782. o-*Mercapto-azo-compounds. Part XII.** *Preparation and Debenzylation of* 1-*Benzylthio*-2-o- *and* -p-*nitrophenylazonaphthalene.*

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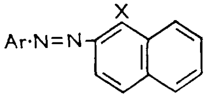
The preparation and debenzylation of 1-benzylthio-2-*o*- and -*p*-nitrophenylazonaphthalene have been investigated. The preparation and properties of the corresponding 1-sulphenyl bromides, tribromides, iodides, thiocyanates, perchlorates, cyanides, the 1-sulphinic acids and 1-thiols, as well as of the disulphides and thiolsulphonates are reported.

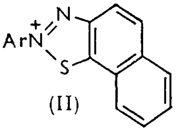
Our earlier investigation [1] of the debenzylation of 1-benzylthio-2-phenylazonaphthalene has been extended to its *o*- and *p*-nitrophenylazo-analogues (I; $X = S{\cdot}CH_2Ph$) which are obtained in good yield by condensing 1-benzylthio-2-naphthylamine with *o*- and *p*-nitronitrosobenzene respectively in acetic acid. It is noteworthy that previous attempts to prepare azo-compounds of the naphthalene series by this method were unsuccessful.[2]

The *p*-nitro-derivative when heated with 1 and 2 mols. of bromine in acetic acid, gives almost quantitatively 2-*p*-nitrophenylazonaphthalene-1-sulphenyl bromide (I; $X = SBr$) and tribromide (I; $X = SBr_3$) respectively. The tribromide is only moderately stable; it dissociates into the sulphenyl bromide and bromine on crystallisation from nitrobenzene, acetic acid, or benzene and more slowly on storage at room temperature.

In contrast, the *o*-nitro-analogue yields only the sulphenyl tribromide (I; $X = SBr_3$), even when only 1 mol. of bromine is used (part of the starting material being then recovered). This is due to the exceptional stability of this tribromide which can be crystallised without decomposition from boiling nitrobenzene or acetic acid and dissociates in a vacuum only above 160° into bromine and 2-*o*-nitrophenylazonaphthalene-1-sulphenyl bromide (I; $X = SBr$). Indeed, this process is the best for preparation of the latter compound. The sulphenyl bromide crystallises as yellow needles with 2 mols. of water which are lost in a vacuum over phosphoric oxide, slowly at room temperature and rapidly at 100°, the crystals becoming orange. The process is reversed on exposure to air. This behaviour is similar to that observed for 4′-nitroazobenzene-2-sulphenyl thiocyanate.[3]



(I)



(II)

$Ar = NO_2{\cdot}C_6H_4$

Both sulphenyl bromides and tribromides behave in other respects like the parent 2-phenylazonaphthalene-1-sulphenyl bromide and tribromide respectively. The sulphenyl bromides are stable to heat, soluble in water, and converted in aqueous solution by double decomposition with the corresponding potassium salts into the stable water-soluble iodides, thiocyanates, and perchlorates, as well as the water-insoluble cyanides. Except for the non-ionic cyanides, these water-soluble substances exist in the solid state and in solutions completely or partly as true salts of structure (II), involving a 2-*p*- or 2-*o*-nitrophenylnaphtho(2′, 1′ : 4, 5-)-1, 2, 3-thiadiazolium cation (see ref. 4).

The preparation and properties of the 2-*p*- and 2-*o*-nitrophenylazonaphthalene-1-sulphinic acids, as well as of the thiolsulphonates (disulphoxides), disulphides, monosulphides, and thiols are described in the Experimental section. Similar structures and properties of the corresponding parent substances have been discussed previously.[1,5]

* Part XI, *J.*, 1956, 653.

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

[2] Zollinger, " Chemie der Azofarbstoffe," Birkhäuser Verlag, 1958, p. 114.

[3] Burawoy, Chaudhuri, and Vellins, *J.*, 1956, 90.

