131. o-*Mercapto-azo-compounds. Part XI.* Action of Alkali on Azobenzene-2-sulphenyl Bromide and its Derivatives.*

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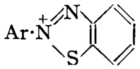
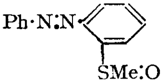
The action of aqueous sodium hydrogen carbonate, aqueous sodium hydroxide, and (wet) liquid ammonia on azobenzene-2-sulphenyl bromide and its derivatives is investigated. According to conditions, the corresponding disulphides and either disulphoxides (reaction 1) or sulphinates (3) are formed. The preparation of the disulphoxides from the corresponding sulphenyl bromides and sodium sulphinates in water is described. The reactions of 2-phenylazonaphthalene-1-sulphenyl bromide with alkalis are complicated by the tendency of di-(2-phenylazo-1-naphthyl) disulphoxide (III) to decompose readily into di-(2-phenylazo-1-naphthyl) sulphide (IV) and sulphur dioxide.

Zincke and Farr [1] found that *o*-nitrobenzenesulphenyl chloride forms with 2 mol. of sodium hydroxide the corresponding disulphide and disulphoxide, and that with an excess of sodium hydroxide the disulphoxide is then converted into more disulphide and the sodium sulphinate. They also observed that the latter reaction, now recognised to be characteristic of all sulphenyl halides and thiocyanates,[2] is accompanied by the transient appearance of a blue colour attributed to the sodium sulphenate formed as an intermediate.

As recently shown,[3, 4, 5] azobenzene-2-sulphenyl bromide and its *o*-nitro-, *p*-nitro-, and *o*-benzylthio-derivatives in aqueous or ethanolic solutions, in which they exist as true salts involving 2-arylbenzo-1-thia-2 : 3-diazolium ions (I), similarly form on addition of excess of sodium hydroxide the soluble blue-violet or blue sodium sulphenates, which cannot be isolated but have been identified by conversion into the stable 2-arylazophenyl methyl sulphoxides on rapid treatment with methyl sulphate. The formation of the parent methyl *o*-phenylazophenyl sulphoxide (II), not yet reported, is described on p. 656.

The blue colour of the solutions disappears slowly, the sulphenates being replaced by the corresponding disulphides and sodium sulphinates. In order to obtain further information about the action of alkali on these sulphenyl bromides, the effect of stoicheiometric quantities and of weaker alkalis has been investigated. Addition of slightly more than 1 mol. of sodium hydrogen carbonate or sodium hydroxide to an aqueous solution of azobenzene-2-sulphenyl bromide quickly yields a precipitate of di-(*o*-phenylazophenyl) disulphide and disulphoxide according to equation (1); this mixture can be quantitatively separated by chromatography with a benzene solution and a silica gel column.

(I) 

 (II)

With 1·75 mol. of sodium hydroxide the disulphoxide, initially formed, is converted into more disulphide and the sodium azobenzene-2-sulphinate according to (2). The total

$$\begin{aligned}
&(1)\ 12ArSBr + 12NaOH &&= 3ArS{\cdot}SAr + 3ArSO_2{\cdot}SAr + 12NaBr + 6H_2O\\
&(2)\ 3ArSO_2{\cdot}SAr + 4NaOH &&= ArS{\cdot}SAr + 4ArSO_2^-Na^+ + 2H_2O\\
&(3)\ 12ArSBr + 16NaOH &&= 4ArS{\cdot}SAr + 4ArSO_2^-Na^+ + 12NaBr + 8H_2O
\end{aligned}$$

result (3) is similar to that already [3] reported for the action of a great excess of sodium hydroxide, but in these less alkaline conditions no, or only a very transient, blue-violet

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* Part X, preceding paper.

[1] Zincke and Farr, *Annalen*, 1912, **391**, 55.

[2] Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 269.

[3] Burawoy and Vellins, *J.*, 1954, 90.

[4] Burawoy, Chaudhuri, and Vellins, *J.*, 1955, 3798.

[5] *Idem*, *J.*, 1956, 90.

colour of the sodium azobenzene-2-sulphenate (appearing sometimes on contact of the drops of sodium hydroxide with the solution) is observed and the reaction is much faster, indicating that the disproportionation is a property of the undissociated sulphenic acid and not of the sulphenate ion, the instability of which is only apparent, being due to partial hydrolysis.

