained by reducing di-*o*-(2-hydroxy-1-naphthylazo)phenyl disulphide (XV) with sodium sulphide in cold ethyl alcohol (cf. Part I) and treating the sodium salt of 1-*o*-mercaptophenylazo-2-naphthol (XVI) thus obtained with benzyl chloride. Recrystallisation of this product from ethyl alcohol gave red needles, m. p. 161—162°, not depressed on admixture with the product obtained as above.

Coupling of Diazotised o-*Aminophenyl Benzyl Sulphide with Phenol.*—A diazonium solution prepared from *o*-aminophenyl benzyl sulphide (2 g.) and nitrosylsulphuric acid as above was slowly added to phenol (3 g.) and sodium carbonate (65 g.) in water and ice (1500 g.). A tar, smelling strongly of benzothiadiazole, was obtained, filtered off, and treated with 5% aqueous sodium hydroxide (100 c.c.). On stirring, part of the tar dissolved, leaving yellow crystals of 4-*benzyloxy*-2′-*benzylthioazobenzene* (XVIII) (0·55 g., 15%). Recrystallisation from ethyl alcohol yielded orange-yellow needles, m. p. 143—144° (Found: C, 76·0; H, 5·3; N, 6·6. $C_{26}H_{22}ON_2S$ requires C, 76·1; H, 5·4; N, 6·8%). Acidification of the alkaline mother-liquor yielded a tar which was filtered off and extracted with boiling light petroleum (b. p. 60—80°). On concentration of this solution 2-*benzylthio*-4′-*hydroxyazobenzene* (XVII) crystallised (0·3 g., 10%). Recrystallisation from the same solvent gave orange needles, m. p. 107—109° (Found : C, 72·2; H, 5·1; N, 8·7. $C_{19}H_{16}ON_2S$ requires C, 71·3; H, 5·0; N, 8·7%).

Coupling in presence of sodium hydroxide (35 g.) instead of sodium carbonate gave the same products (yields : 4-benzyloxy-2′-benzylthioazobenzene, 1·2 g., 33%; 2-benzylthio-4′-hydroxyazobenzene, 0·05 g., 2%).

Conversion of 2-*Benzylthio*-4′-*hydroxyazobenzene into* 4-*Benzyloxy*-2′-*benzylthioazobenzene.*—2-Benzylthio-4′-hydroxyazobenzene (0·45 g.) was dissolved in water (3 c.c.) containing sodium hydroxide (0·25 g.). Benzyl chloride (9·75 g.) and ethyl alcohol (9 c.c.) were added, and the mixture kept at room temperature for 48 hr. It was then warmed gradually to 70° during 4 hr. 4-Benzyloxy-2′-benzylthioazobenzene separated on cooling. Recrystallisation from ethyl alcohol gave a product of m. p. 143—144°, not depressed on admixture with the compound obtained directly in the coupling reaction as above.

Di-(2-*acetamido*-1-*naphthyl*) *Disulphide* (XXIII).—2-Naphthylamine (71 g.) in 96% acetic acid (450 c.c.) was mixed with sodium thiocyanate (160 g.) in 96% acetic acid (1200 c.c.) and cooled to −5°. Bromine (25 c.c.) in acetic acid (350 c.c.) was added dropwise, with vigorous stirring. The precipitate, consisting of the salts of 1-thiocyanato-2-naphthylamine and 2-aminonaphthothiazole, was filtered off, washed with 10% sodium hydroxide, and finally with water, and dried (cf. Kaufmann and Oehring, *Ber.*, 1926, **59**, 187). This product was fused with potassium hydroxide (300 g.) for 1 hr. at 200—220°. The cooled melt was dissolved in water (1500 c.c.), the solution was filtered, and air passed through it for 24 hr. The precipitate of di-(2-amino-1-naphthyl) disulphide formed was boiled under reflux with a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (40 c.c.) for 1 hr. Addition of the resulting solution to a large amount of water yielded *di*-(2-*acetamido*-1-*naphthyl*) *disulphide* (66 g., 61% calc. from 2-naphthylamine). Recrystallisation from chlorobenzene or glacial acetic acid gave yellow plates, m. p. 223—224° (Found : C, 66·5; H, 4·6; N, 6·8. $C_{24}H_{20}O_2N_2S_2$ requires C, 66·7; H, 4·6; N, 6·5%).

