19. o-*Mercapto-azo-compounds. Part IX.* Debenzylation of 1-Benzylthio-2-phenylazonaphthalene.*

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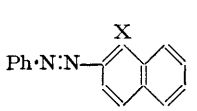
The debenzylation of 1-benzylthio-2-phenylazonaphthalene by bromine in glacial acetic acid and the action of sodium in liquid ammonia on 2-benzylthioazobenzene, 1-benzylthio-2-phenylazonaphthalene, and 2 : 2′-dibenzylthioazobenzene are investigated. The preparation and the properties of 2-phenylazonaphthalene-1-sulphenyl bromide and its derivatives, of 2-phenylazonaphthalene-1-sulphinic acid, and of 1-mercapto-2-phenylazonaphthalene are discussed.

The investigation of the debenzylation of 2-benzylthioazobenzene and its derivatives (Parts V—VIII *) has been extended to 1-benzylthio-2-phenylazonaphthalene (I; X = S·CH_2Ph) which is obtained by condensing 1-benzylthio-2-naphthylamine with nitrosobenzene in acetic acid. Heating with 1 and 2 mols. of bromine in acetic acid yields almost quantitatively 2-phenylazonaphthalene-1-sulphenyl bromide and tribromide respectively (I; X = SBr and SBr_3).

The sulphenyl bromide is stable to heat, soluble in water, and converted in aqueous solution by double decomposition into the chloride, iodide, thiocyanate, perchlorate, and water-insoluble cyanide. The iodide is sufficiently stable to allow crystallisation from ethanol and shows characteristic colour changes in solvents similar to those already observed for azobenzene-2-sulphenyl iodide (see Part VI). The chloride crystallises with 1 mol. of water which cannot be removed without decomposition which starts slowly above 100°; but its identity is not in doubt, since it is easily soluble in water and converted quantitatively by potassium cyanide in aqueous solution into the almost pure cyanide (1-thiocyanato-2-phenylazonaphthalene).

The properties of these compounds are very similar to those of the corresponding azobenzene-2-sulphenyl derivatives (see Part VI). Like the latter, except for the cyanide, they will exist in the solid state and in solution completely or partly as true salts of structure (II), involving a 2-phenylnaphtho(2′ : 1′-4 : 5)-1-thia-2 : 3-diazolium cation.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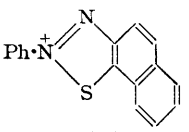
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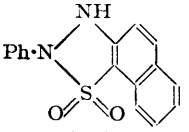
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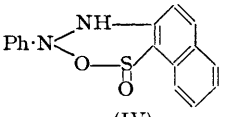
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2-Phenylazonaphthalene-1-sulphenyl tribromide (in dilute ethanol) is converted almost quantitatively by sodium hydroxide into the orange sodium 2-phenylazonaphthalene-1-sulphinate (I; X = SO_2Na), but the free acid obtained by acidification crystallises from benzene and light petroleum as colourless plates, indicating the absence of an azo-group. Being similar to the almost colourless azobenzene-2-sulphinic acid (see Part V), it should possess the cyclic structure (III) or (IV). However, whereas the azobenzene derivative is fairly stable and can be crystallised from dilute ethanol, 2-phenylazonaphthalene-1-sulphinic acid in chloroform, ether, or ethanol dissociates, slowly at room temperature, quickly on heating, into 2-phenylazonaphthalene (I; X = H) and sulphur dioxide and, thus, cannot be crystallised from these solvents.

The sulphinic acid also dissociates when melted or when its alkaline solution is heated. Attempts to prepare the 4-nitrobenzyl and methyl sulphones by treating the aqueous solutions of the sodium sulphinate at room temperature with 4-nitrobenzyl chloride and methyl sulphate respectively also failed, 2-phenylazonaphthalene being the only product isolated. The stability of the sulphinic acid in non-polar solvents such as benzene and light petroleum, and the qualitative observation that the rate of dissociation increases in