Di-(*o*-phenylazophenyl) disulphoxide has been identified by its unambiguous preparation from azobenzene-2-sulphenyl bromide and sodium azobenzene-2-sulphinate in aqueous solution. The solubility and stability of the sulphenyl bromide in water allow this simplification of the usual method for the preparation of disulphoxides, the reaction of a silver sulphinate with a sulphenyl halide in ether solution, first used by Zincke and Farr[1] for the preparation of di-(*o*-nitrophenyl) disulphoxide. Di-(*o*-phenylazophenyl) disulphoxide is sparingly soluble in water and forms with 1 equiv. of sodium hydroxide in aqueous suspension, or more slowly with a considerable excess of sodium hydroxide in dilute methanol, the disulphide and the sodium sulphinate according to (2). In the latter case, however, the reaction is preceded by development of the rather persistent blue-violet colour of the sodium sulphenate.

The action of liquid ammonia below —50° on azobenzene-2-sulphenyl bromide has also been investigated, the original aim having been the preparation of azobenzene-2-sulphenamide. This is not formed, but the small amount of water present in commercial liquid ammonia rapidly converts the sulphenyl bromide into the disulphide and the disulphoxide (as 1). If the reaction is allowed to proceed for a longer time (until a test sample, on addition of sodium hydroxide, failed to show the blue-violet colour characteristic of the sodium sulphenate, indicating complete disappearance of the disulphoxide), the disulphoxide is further converted into more disulphide and the ammonium sulphinate (as 2). The same result is obtained with the disulphoxide as starting material. The blue-violet colour of the sulphenate ion is not observed at any stage in these experiments.

2-Nitro-, 4-nitro-, and 2-benzylthio-azobenzene-2′-sulphenyl bromides behave like the parent substance, except that the disulphoxides, all of which have been also synthesised from the corresponding sulphenyl bromides and sodium sulphinates, are completely insoluble in water, and in aqueous suspension are not affected at room temperature by an equimolecular amount and only slightly by a great excess of sodium hydroxide.

These observations show that the action of alkali on azobenzene-2-sulphenyl bromide and its derivatives (and probably on other sulphenyl halides or thiocyanates) can proceed in at least three stages : (i) Formation of the sulphenic acid (which, with an excess of sodium hydroxide, is in equilibrium with the coloured sodium sulphenate) (4). (ii) Disproportionation of the sulphenic acid into the disulphoxide and disulphide, the mechanism of which requires further elucidation, but which is probably initiated by the intermediate formation of the sulphenic anhydride (5). (iii) Cleavage of the disulphoxide into the sulphinate and the sulphenic acid (being, again, with an excess of sodium hydroxide in equilibrium with the blue sodium sulphenate) (6) which re-enters the reaction cycle.

$$(4)\ \mathrm{ArSBr} \longrightarrow \mathrm{ArS{\cdot}OH}$$

$$(5)\ 4\mathrm{ArS{\cdot}OH} \longrightarrow (2\mathrm{ArSO{\cdot}SAr}) \longrightarrow \mathrm{ArSO_2{\cdot}SAr} + \mathrm{ArS{\cdot}SAr}$$

$$(6)\ \mathrm{ArSO_2{\cdot}SAr} \longrightarrow \mathrm{ArSO_2^-Na^+(NH_4^+)} + \mathrm{Ar{\cdot}S{\cdot}OH}$$

The action of alkali on 2-phenylazonaphthalene-1-sulphenyl bromide is complicated by the instability of di-(2-phenylazo-1-naphthyl) disulphoxide (III). This separates when aqueous solutions of the sulphenyl bromide and the sodium sulphinate are mixed, and, if quickly filtered off, is obtained almost pure, but it cannot be crystallised, since on standing either as solid or in solution, it decomposes at room temperature, and more rapidly on heating, into di-(2-phenylazo-1-naphthyl) sulphide (IV) and sulphur dioxide. This is similar to the tendency[6] of 2-phenylazonaphthalene-1-sulphinic acid to decompose into 2-phenylazonaphthalene and sulphur dioxide.