[4] Burawoy, Liversedge, and Vellins, *J.*, 1954, 4481.

[5] Burawoy and Chaudhuri, *J.*, 1956, 653.

EXPERIMENTAL

1-*Benzylthio*-2-o-*nitrophenylazonaphthalene*.—*o*-Nitronitrosobenzene (6·3 g.) in hot acetic acid (50 c.c.) was added to 1-benzylthio-2-naphthylamine (10 g.) in acetic acid (10 c.c.). The mixture was kept at room temperature overnight. The precipitate of almost pure 1-*benzylthio*-2-o-*nitrophenylazonaphthalene* (10·5 g., 70%) was washed with a little acetic acid and light petroleum. Crystallisation from acetic acid gave red needles, m. p. 131—132° (Found: C, 69·1; H, 4·0; N, 10·3. $C_{23}H_{17}O_2N_3S$ requires C, 69·2; H, 4·3; N, 10·5%).

1-*Benzylthio*-2-p-*nitrophenylazonaphthalene*, similarly prepared (9·8 g., 65%), formed reddish-brown needles (from ethanol), m. p. 177—178° (Found: C, 69·2; H, 4·2; S, 8·2. $C_{23}H_{17}O_2N_3S$ requires C, 69·2; H, 4·3; S, 8·0%).

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl Tribromide*.—(i) 1-Benzylthio-2-*o*-nitrophenylazonaphthalene (5 g.), bromine (5 g., 2·5 mol.), and acetic acid (70 c.c.) were refluxed for 5 min. On cooling, almost pure *tribromide* separated (6·6 g., 95%). Crystallisation from nitrobenzene gave orange-yellow plates, m. p. 201—202° (decomp.) (Found: C, 35·3; H, 1·6; N, 7·9; S, 5·6. $C_{16}H_{10}O_2N_3SBr_3$ requires C, 35·1; H, 1·8; N, 7·7; S, 5·8%).

(ii) 1-Benzylthio-2-*o*-nitrophenylazonaphthalene (1 g.), bromine (0·42 g., 1 mol.), and acetic acid (15 c.c.) were refluxed for 30 min. After cooling, light petroleum (100 c.c.) was added and the precipitated oily product washed with more light petroleum till it solidified. The solid was extracted with benzene and the residue crystallised once from nitrobenzene, to give almost pure orange-yellow plates, m. p. 199—200° (decomp.) not depressed on addition of the pure tribromide prepared in the preceding experiment (0·4 g., 55%). Removal of the solvent from the benzene extract and crystallisation of the residue (0·1 g.) from acetic acid gave red needles, m. p. 131—132°, not depressed on addition of the starting material.

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl Bromide*.—2-*o*-Nitrophenylazonaphthalene-1-sulphenyl tribromide (10 g.) was heated in a vacuum at 160—165° until of constant weight (~3 hr.). The residual *sulphenyl bromide* crystallised from water as yellow needles, m. p. 261—262°, containing 2 mols. of water (Found: C, 45·6; H, 3·4; N, 10·2. $C_{16}H_{10}O_2N_3SBr,2H_2O$ requires C, 45·3; H, 3·3; N, 9·9%). On drying at 110° (P_2O_5) in a vacuum, the crystals lost the water and the colour changed to orange (Found: C, 49·1; H, 2·6; N, 10·8; S, 8·2. $C_{16}H_{10}O_2N_3SBr$ requires C, 49·5; H, 2·6; N, 10·8; S, 8·2%). On exposure to the atmosphere, the process was reversed.

2-p-*Nitrophenylazonaphthalene*-1-*sulphenyl Bromide*.—A solution of 1-benzylthio-2-*o*-nitrophenylazonaphthalene (6·5 g.) and bromine (3·12 g., 1·2 mol.) in acetic acid (80 c.c.) was refluxed for 15 min. On cooling, almost pure *sulphenyl bromide* separated in nearly quantitative yield. Crystallisation from water gave red needles, m. p. 257—258° (Found: C, 49·9; H, 2·9; N, 10·5. $C_{16}H_{10}O_2N_3SBr$ requires C, 49·5; H, 2·6; N, 10·8%).