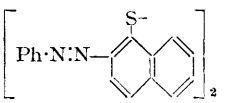
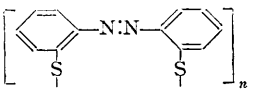
* Parts V—VIII, *J.*, 1954, 90, 4481; 1955, 3798; preceding paper.

the order of solvents chloroform < ether < ethanol, suggest that the decomposition is initiated by ionisation and subsequent tautomerisation to the true, but unstable, 2-phenylazonaphthalene-1-sulphinic acid (I; X = SO_2H). This is similar to the slow conversion of the colourless " azobenzene-2-sulphinic acid " in chloroform or ethanol into the orange-yellow, but in this case stable, true azo-tautomer. Kharasch, King, and Bruice (*J. Amer. Chem. Soc.*, 1955, **77**, 981) recently reported that 2 : 4-dinitrobenzenesulphenyl chloride on treatment with alkali or acid yields, in place of the expected sulphinic acid, only *m*-dinitrobenzene. The instability of both these sulphinic acids should be due to the strain resulting from intramolecular steric hindrance between the SO_2H group and the large *ortho*-substituents.

The structures of the sulphenyl derivatives and of the colourless tautomers of the sulphinic acids, and the quantitative aspects of their solvent-dependent equilibria and gradual tautomeric changes, are being further investigated.

On addition of an excess of sodium hydroxide, azobenzene-2-sulphenyl bromide and its derivatives in dilute ethanol are converted into the corresponding blue sodium sulphenates which at room temperature only slowly disproportionate to the insoluble disulphides and soluble sodium sulphinates. In contrast, 2-phenylazonaphthalene-1-sulphenyl bromide, when similarly treated, immediately yields a precipitate of di-(2-phenylazo-1-naphthyl) disulphide (V), also obtained by the action of zinc, and the soluble sodium 2-phenylazonaphthalene-1-sulphinate (I; X = SO_2Na), the intermediate formation of a blue sodium sulphenate (I; X = SONa) not being observed. Unexpectedly, a very small amount of 2-phenylazo-1-naphthol was also isolated.

The debenzylation of the *o*-benzylthioazo-compounds with sodium in liquid ammonia, a method originally applied by Sifferd and du Vigneaud (*J. Biol. Chem.*, 1935, **108**, 757) to the cleavage of benzylcysteine, has also been investigated. Whereas 2-benzylthioazobenzene itself, probably owing to its insolubility, remains unchanged even in presence of ether, 1-benzylthio-2-phenylazonaphthalene is easily debenzylated, the disulphide (V) or, in presence of an excess of sodium, the sodium salt (I; X = SNa) of 1-mercapto-2-phenylazonaphthalene being formed. The latter is also obtained by reduction of the disulphide with ethanolic sodium sulphide.

(V)   (VI)

Like 2-mercaptoazobenzene, the crude thiol formed on acidification could not be purified, being readily reoxidised on storage or attempted crystallisation to the disulphide, but its identity has been established by conversion into the original 1-benzylthio-2-phenylazonaphthalene.

Similarly, 2 : 2′-dibenzylthioazobenzene yields, depending on the quantity of sodium used, the polysulphide (VI) or the sodium salt of 2 : 2′-dimercaptoazobenzene, the preparations of which, by the action of zinc or sodium hydroxide on di-[*o*-(*o*-bromothio)-phenylazophenyl] disulphide and by the reduction of the polysulphide with sodium sulphide respectively, have already been described (see Part VII).

Experimental

1-Benzylthio-2-phenylazonaphthalene.—A solution of 1-benzylthio-2-naphthylamine (8 g.) and nitrosobenzene (4·0 g.) in acetic acid (60 c.c.) was kept for 24 hr. at room temperature. The precipitate of *1-benzylthio-2-phenylazonaphthalene* was filtered off and washed with a little acetic acid and light petroleum (7·5 g., 70%). Crystallisation from ethanol gave orange-red needles, m. p. 122° (Found : C, 78·2; H, 5·2; N, 7·9. $C_{23}H_{18}N_2S$ requires C, 78·0; H, 5·1; N, 7·9%).