2-Phenylazonaphthalene-1-sulphenyl bromide in aqueous solution with 1 mol. of sodium hydroxide instantaneously forms a mixture of the disulphide and the unstable disulphoxide

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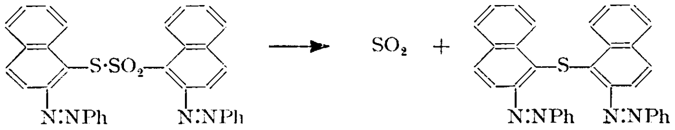
[6] Burawoy, Chaudhuri, and Hyslop, *J.*, 1956, 96.

(and/or monosulphide) which are separated and isolated most economically by reduction of the disulphide with sodium sulphide to the water-soluble sodium mercaptide. The latter, after separation of the insoluble monosulphide, readily yields the disulphide in air.[6]

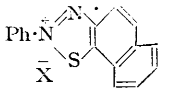
In contrast, the reaction is very slow with 1 mol. of sodium hydrogen carbonate, the solution remaining clear for about 2 hr. This can only be attributed to the presence in solution of 2-phenylnaphtho(1′ : 2′ : 5 : 4)-1-thia-2 : 3-diazolium hydrogen carbonate (V) and to the greater basicity of 2-phenylazonaphthalene-1-sulphenic acid than of azobenzene-2-sulphenic acid and its derivatives (see also below). Moreover, the reaction remains incomplete, since the sulphur dioxide, liberated by decomposition of the disulphoxide formed, increases the acidity of the solution and finally inhibits hydrolysis. A small amount of the 2-phenylnaphthothiadiazolium sulphite (V) or its covalent isomer 2-phenylazonaphthalene-1-sulphenyl sulphite (VI) is also precipitated, together with the disulphide and monosulphide. It has been identified with an authentic sulphite prepared from the sulphenyl bromide by double decomposition with sodium sulphite.

(III)

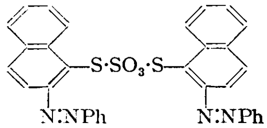


(IV)

(V)



(X = HCO$_3$ or $\frac{1}{2}$SO$_3$)



(VI)

Treatment of the sulphenyl bromide with liquid ammonia quickly gives a mixture of the disulphide and the monosulphide, but no sulphinic acid. The result is the same if the solution is allowed to stand. This indicates that in these weakly alkaline conditions the decomposition of the disulphoxide to the monosulphide is faster than cleavage to the sulphinate and the sulphenic acid (as 6).

On the other hand, as already shown,[6] an appreciable excess of sodium hydroxide converts the sulphenyl bromide in water almost instantaneously into the disulphide and sodium sulphinate. In these strongly alkaline conditions cleavage of the disulphoxide, initially formed, is very fast and takes preference over decomposition. The rapidity of this reaction and the non-appearance of the blue colour of the sulphenate ion, which is in contrast to the behaviour of azobenzene-2-sulphenyl bromide and its substituted derivatives,[3, 4, 5] indicates an appreciably lower acidity of the 2-phenylazonaphthalene-1-sulphenic acid in agreement with the greater basicity of this amphoteric compound as indicated by the stability of its hydrogen carbonate (cf. above).

EXPERIMENTAL

Di-(o-phenylazophenyl) Disulphoxide.—An aqueous solution of sodium azobenzene-2-sulphinate (0·2 g. in 20 c.c.) was added to azobenzene-2-sulphenyl bromide (0·2 g.) in water (60 c.c.). The *disulphoxide* separated immediately (0·3 g., 91%). Crystallisation from light petroleum (b. p. 60—80°) gave orange needles, m. p. 103—104° (Found : C, 62·8; H, 3·8; N, 12·1. $C_{24}H_{18}O_2N_4S_2$ requires C, 62·8; H, 3·9; N, 12·2%). The disulphoxide is slightly soluble in water, and when stirred in aqueous suspension with an equivalent amount of sodium hydroxide is readily converted into the disulphide and sodium azobenzene-2-sulphinate.