2-p-*Nitrophenylazonaphthalene*-1-*sulphenyl Tribromide*.—The preceding experiment was repeated with 6·5 g. of bromine (2·5 mol.). The precipitate of the yellow-orange tribromide (86%) was filtered off, but dissociated slowly at room temperature and during drying into the monobromide and bromine. Crystallisation from solvents such as acetic acid or benzene gave pure monobromide.

The following derivatives were obtained almost quantitatively by the addition of potassium iodide, thiocyanate, perchlorate, and cyanide respectively to aqueous solutions of the sulphenyl bromides.

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl iodide*, dark brown needles (from water), m. p. 194—195°, soluble in water, ethanol, benzene, and chloroform with yellow, orange, green, and dark green colours respectively (Found: C, 44·2; H, 2·3; N, 9·7. $C_{16}H_{10}O_2N_3SI$ requires C, 44·1; H, 2·3; N, 9·6%). 2-p-*Nitrophenylazonaphthalene*-1-*sulphenyl iodide*, red-brown needles (from water), m. p. 236—237° (colours in solution are similar to those of its *o*-nitro-isomer) (Found: C, 44·4; H, 2·3; N, 9·9%).

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl thiocyanate*, reddish-orange granules (from ethanol), m. p. 176—177° (decomp.) (Found: C, 55·5; H, 2·5; N, 15·1. $C_{17}H_{10}O_2N_4S_2$ requires C, 55·7; H, 2·7; N, 15·3%). para-*Isomer*, dark red plates (from ethanol), m. p. 212—213° (decomp.) (Found: C, 56·0; H, 3·0; N, 15·0%).

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl cyanide* (1-*thiocyanato*-2-o-*nitrophenylazonaphthalene*), yellow needles (from benzene–light petroleum), m. p. 185—186° (Found: C, 61·8; H, 3·0; N, 16·5. $C_{17}H_{10}O_2N_4S$ requires C, 61·2; H, 3·0; N, 16·8%). para-*Isomer*, red needles (from benzene), m. p. 196—197° (Found: C, 61·5; H, 3·1; N, 16·7%).

2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl perchlorate*, yellow plates (from nitrobenzene), m. p. 274—275° (decomp.) (Found: C, 47·7; H, 2·7; N, 10·4. $C_{16}H_{10}O_6N_3SCl$ requires C, 47·1; H, 2·5; N, 10·3%). para-*Isomer*, orange-yellow needles (from water), m. p. 283—284° (decomp.) (Found: C, 47·0; H, 2·7; N, 10·4%).

Di-(2-o-*nitrophenylazo*-1-*naphthyl*) *Disulphide*.—A suspension of 2-*o*-nitrophenylazonaphthalene-1-sulphenyl bromide (0·5 g.) and zinc dust (4 g.) in benzene (50 c.c.) was refluxed for 10 min., then filtered whilst hot and evaporated. The residual *disulphide* (0·35 g., 88%) crystallised from benzene–light petroleum as red needles, m. p. 220—221° (Found: C, 62·7; H, 3·3; S, 10·4. $C_{32}H_{20}O_4N_6S_2$ requires C, 62·3; H, 3·3; S, 10·4%). A similar result was obtained on treatment of the sulphenyl tribromide with zinc dust for a longer period.

Di-(2-p-*nitrophenylazo*-1-*naphthyl*) *Disulphide*.—A suspension of the sulphenyl bromide (1·5 g.) and zinc dust (10·5 g.) in benzene (150 c.c.) was refluxed for 30 min. and worked up as in the preceding experiment (yield 0·8 g., 67%). Crystallisation as before gave dark brown needles, m. p. 234—235° (Found: C, 62·6; H, 3·4%).