2-Phenylazonaphthalene-1-sulphenyl Bromide.—A solution of 1-benzylthio-compound (5 g.) and bromine (2·26 g., 1 mol.) in glacial acetic acid (80 c.c.) was refluxed for 3 min. On cooling, almost pure *sulphenyl bromide* separated (4 g., 82%). Less pure product (0·3 g.) was obtained by extracting the filtrate with chloroform. Crystallisation from acetic acid gave long yellow needles, m. p. 245°. The bromide is soluble in water, alcohol, chloroform, and sparingly so in benzene (Found : C, 56·2; H, 2·9; N, 8·3. $C_{16}H_{11}N_2SBr$ requires C, 56·0; H, 3·2; N, 8·2%).

2-*Phenylazonaphthalene*-1-*sulphenyl Chloride*.—A solution of the bromide (0·5 g.) in water (200 c.c.) and concentrated hydrochloric acid (50 c.c.) was extracted with chloroform. The extract was concentrated, and the *sulphenyl chloride* (0·3 g., 69%) precipitated by addition of light petroleum. Crystallisation from chlorobenzene gave hydrated yellow needles, m. p. 222°, easily soluble in water (Found : C, 60·7; H, 4·0; Cl, 11·5. $C_{16}H_{11}N_2SCl,H_2O$ requires C, 60·6; H, 4·1; Cl, 11·2%). No loss of weight was observed at 100° in 6 hr. and slow decomposition above this temperature.

2-*Phenylazonaphthalene*-1-*sulphenyl Iodide*.—Potassium iodide (1 g.) in water (20 c.c.) was added to a solution of the sulphenyl bromide (0·5 g.) in water (200 c.c.). The precipitate of the *iodide* (formed almost quantitatively) crystallised from ethanol as almost black needles, m. p. 228°, sparingly soluble in solvents with the following colours : water, yellow; ethanol, orange; chloroform, deep green; benzene, green (Found : C, 48·4; H, 2·8. $C_{16}H_{11}N_2SI$ requires C, 49·0; H, 2·8%).

2-*Phenylazonaphthalene*-1-*sulphenyl Perchlorate*.—Sodium perchlorate (1 g.) in water (10 c.c.) was added to a solution of the sulphenyl bromide (0·3 g.) in water (100 c.c.). The precipitated *perchlorate* (formed almost quantitatively) was crystallised from ethanol as yellow needles, m. p. 216° (decomp.) (Found : C, 52·6; H, 3·0; N, 8·0. $C_{16}H_{11}O_4N_2SCl$ requires C, 52·9; H, 3·0; N, 7·7%).

2-*Phenylazonaphthalene*-1-*sulphenyl Thiocyanate*.—Potassium thiocyanate (1 g.) in water (20 c.c.) was added to a solution of the sulphenyl bromide (0·5 g.) in water (200 c.c.). The precipitated *thiocyanate* (0·35 g., 74%) crystallised from ethanol as orange needles, m. p. 160° (Found : C, 63·6; H, 3·4; N, 13·0. $C_{17}H_{11}N_3S_2$ requires C, 63·5; H, 3·4; N, 13·0%).

2-*Phenylazonaphthalene*-1-*sulphenyl Cyanide* (1-*Thiocyanato*-2-*phenylazonaphthalene*).—The above experiment was repeated, but potassium thiocyanate was replaced by potassium cyanide. The insoluble 1-*thiocyanato*-2-*phenylazonaphthalene* was collected (0·4 g., 95%). Crystallisation from ethanol gave orange needles, m. p. 116° (Found : C, 70·8; H, 3·9; N, 14·1. $C_{17}H_{11}N_3S$ requires C, 70·6; H, 3·8; N, 14·5%). 2-Phenylazonaphthalene-1-sulphenyl chloride hydrate was similarly and quantitatively converted into the cyanide.

2-*Phenylazonaphthalene*-1-*sulphenyl Tribromide*.—A solution of 1-benzylthio-2-phenylazonaphthalene (2 g.) and bromine (1·9 g., 2·1 mols.) in acetic acid (45 c.c.) was refluxed for 3 min. On cooling, pure 2-*phenylazonaphthalene*-1-*sulphenyl tribromide* separated (2·2 g., 76%). Crystallisation from acetic acid containing a drop of bromine gave yellow-brown plates, m. p. 170—171° (Found : C, 38·4; H, 2·3; Br, 47·1. $C_{16}H_{11}N_2SBr_3$ requires C, 38·2; H, 2·2; Br, 47·6%).