Action of Sodium Hydrogen Carbonate or Hydroxide (1 Mol.) on Azobenzene-2-sulphenyl Bromide.—Sodium hydrogen carbonate (0·01N; 350 c.c., ~1 mol.) was added slowly to a well-stirred aqueous solution of azobenzene-2-sulphenyl bromide (1 g. in 200 c.c.). At no stage was the blue-violet colour characteristic of sodium azobenzene-2-sulphenate observed. After a few hours, the precipitate of di-(*o*-phenylazophenyl) disulphide and disulphoxide was filtered off (0·7 g.). The disulphoxide was extracted with cold methanol and the insoluble disulphide collected (0·3 g., 84%). Crystallisation from light petroleum (b. p. 60—80°) gave orange needles, m. p. and mixed m. p. 142° (Burawoy and Vellins [3] give 142°) The disulphoxide was isolated from the methanol extract and from an ether extract of the original aqueous filtrate (0·3 g., 78%; m. p. and mixed m. p. 103—104°, from light petroleum).

A similar result was obtained with sodium hydroxide (0·01N; 350 c.c., ~1 mol.), except that a very transient appearance of the blue-violet colour could not be avoided in the last stages of the addition on contact of the sodium hydroxide with the solution, and that a very small amount of azobenzene-2-sulphinic acid (<0·05 g.) was also formed and isolated from the acidified original mother-liquor.

The experiment was repeated, but sodium hydrogen carbonate was added to a solution of the sulphenyl bromide in benzene (200 c.c.). The benzene layer containing the disulphide and disulphoxide, after being washed and dried (Na_2SO_4), was chromatographed on a column of silica gel. The disulphide passed quickly through the column and was recovered (almost pure) from the benzene solution (0·3 g., 84%; m. p. and mixed m. p. 142°, from light petroleum). The disulphoxide, adsorbed at the top of the column, was eluted with chloroform (0·3 g., 78%; m. p. and mixed m. p. 103—104°, from light petroleum). The separation is quantitative.

Action of Sodium Hydroxide (1·75 *Mol.*) *on Azobenzene-2-sulphenyl Bromide.*—Aqueous sodium hydroxide (0·01N; 600 c.c., 1·75 mol.) was added slowly to a well-stirred solution of the sulphenyl bromide (1 g.) in water (200 c.c.). The disulphide was quickly precipitated and was filtered off (0·45 g., 91%; m. p. and mixed m. p. 142°, from light petroleum). The filtrate was acidified with hydrochloric acid and extracted with ether which, on evaporation, yielded azobenzene-2-sulphinic acid (0·2 g., 74%; m. p. and mixed m. p. 104°, from dilute methanol; Burawoy and Vellins [3] give 104°).

Action of Sodium Hydroxide (*Excess*) *on Di-*(o*-phenylazophenyl*) *Disulphoxide.*—10% Aqueous sodium hydroxide (20 c.c.) was added to a solution of the disulphoxide (0·5 g.) in methanol (100 c.c.). After disappearance of the blue-violet colour which developed immediately, the precipitated disulphide was filtered off (0·15 g., 96%; m. p. and mixed m. p. 142°, from light petroleum). The filtrate was diluted with water and acidified with hydrochloric acid. The precipitate of azobenzene-2-sulphinic acid was collected (0·25 g., 70%; m. p. and mixed m. p. 104°, from aqueous methanol).

Methyl 2-Phenylazophenyl Sulphoxide.—40% Aqueous sodium hydroxide (5 c.c.) was added to a solution of azobenzene-2-sulphenyl bromide (0·5 g.) in methanol (50 c.c.). The blue-violet solution was immediately shaken with methyl sulphate (3 c.c.) until the blue colour had disappeared. Water was added and the precipitate of *methyl 2-phenylazophenyl sulphoxide* was filtered off (0·3 g., 72%). Crystallisation from aqueous methanol gave orange-yellow needles, m. p. 58—59° (Found: C, 64·3; H, 5·1; N, 11·4. $C_{13}H_{12}ON_2S$ requires C, 63·9; H, 4·9; N, 11·3%).

*Di-*o*-*(*2-nitrophenylazophenyl*) *Disulphoxide.*—Sodium 2-nitroazobenzene-2′-sulphinate (0·5 g.) in water (50 c.c.) was added to 2-nitroazobenzene-2′-sulphenyl bromide (0·5 g.) in water (500 c.c.). The *disulphoxide* separated immediately (0·8 g., 98%). Crystallisation from benzene gave reddish-brown prisms, m. p. 198° (Found: C, 52·4; H, 2·9; N, 15·8. $C_{24}H_{16}O_6N_6S_2$ requires C, 52·6; H, 2·9; N, 15·6%). The disulphoxide is insoluble in water and its suspension is only very slowly, if at all, affected even by an excess of aqueous sodium hydroxide.