2-o-*Nitrophenylazonaphthalene*-1-*sulphinic Acid*.—An excess of 10% aqueous sodium hydroxide (10 c.c.) was added to a suspension of the tribromide (0·5 g.) in ethanol (50 c.c.). The resultant deep red solution was diluted with cold water (200 c.c.) and, after filtration, acidified with dilute hydrochloric acid. The precipitated *sulphinic acid* was washed with a small amount of water and with light petroleum (0·3 g., 90%). Crystallisation from benzene gave yellow prisms, m. p. 168—169° (decomp.) (Found: C, 56·5; H, 3·2; N, 12·7. $C_{16}H_{11}O_4N_3S$ requires C, 56·3; H, 3·2; N, 12·3%).

The acid at its m. p. and in ethanol, methanol, or chloroform solution, slowly at room temperature and rapidly when heated, dissociated into 2-o-*nitrophenylazonaphthalene* and sulphur dioxide. Crystallisation from ethanol gave reddish-brown needles, m. p. 100—101° (Found: C, 69·4; H, 3·9; N, 15·4. $C_{16}H_{11}N_3O_2$ requires C, 69·3; H, 4·0; N, 15·2%).

The para-*isomer* was obtained similarly by action of sodium hydroxide on freshly prepared sulphenyl tribromide without prior drying and crystallisation. Crystallisation from benzene gave white needles, m. p. 193—194° (Found: C, 56·3; H, 3·2%). Its behaviour is analogous to that of the *o*-nitro-isomer. 2-p-*Nitrophenylazonaphthalene* crystallised from light petroleum (b. p. 60—80°) as red needles, m. p. 196—197° (Found: C, 69·2; H, 3·9%).

Di-(2-o-*nitrophenylazo*-1-*naphthyl*) *Sulphide and the Derived Thiolsulphonate*.—2-*o*-Nitrophenylazonaphthalene-1-sulphinic acid (0·5 g.) was dissolved in warm water (350 c.c.) containing sodium hydroxide (0·058 g., 1 mol.). The solution, after cooling, was added to 2-*o*-nitrophenylazonaphthalene-1-sulphenyl bromide (0·5 g.) in water (400 c.c.) with stirring. The dark-orange precipitate of the crude thiolsulphonate was quickly filtered off. It decomposes slowly at room temperature or rapidly when heated into the sulphide and sulphur dioxide (Found for crude disulphoxide: C, 58·1; H, 3·1; N, 13·3. Calc. for $C_{32}H_{20}O_6N_6S_2$: C, 59·2; H, 3·1; N, 13·0%). Crystallisation from benzene gave red-brown prisms of the *monosulphide*, m. p. 275—276° (decomp.) (Found: C, 65·3; H, 3·3; N, 14·3. $C_{32}H_{20}O_4N_6S$ requires C, 65·7; H, 3·4; N, 14·4%).

The analogous *p*-nitro-thiolsulphonate, when crystallised from benzene, yielded deep red plates of the *sulphide*, m. p. 268—269° (Found: C, 65·5; H, 3·5%).

Action of Sodium Hydroxide (*Excess*) *on* 2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl Bromide*.—10% Aqueous sodium hydroxide (20 c.c.) was added to a solution of the sulphenyl bromide (2 g.) in water (300 c.c.). The precipitate of disulphide was collected (0·9 g., 85%). Crystallisation from benzene and light petroleum gave dark red crystals, m. p. 220—221°, not depressed on addition of the disulphide obtained by the action of zinc. The alkaline fitrate was acidified with dilute hydrochloric acid, and the pink precipitate consisting almost exclusively of the sulphinic acid was filtered off and washed with water (0·5 g., 86%). Crystallisation from benzene gave yellow prisms, m. p. and mixed m. p. 168—169°.

Results with the *para*-isomer were similar.