2-*Acetamido*-1-*naphthyl Benzyl Sulphide* (XXV).—To a boiling solution of di-(2-acetamido-1-naphthyl) disulphide (60 g.) in ethyl alcohol (2 l.), sodium sulphide nonahydrate (120 g.) in water (600 c.c.) was gradually added. The solution was filtered and benzyl chloride (90 c.c.) slowly added under reflux. After 15 min., water (2 l.) was added, the mixture cooled, and the precipitate of 2-*acetamido*-1-*naphthyl benzyl sulphide* collected in almost quantitative yield. Recrystallisation from ethyl alcohol gave colourless needles, m. p. 100—101° (Found : C, 74·2; H, 5·6; N, 4·5. $C_{19}H_{17}ONS$ requires C, 74·3; H, 5·5; N, 4·6%).

2-*Amino*-1-*naphthyl Benzyl Sulphide* (XXVI).—Sodium hydroxide (300 g.) in water (1 l.) was added to 2-acetamido-1-naphthyl benzyl sulphide (80 g.) in ethyl alcohol (2 l.) and the mixture boiled for 3—4 hr. Water (2 l.) was added, and after cooling the precipitate of 2-*amino*-1-*naphthyl benzyl sulphide* obtained in almost quantitative yield was filtered off and washed with water. It crystallised from dilute alcohol as colourless needles, m. p. 64—65° (Found : C, 77·0; H, 6·0; N, 5·2. $C_{17}H_{15}NS$ requires C, 77·0; H, 5·6; N, 5·3%).

Action of Water on Diazotised 2-*Amino*-1-*naphthyl Benzyl Sulphide.*—Well-powdered 2-amino-1-naphthyl benzyl sulphide (1 g.) was added to well-stirred nitrosylsulphuric acid (0·4 g. of sodium nitrite in 5 c.c. of concentrated sulphuric acid) at 0°, stirring being continued for 30 min. Addition to water and ice (100 g.) resulted in the immediate formation of a precipitate of naphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazole (0·45 g., 64%). Recrystallisation from light petroleum (b. p. 60—80°) gave yellow needles, m. p. 88° (Jacobson and Schwartz, *Annalen*, 1893, **277**, 260, give 89°). It was also formed directly by diazotisation of the sulphide in aqueous conditions.

Coupling of Diazotised 2-*Amino*-1-*naphthyl Benzyl Sulphide with* 2-*Naphthol.*—A diazonium solution formed from 2-amino-1-naphthyl benzyl sulphide (5 g.) in nitrosylsulphuric acid (2 g. of sodium nitrite in 50 c.c. of concentrated sulphuric acid) was added to 2-naphthol (15 g.), sodium hydroxide (5 g.), and sodium carbonate (300 g.) in water and ice (2000 g.) with stirring. After a few minutes, sodium hydroxide (80 g.) was added, and the red precipitate of 1-(1-*benzylthio*-2-*naphthylazo*)-2-*naphthol* (XXIX) filtered off and washed with dilute sodium hydroxide and, finally, with water (yield, 3·6 g., 45%). Recrystallisation from glacial acetic acid gave red needles with a green lustre, m. p. 205° (Found : C, 76·7; H, 4·7; N, 6·6. $C_{27}H_{20}ON_2S$ requires C, 77·1; H, 4·8; N, 6·7%). Steam-distillation of the mother liquor yielded naphthothiadiazole (1·8 g., 53%) of m. p. 88°.