Action of Sodium Hydrogen Carbonate or Hydroxide (1 *Mol.*) *on 2-Nitroazobenzene-2′-sulphenyl Bromide.*—Aqueous sodium hydrogen carbonate or sodium hydroxide (0·01N; 150 c.c., ~1 mol.) was added slowly to a well-stirred suspension of the sulphenyl bromide (0·5 g.) in water (300 c.c.). No blue colour developed. The precipitate of di-(*o*-2-nitrophenylazophenyl) disulphide and disulphoxide, formed instantaneously, was filtered off (0·35 g.). The mixture was quantitatively separated chromatographically by means of benzene and a column of silica gel. The disulphide (0·15 g., 79%) crystallised from benzene as yellow needles, m. p. and m. p. 172—173° (Burawoy, Chaudhuri, and Vellins [5] give 172—173°). The disulphoxide was eluted with chloroform (0·15 g., 75%; m. p. and mixed m. p. 198°, from benzene). The same result was obtained with 2 mol. of sodium hydroxide, no sulphinic acid being formed.

Action of Sodium Hydroxide (*Excess*) *on Di-*(o*-2-nitrophenylazophenyl*) *Disulphoxide.*—10% Aqueous sodium hydroxide (20 c.c.) was added to the disulphoxide (0·5 g.) in methanol (100 c.c.). The solution was kept until disappearance of the deep blue colour which developed immediately. The precipitate of the disulphide was filtered off (0·14 g., 90%; m. p. and mixed m. p. 172—173°, from benzene). The filtrate was diluted with water and acidified. The precipitate of 2-nitroazobenzene-2′-sulphinic acid was collected (0·25 g., 70%; m. p. and mixed m. p. 144—145°, from aqueous methanol; Burawoy, Chaudhuri, and Vellins [5] give 144—145°).

Di-(o-4-*nitrophenylazophenyl*) *Disulphoxide.*—Sodium 4-nitroazobenzene-2′-sulphinate (0·5 g.) in water (50 c.c.) was added to 4-nitroazobenzene-2′-sulphenyl bromide (0·5 g.) in water (300 c.c.). The almost quantitative precipitate of the *disulphoxide* (0·8 g.) crystallised from benzene and light petroleum (b. p. 60—80°) as reddish-brown prisms, m. p. 172° (Found : C, 53·0; H, 2·9; N, 15·6. $C_{24}H_{16}O_6N_6S_2$ requires C, 52·6; H, 2·9; N, 15·6%), insoluble in water and, in suspension, only very slowly attacked by an excess of sodium hydroxide.

Action of Sodium Hydrogen Carbonate or Hydroxide (1 *Mol.*) *on* 4-*Nitroazobenzene*-2′-*sulphenyl Bromide.*—A suspension of the bromide (0·5 g.) in water (500 c.c.) was treated, as described for the 2-nitro-isomer, with sodium hydrogen carbonate or hydroxide. The disulphide (0·15 g., 79%; m. p. and mixed m. p. 228°, from benzene; Burawoy, Chaudhuri, and Vellins [5] give 228°) and the disulphoxide (0·15 g., 75%; m. p. and mixed m. p. 172°, from benzene and light petroleum) were isolated after quantitative chromatographic separation. No sulphinic acid was formed. The same result was obtained with 2 mol. of sodium hydroxide.

Action of Sodium Hydroxide (*Excess*) *on Di-*(o-4-*nitrophenylazophenyl*) *Disulphoxide.*—A solution of the disulphoxide (0·5 g.) in methanol (100 c.c.) was treated with sodium hydroxide, as described for the 2-nitro-isomer. The disulphide (m. p. and mixed m. p. 228°, from benzene) and the sulphinic acid (m. p. and mixed m. p. 133°, from methanol; Burawoy, Chaudhuri, and Vellins [5] give 133°) were obtained in similar yields.