2-*Phenylazonaphthalene*-1-*sulphinic Acid*.—An excess of 10% aqueous sodium hydroxide (10 c.c.) was added to a suspension of 2-phenylazonaphthalene-1-sulphenyl tribromide (0·5 g.) in ethanol (50 c.c.). The resultant deep red solution was diluted with water (200 c.c.) and acidified with hydrochloric acid. The precipitated 2-*phenylazonaphthalene*-1-*sulphinic acid* was washed with light petroleum (0·2 g., 66%). Crystallisation from benzene–light petroleum (b. p. 60—80°) gave colourless plates, m. p. 146—148° (Found : C, 65·0; H, 4·1; N, 9·3; active H, 0·32. $C_{16}H_{11}N_2{\cdot}SO_2H$ requires C, 64·9; H, 4·1; N, 9·4; active H, 0·34%). The sulphinic acid, when heated at its m. p. for a few minutes, dissociated quantitatively into 2-phenylazonaphthalene and sulphur dioxide. Crystallisation from ethanol gave orange-yellow needles, m. p. 84° [Bucherer and Rauch (*J. prakt. Chem.*, 1931, **132**, 259) give m. p. 84°] (Found : C, 82·4; H, 5·1; N, 12·4. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·1; N, 12·1%).

Di-(2-*phenylazo*-1-*naphthyl*) *Disulphide*.—A solution of 2-phenylazonaphthalene-1-sulphenyl bromide (1 g.) in water (400 c.c.) and benzene (50 c.c.) was stirred for 3 hr. with zinc dust (7 g.). After filtration, the benzene layer was dried and concentrated to a small volume. The *disulphide* was collected (0·6 g., 80%) and crystallised from benzene as red prisms, m. p. 205° (Found : C, 73·1; H, 4·2; N, 10·5. $C_{32}H_{22}N_4S_2$ requires C, 73·0; H, 4·2; N, 10·6%). Treatment of the tribromide with zinc gave the same disulphide.

1-*Mercapto*-2-*phenylazonaphthalene*.—A solution of sodium sulphide nonahydrate (1 g.) in water (10 c.c.) was added to a suspension of finely ground disulphide (0·5 g.) in ethanol (50 c.c.). After 24 hours' stirring, water (150 c.c.) was added and the filtered red solution acidified with hydrochloric acid. The precipitated crude 1-mercapto-2-phenylazonaphthalene was dried (0·33 g., 70%). It slowly lost its solubility in ethanolic sodium hydroxide. Crystallisation from light petroleum (b. p. 40—60°) or from benzene yielded the pure disulphide, m. p. 205°.

The experiment was repeated, but 10% aqueous sodium hydroxide (10 c.c.) and benzyl chloride (2 c.c.) were added with stirring to the filtered red solution. After 15 min., the precipitate of 1-benzylthio-2-phenylazonaphthalene was collected [0·6 g., 89%; m. p. and

mixed m. p. 122° (from ethanol)]. The same product (0·08 g., 75%) was obtained on stirring a filtered solution of freshly prepared crude 1-mercapto-2-phenylazonaphthalene (0·08 g.) in cold ethanol (50 c.c.) and 10% aqueous sodium hydroxide (5 c.c.) with a drop of benzyl chloride and subsequent addition of water.

Action of Sodium Hydroxide on 2-Phenylazonaphthalene-1-sulphenyl Bromide.—10% Aqueous sodium hydroxide (20 c.c.) was added to 2-phenylazonaphthalene-1-sulphenyl bromide (2 g.) in cold ethanol (50 c.c.). The precipitate of disulphide formed immediately was collected (0·8 g., 78%). Crystallisation from benzene gave red prisms, m. p. 205°, identical with the disulphide obtained by the action of zinc.