1-(1-Benzylthio-2-naphthylazo)-2-naphthol was also prepared by reduction of di-[2-(2-

hydroxy-1-naphthylazo)-1-naphthyl] disulphide with sodium sulphide in boiling ethyl alcohol (cf. Part II), and treating the solution of the sodium salt of 1-(1-mercapto-2-naphthylazo)-2-naphthol thus obtained with benzyl chloride. Recrystallisation of the product from glacial acetic acid gave red needles, m. p. 205°, not depressed on admixture with the product obtained above.

Action of Hydrobromic Acid on 1-o-*Benzylthiophenylazo*-2-*naphthol*.—1-*o*-Benzylthiophenylazo-2-naphthol (0·5 g.) in acetic acid (25 c.c.) was heated under reflux, and hydrobromic acid (48%; 25 c.c.) was added. Boiling was continued for 30 min., the solution poured into ice-water, and the precipitate filtered off and washed with water. This proved to be the starting material recovered in almost quantitative yield.

Action of Aluminium Bromide on 1-o-*Benzylthiophenylazo*-2-*naphthol*.—1-*o*-Benzylthiophenylazo-2-naphthol (2·5 g.) in dry benzene (200 c.c.) was treated with aluminium bromide (2·8 g.) in dry benzene (25 c.c.) and set aside for 24 hr. The purple precipitate formed was filtered off, freed from benzene *in vacuo* over paraffin wax, and slowly added to stirred concentrated hydrochloric acid (20 c.c.) and ice (400 g.). The red precipitate of 1-*o*-mercaptophenylazo-2-naphthol (XXXII), obtained in almost quantitative yield, was recrystallised from benzene by evaporation at room temperature under a reduced pressure of carbon dioxide as red plates, sintering at 118° and melting at 183—185°. It is identical with the product already described (Parts I and II) as shown by mixed m. p., oxidation in boiling xylene to *o*-(2-hydroxy-1-naphthylazo)benzenesulphenic anhydride (XXXIII), m. p. 241—243°, and formation of 1-*o*-methylthiophenylazo-2-naphthol, m. p. 163—164°, when shaken with sodium sulphide (added to prevent oxidation), sodium hydroxide, and methyl sulphate.

Conversion of o-(2-*Hydroxy*-1-*naphthylazo*)*benzenesulphenic Anhydride into Di*-o-(2-*hydroxy*-1-*naphthylazo*)*phenyl Disulphide*.—Concentrated hydrobromic acid (1 c.c.) was added to a suspension of *o*-(2-hydroxy-1-naphthylazo)benzenesulphenic anhydride (0·25 g.) in boiling glacial acetic acid (15 c.c.), and boiling allowed to proceed for 10 min. until the solid completely dissolved. After cooling, water (150 c.c.) and 10% sodium hydroxide solution (5 c.c.) were added, and the precitate formed (0·19 g., 81%) was recrystallised from benzene, giving dark red needles of di-*o*-(2-hydroxy-1-naphthylazo)phenyl disulphide, m. p. 233—234°, not depressed on admixture with a sample prepared from tetrazotised 2 : 2′-diaminodiphenyl disulphide and 2-naphthol (cf. Part I).

Action of Hydrobromic Acid on 1-(1-*Benzylthio*-2-*naphthylazo*)-2-*naphthol*.—1-(1-Benzylthio-2-naphthylazo)-2-naphthol (0·5 g.) in glacial acetic acid (20 c.c.) was heated under reflux, and 48% hydrobromic acid (20 c.c.) added. Boiling was continued for 30 min. and the mixture poured into ice water. The red precipitate of the starting material was recovered almost quantitatively.