Di-(o-2-*benzylthiophenylazophenyl*) *Disulphoxide.*—Solutions of sodium 2-benzylthioazobenzene-2′-sulphinate (0·5 g.) in water (50 c.c.) and of 2-benzylthioazobenzene-2′-sulphenyl bromide (0·5 g.) in ethanol (100 c.c.) were mixed, and the precipitated *disulphoxide* (0·6 g., 71%) crystallised from ethanol as reddish-brown needles, m. p. 135° (Found : C, 64·8; H, 4·1; N, 8·4. $C_{38}H_{30}O_2N_4S_4$ requires C, 65·0; H, 4·3; N, 8·0%), insoluble in water and, in aqueous suspension, not attacked by sodium hydroxide at room temperature.

Action of Sodium Hydrogen Carbonate or Hydroxide (1 *Mol.*) *on* 2-*Benzylthioazobenzene*-2′-*sulphenyl Bromide.*—A suspension of the sulphenyl bromide (0·5 g.) in 10% aqueous ethanol (400 c.c.) was treated, as described for the nitro-derivatives, with sodium hydrogen carbonate or hydroxide (0·01N; 121 c.c., ~1 mol.). The disulphide (0·15 g., 75%; m. p. and mixed m. p. 231°, from benzene; Burawoy, Chaudhuri, and Vellins [4] give 231°) and the disulphoxide (0·15 g., 65%; m. p. and mixed m. p. 135°, from ethanol) were isolated after chromatographic separation. No sulphinic acid was formed.

Action of Sodium Hydroxide (*Excess*) *on Di-*(o-2-*benzylthiophenylazophenyl*) *Disulphoxide.*—10% Aqueous sodium hydroxide (20 c.c.) was added to a methanolic solution of the disulphoxide (0·5 g. in 100 c.c.). After disappearance of the blue colour, the disulphide (m. p. and mixed m. p. 231°, from benzene) and the sulphinic acid (m. p. and mixed m. p. 126°, from ethanol; Burawoy, Chaudhuri, and Vellins [4] give m. p. 126°) were isolated.

Action of (*Wet*) *Liquid Ammonia on Azobenzene*-2-*sulphenyl Bromide, Di-*(o-*phenylazophenyl*) *Disulphoxide, and their Derivatives.*—(i) Azobenzene-2-sulphenyl bromide or its 2-nitro- or 4-nitro- or 2-benzylthio-derivative (0·5 g.) was added to well-stirred liquid ammona (30—50 c.c.) below −50°. After 30 min., ammonia was evaporated off. The residue, consisting of the corresponding disulphide (75—85%) and disulphoxide (66—78%), was separated chromatographically as described earlier.

(ii) The experiments were repeated, but the reaction allowed to proceed for 12—30 hr., until a test sample failed to develop a blue colour with ethanolic sodium hydroxide, showing complete disappearance of the disulphoxide formed initially. After evaporation of the ammonia, the residue was extracted with water or dilute aqueous sodium hydroxide, and the residual insoluble disulphide was collected (70—80%). On acidification of the alkaline extracts the sulphinic acid was obtained (65—70%).

(iii) Di-(*o*-phenylazophenyl) disulphoxide or its 2-nitro- or 4-nitro- or 2-benzylthio-derivative (0·5 g.) was treated with liquid ammonia (30—50 c.c.) below −50° for 5 hr., a test with ethanolic sodium hydroxide then showing complete conversion of the starting material. The mixture was worked up as under (ii), and the corresponding disulphide (85—90%) and sulphinic acid (75—85%) isolated.

The products obtained in all experiments were crystallised and identified as described earlier. At no stage was the blue colour of the sulphenate ion observed.

Di-(2-*phenylazo*-1-*naphthyl*) *Disulphoxide and Sulphide.*—Aqueous solutions of sodium 2-phenylazonaphthalene-1-sulphinate (0·3 g. in 20 c.c.) and of 2-phenylazonaphthalene-1-sulphenyl bromide (0·3 g. in 200 c.c.) were mixed, and the precipitate of the *disulphoxide* quickly filtered off, washed, and dried (0·4 g., 80%; m. p. 115—120°) (Found : C, 68·1; H, 4·3; N, 10·5. $C_{32}H_{22}O_2N_4S_2$ requires C, 69·1; H, 4·0; N, 10·0%). Attempts to purify the disulphoxide yielded *di-(2-phenylazo-1-naphthyl) sulphide*, which crystallised from light petroleum (b. p. 80—100°) as reddish-brown needles, m. p. 198° (Found: C, 77·9; H, 4·4; N, 11·6. $C_{32}H_{22}N_4S$ requires C, 77·8; H, 4·4; N, 11·3%).