The alkaline filtrate was acidified and the pink precipitate, consisting mainly of 2-phenylazonaphthalene-1-sulphinic acid, was filtered off and washed with light petroleum (0·35 g., 41%). Crystallisation from benzene and light petroleum (b. p. 60—80°) gave colourless plates, m. p. 146—148°, identical with the sulphinic acid obtained by the action of sodium hydroxide on the tribromide. The mother-liquors contained a small amount of 2-phenylazo-1-naphthol which crystallised from ethanol as red needles, m. p. and mixed m. p. 138°.

Action of Sodium in Liquid Ammonia on 2-Benzylthioazobenzene.—2-Benzylthioazobenzene (0·5 g.) or its solution in ether was added to a solution of sodium (0·3 g., 6 atomic proportions) in liquid ammonia (50 c.c.) below −50°. (The ammonia was previously treated with a small amount of sodium until a permanent blue colour was attained.) After 8 hours' stirring, addition of ammonium chloride (0·3 g.), and evaporation of ammonia, unchanged starting material was recovered quantitatively.

Action of Sodium in Liquid Ammonia on 1-Benzylthio-2-phenylazonaphthalene.—1-Benzylthio-2-phenylazonaphthalene (0·5 g.) was added to a solution of sodium (0·1 g., 3 atomic proportions) in liquid ammonia (50 c.c.) below −50°. After 5 hours' stirring ammonium chloride (0·2 g.) was added and ammonia evaporated. The residue of almost pure di-(2-phenylazo-1-naphthyl) disulphide was washed with water and filtered off [0·32 g., 86%; m. p. 198—200° (crude), 205° (from benzene)].

The experiment was repeated with 0·2 g. of sodium and without ammonium chloride. The residue was extracted with cold water and the insoluble disulphide collected [0·11 g., 29%; m. p. 195° (crude)]. The aqueous extract, after addition of 5% aqueous sodium hydroxide (5 c.c.) and ethanol (10 c.c.), was quickly shaken with benzyl chloride (2 c.c.), and the precipitate of 1-benzylthio-2-phenylazonaphthalene collected [0·24 g., 48%; m. p. and mixed m. p. 122° (from ethanol)].

The experiment was repeated, but the aqueous extract quickly acidified. The precipitated 1-mercapto-2-phenylazonaphthalene was filtered off and redissolved in ethanolic sodium hydroxide, and the filtered solution was shaken with benzyl chloride. 1-Benzylthio-2-phenylazonaphthalene was collected [0·22 g., 44%; m. p. 122° (from ethanol)].

Action of Sodium in Liquid Ammonia on 2 : 2′-Dibenzylthioazobenzene.—2 : 2′-Dibenzylthioazobenzene (0·5 g.) was added to a solution of sodium (0·11 g., 4 atomic proportions) in liquid ammonia (50 c.c.) below −50°. After 3 hours' stirring, ammonium chloride (0·1 g.) was added and ammonia allowed to evaporate. The residue of the polysulphide (VI) was washed with water and benzene [0·25 g., 87%; m. p. 266—268° (before and after crystallisation from chlorobenzene–nitrobenzene), not depressed by an authentic specimen (see Part VII)].

The experiment was repeated with 0·2 g. of sodium and without ammonium chloride. The residue, consisting of the sodium salt of 2 : 2′-dimercaptoazobenzene, was dissolved in water, and the solution was filtered and shaken with benzyl chloride (2 c.c.). The precipitate of 2 : 2′-dibenzylthioazobenzene was collected [0·37 g., 74%; m. p. and mixed m. p. 222° (from toluene)].

The last experiment was repeated, but the filtered aqueous solution was acidified. The precipitate of crude 2 : 2′-dimercaptoazobenzene was filtered off, dried in a vacuum desiccator for 20 hr. (0·17 g., 54%), and dissolved in aqueous sodium hydroxide (0·5 g. in 100 c.c.). When the filtered solution was shaken with methyl sulphate, 2 : 2′-dimethylthioazobenzene separated [0·12 g., 38%; m. p. 155° (from ethanol), not depressed by an authentic specimen (see Part VII)].

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