Action of Aluminium Bromide on 1-(1-*Benzylthio*-2-*naphthylazo*)-2-*naphthol*.—A solution of freshly distilled aluminium bromide (2 g.) in dry benzene (100 c.c.) was added to a solution of 1-(1-benzylthio-2-naphthylazo)-2-naphthol (2 g.) in dry benzene (400 c.c.) and the mixture shaken for 60 hr. The dark purple precipitate formed was filtered off, freed from benzene *in vacuo* over paraffin wax, and treated with concentrated hydrochloric acid (15 c.c.) and ice (300 g.), and the red precipitate of 1-(1-mercapto-2-naphthylazo)-2-naphthol (XXXV), obtained in almost quantitative yield, was recrystallised from toluene in an atmosphere of nitrogen, to give small orange plates, m. p. 246—247°, not depressed on admixture with the thiol obtained by the reduction of di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide (Part II, where the m. p. was erroneously given as 232—234°). This was also confirmed by its oxidation to di-[2-(2-hydroxy-1-naphthylazo)-1-naphthyl] disulphide, m. p. 242—244°, and methylation to 1-(1-methylthio-2-naphthylazo)-2-naphthol, m. p. 174° (Part II).

Action of Bromine on 1-o-*Benzylthiophenylazo*-2-*naphthol*.—A solution of 1-*o*-benzylthiophenylazo-2-naphthol (1·5 g.) and bromine (1·3 g., 4 atoms) in chloroform (50 c.c.) was kept for 8 days at room temperature. Dry ether (125 c.c.) was added and the precipitate formed was washed with ether. Treatment with boiling glacial acetic acid (200 c.c.), in order to convert any sulphenyl bromide into the corresponding disulphide, followed by addition of water (1000 c.c.), gave a red precipitate (1·0 g., 69%) consisting mainly of a *dibromodi*-o-(2-*hydroxy*-1-*naphthylazo*)*phenyl disulphide*, which on crystallisation from benzene was obtained as dark red needles with a green lustre, m. p. 235—236° (Found: N, 7·8; Br, 23·3. $C_{32}H_{20}O_2N_4S_2Br_2$ requires N, 7·8; Br, 22·4%). Its m. p. was depressed by that of the unbrominated parent substance (cf. Part I), but otherwise it showed similar properties. It dissolves in organic solvents with a violet colour and in concentrated sulphuric acid with a light brown colour.

The crude disulphide (1 g.) in ethyl alcohol (50 c.c.) was reduced by shaking it with sodium sulphide nonahydrate (2 g.) in water (10 c.c.) at room temperature for 4 hr. On addition of water (150 c.c.) and sodium chloride, the *sodium* salt of a bromo-1-*o*-mercaptophenylazo-2-naphthol was precipitated as dark violet needles with a bronze lustre. Acidification with concentrated hydrochloric acid (20 c.c.) of a suspension of this salt in ethyl alcohol (35 c.c.) and water (150 c.c.) yielded a red *bromo*-1-o-*mercaptophenylazo*-2-*naphthol* in almost quantitative yield. Crystallisation by evaporation of its cold benzene solution under reduced pressure of carbon dioxide gave red plates, sintering at 110°, m. p. 198—200° (Found: C, 54·5; H, 3·5; N, 7·4. $C_{16}H_{11}ON_2SBr$ requires C, 53·5; H, 3·1; N, 7·8%). Crystallisation of the thiol from boiling xylene in the presence of air yielded, as in the case of the unbrominated parent substance (Part ·I), a *dibromo*-o-(2-*hydroxy*-1-*naphthylazo*)*benzenesulphenic anhydride* as brownish-red crystals, m. p. 234—235° (Found: C, 53·5; H, 2·7; N, 7·7. $C_{32}H_{20}O_3N_4S_2Br_2$ requires C, 52·5; H, 2·7; N, 7·7%). This was reconverted into the corresponding disulphide described above (mixed m. p.) by boiling hydrobromic acid in glacial acetic acid.

Treatment of a crude sample of the thiol with aqueous sodium hydroxide and methyl sulphate in the presence of sodium sulphide gave a bromo-1-*o*-methylthiophenylazo-2-naphthol which was not obtained completely free from the corresponding unbrominated compound. Crystallisation from ethyl alcohol gave fine red needles, m. p. 135—136° (Found: C, 58·3; H, 3·7; N, 7·8. Calc. for $C_{17}H_{13}ON_2SBr$: C, 54·7; H, 3·5; N, 7·5. Calc. for $C_{17}H_{14}ON_2S$: C, 69·4; H, 4·8; N, 9·5%).

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