Action of Sodium Hydroxide (1 Mol.) on 2-Phenylazonaphthalene-1-sulphenyl Bromide.—Aqueous sodium hydroxide (0·01N; 146 c.c., ~1 mol.) was added at once to a well-stirred aqueous solution of the sulphenyl bromide (0·5 g. in 200 c.c.). After 30 min., the precipitate of the disulphide and the disulphoxide (and/or monosulphide), formed almost instantaneously, was filtered off (0·35 g.; m. p. 155—175°). The mixture was refluxed with ethanol (50 c.c.) for 1 hr. in order to ensure complete conversion of any disulphoxide into monosulphide, sodium sulphide nonahydrate (0·3 g.) and sodium hydroxide (0·25 g.) in water (15 c.c.) were added, and, after 3 min., the solution was cooled and diluted with water. The precipitated monosulphide was filtered off (0·08 g., 46%; m. p. and mixed m. p. 198°, from light petroleum). The mother-liquor containing the sodium mercaptide was acidified and extracted with benzene. The benzene layer was dried and concentrated to a small volume, and the precipitate of almost pure disulphide was collected (0·12 g., 65%; m. p. and mixed m. p. 205°, from benzene; Burawoy, Chaudhuri, and Hyslop [6] give 205°). The original mother-liquor did not contain any sulphinic acid.

Action of (Wet) Liquid Ammonia on 2-Phenylazonaphthalene-1-sulphenyl Bromide.—The sulphenyl bromide (0·5 g.) was added to well-stirred liquid ammonia (30 c.c.) below −50°. After 30 min., the ammonia was evaporated off, and the residue of the disulphide and the monosulphide washed with water. Treatment of a sample with cold aqueous sodium hydroxide did not yield any sulphinic acid. The mixture (0·32 g.; m. p. 155—190°) was separated by means of sodium sulphide as in the preceding experiment, yielding monosulphide (0·06 g., 35%; m. p. and mixed m. p. 198°, from light petroleum) and disulphide (0·12 g., 65%; m. p. and mixed m. p. 205°, from benzene). The same result was obtained when the reaction was allowed to proceed for 5 hr.

Action of Sodium Hydrogen Carbonate (1 Mol.) on 2-Phenylazonaphthalene-1-sulphenyl Bromide.—Sodium hydrogen carbonate (0·25 g., 1 mol.) in water (10 c.c.) was added at once to a well-stirred aqueous solution of the sulphenyl bromide (1·0 g. in 400 c.c.) which after 2 hr. started to become turbid. The reaction was allowed to proceed for 48 hr., and the precipitate of the disulphide, monosulphide, and *2-phenylazonaphthalene-1-sulphenyl sulphite* filtered off. The sulphides (0·33 g., 43%) were removed by extraction with boiling benzene and separated and identified as in the preceding experiment. The benzene-insoluble sulphite (0·07 g., 8%) formed from ethanol reddish-brown solvated needles, m. p. 127—128° (Found: C, 62·7; H, 4·3; N, 8·9. $C_{32}H_{22}O_3N_4S_3,C_2H_6O$ requires C, 62·6; H, 4·3; N, 8·6%). The ethanol could not be removed below 100°. The original mother-liquor remained clear on storage, but contained an appreciable amount of unchanged 2-phenylnaphthothiadiazolium salt which, after 50 hr., was recovered, on addition of sodium perchlorate, as the sparingly soluble perchlorate (0·34 g., 32%; m. p. 214°; Burawoy, Chaudhuri, and Hyslop [6] give m. p. 216°).

2-Phenylazonaphthalene-1-sulphenyl Sulphite.—Sodium sulphite (0·08 g.) in water (10 c.c.) was added to 2-phenylazonaphthalene-1-sulphenyl bromide (0·4 g.) in water (200 c.c.). The precipitated sulphite (0·27 g., 76%) crystallised from ethanol as reddish-brown needles, m. p. 127—128°, not depressed by mixing with the product described in the preceding experiment. Crystallisation from methanol gave similar needles of *solvate*, m. p. 127—128° (Found: C, 62·0; H, 4·0; N, 9·0. $C_{32}H_{22}O_3N_4S_3,CH_4O$ requires C, 62·1; H, 4·1; N, 8·8%).

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