Action of Sodium Hydrogen Carbonate (1 *Mol*.) *on* 2-o-*Nitrophenylazonaphthalene*-1-*sulphenyl Bromide*.—A solution of sodium hydrogen carbonate (0·084 g.) in water (1 c.c.) was added to the sulphenyl bromide (0·4 g.) in water (250 c.c.). After 3 hours' stirring, the precipitate consisting of the disulphide, thiolsulphonate, and/or sulphide, was collected, washed with water, and dried (0·3 g.). The mixture was suspended in ethanol (20 c.c.) and refluxed for 4 min. with a solution of sodium sulphide nonahydrate (0·3 g.) in 5% aqueous sodium hydroxide (4 c.c.). After addition of water, the insoluble monosulphide (0·1 g.) was collected. Crystallisation from benzene gave dark red prisms, m. p. and mixed m. p. 275—276°. The filtrate was acidified with dilute hydrochloric acid. The precipitate of thiol (see below) was collected (~0·1 g.). Crystallisation from benzene gave red needles of disulphide, m. p. and mixed m. p. 220—221°.

In another experiment, the mixture of the disulphide and monosulphide was separated by a more tedious fractional crystallisation from benzene, the monosulphide being much less soluble than the disulphide. Pure specimens were obtained in moderate yields.

1-*Mercapto*-2-o-*nitrophenylazonaphthalene*.—A solution of sodium sulphide nonahydrate (0·4 g.) in 5% aqueous sodium hydroxide (8 c.c.) was added to a suspension of the disulphide (0·6 g.) in ethanol (70 c.c.). The mixture was refluxed for 5 min. After cooling and addition of oxygen-free water (70 c.c.), the dark reddish-brown solution was filtered and acidified with hydrochloric acid. The precipitated crude 1-*mercapto*-2-o-*nitrophenylazonaphthalene* was quickly collected, washed with water, and dried (P_2O_5) (0·4 g., 66%; m. p. 105—115°) (Found: C, 62·2; H, 3·5; N, 14·6. $C_{16}H_{11}O_2N_3S$ requires C, 62·1; H, 3·6; N, 13·6%). On storage its solubility in ethanolic sodium hydroxide decreased and its m. p. rose (*e.g.*, 138—145° after 3 days; 170—180° after 3 weeks). Crystallisation from benzene and light petroleum yielded, in spite of precautions to exclude oxygen, red needles of the disulphide, m. p. and mixed m. p. 220—221°. The experiment was repeated with half the quantities, but 10% aqueous sodium hydroxide (10 c.c.) and benzyl chloride (2 c.c.) were added with stirring to the filtered red solution. The mixture was heated on a water-bath for 1 hr. and set aside for 20 hr. The precipitate of 1-benzylthio-2-*o*-nitrophenylazonaphthalene was collected (0·35 g., 88%). Crystallisation from acetic acid gave red needles, m. p. and mixed m. p. 131—132°.

The same product (0·1 g., 50%) was obtained by heating, on a water-bath, a filtered solution of freshly prepared crude 1-mercapto-2-*o*-nitrophenylazonaphthalene (0·15 g.) in ethanol (25 c.c.) and 10% aqueous sodium hydroxide (10 c.c.) with benzyl chloride (1 c.c.), with subsequent addition of water.

1-*Mercapto*-2-p-*nitrophenylazonaphthalene*.—Reduction of the disulphide (0·4 g.) carried out as for the *o*-nitro-isomer yielded the *thiol* (0·2 g., ~50%; m. p. 90—98° immediately after separation, 110—120° after 24 hr. and 195—210° after 5 days). Crystallisation from benzene and light petroleum gave brown needles of the disulphide, m. p. and mixed m. p. 234—235°. In another experiment, treatment of the filtered solution with benzyl chloride yielded 1-benzylthio-2-*p*-nitrophenylazonaphthalene (80%), red needles (from acetic acid), m. p. and mixed m. p. 177—178°. The same product (0·04 g., 31%) was obtained on benzylation of an alkaline solution of freshly isolated crude thiol (0·1 g.).

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