The same isomer (XVIa) was obtained in 50% yield by reduction with 4 equiv of sodium dithionite in acetonitrile at room temperature for 1 hr. In diglyme, the yield was 64% after 3 hr. Stirring with zinc dust (4 equiv) in benzene under nitrogen for 12 hr gave 51% while in diglyme the yield was 68%.

Reaction of XV with *tert*-butylmagnesium chloride has been reported[3] not only to give XVIa in 12% yield, but also the stereoisomer XVIb, mp 199–200°, in 10% yield, with the same uv and nmr spectra.

Anal. Found: C, 73.12; H, 4.60; S, 21.95.

Oxidation of XVIa (100 mg) in 6 ml of 2:1 70% perchloric acid–acetic acid by heating to boiling gave a dark red-green solution which was quickly cooled to 0° and then 20 ml of ether, precooled to −78°, was added slowly to give 136 mg (72%) of dark green crystals of XV, mp 192–195°.

Oxidation of XVIa[3] (339 mg) in 4 ml of boiling acetic acid by dropwise addition of 1 ml of 50% H_2O_2 gave, on cooling, pale yellow crystals. Recrystallization from acetic acid yielded 317 mg (77%) of the disulfone XVII: mp 261–262°; sulfone bands at 1290 and 1112 cm^{-1}; uv λ_{max} (log ϵ) 284 (4.06) nm.

Anal. Calcd for $C_{18}H_{14}S_2O_4$: C, 60.32; H, 3.94; S, 17.86. Found: C, 60.57; H, 4.13; S, 17.90.

Disproportionations.—All disproportionation reactions were carried out under vacuum at 40–50° in diglyme first dried over calcium hydride and then distilled from a 5:1 potassium–sodium alloy into an evacuated flask containing the reactants and a Teflon-coated magnetic stirring bar. Some reactions involving thioxanthene were carried out in the dark to avoid its possible photodimerization.[24]

A solution of 1.00 g of I and 655 mg of III (protected from light) turned red-violet after 5 days. Filtration yielded 355 mg (27%) of II, mp 330–332°, after recrystallization from xylene.[2] Evaporation of the diglyme, benzene extraction of the black residue, benzene elution from a neutral alumina column, and recrystallization from $CHCl_3$–ethanol recovered 534 mg of III, mp 126–128°. Duplicate reactions not protected from light turned black within 3 days and yielded 181 mg (126 mg) of II and 674 mg (818 mg) of III. An aliquot of this reaction mixture (0.500 g, 1.68 mequiv of I, 0.333 g, 1 mequiv of III) was added to distilled water and titrated with 0.01 *N* NaOH, indicating the formation of 1.33 mequiv (79%) of free perchloric acid.

A similar reaction of 500 mg of I and 333 mg of III carried out in the presence of 1 equiv of pyridine (to neutralize perchloric acid formed) gave a pale pink reaction mixture in 4 hr. The white precipitate (670 mg) was collected. The acetone-soluble fraction gave, after addition of benzene, 233 mg (75%) of pyridinium perchlorate: mp 299–300°; uv (MeOH) λ_{max}, nm (log ϵ), 250 (4.69), 255 (4.73), 262 (4.56).

Anal. Calcd for $C_5H_6ClNO_4$: C, 33.42; H, 3.37; N, 7.79. Found: C, 33.66; H, 3.40; N, 7.66.

The acetone-insoluble solid gave 204 mg (30%) of II on recrystallization from xylene.

A solution of 378 mg of I and 600 mg of XI was red-violet after 5 days. Filtration gave 110 mg (45%) of II. Evaporation of the diglyme solvent, extraction with chloroform, charcoal treatment, filtration, evaporation, and recrystallization recovered 230 mg of XI.

A solution of 500 mg of VI and 531 mg of III gave a red-violet solution in 4 days, either in the light or dark. Filtration gave 184–190 mg (69–71%) of II. Vacuum evaporation of solvent, benzene extraction, benzene elution from neutral alumina, evaporation, and recrystallization from methanol gave 307–328 mg (86–93%) of XI, mp 99°. A similar reaction mixture containing 1 equiv of pyridine to neutralize perchloric acid formed gave no reaction; both starting materials were recovered unchanged.

Reaction of 500 mg of I, 330 mg of III, and 71 mg of $MgCO_3$ in diglyme gave a red reaction mixture which faded to a clear pale yellow overnight. After vacuum distillation of the solvent, the residue was placed on a neutral alumina column and eluted with CCl_4 to give 436 mg of III after recrystallization from ethanol, mp 126–128°. Methanol elution gave 250 mg (71%) of thioxanthone after recrystallization from ethanol as pale yellow needles, mp 216–217°.

Reaction of 250 mg of VI, 134 mg of III, and 28.5 mg of $MgCO_3$ turned from red to colorless overnight. Similar work-up gave 293 mg of what appeared to be a mixture of III and XI (by its infrared spectrum) and 59 mg (22%) of thioxanthone, mp 216–218°.

Registry No.—I, 26401-81-0; II, 10496-86-3; VI disulfone, 26430-92-2; VII, 3166-15-2; VIII, 26430-88-6; IX, 26430-89-7; X disulfone, 26430-90-0; XV, 7432-88-4; XVIa, 25548-01-0; XVIb, 26372-65-6; XVII, 26438-45-9; pyridinium perchlorate, 15598-34-2.

(24) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

Chemistry of the Sulfur–Nitrogen Bond. I. Thermal Reactions of Nitrobenzenesulfenanilides[1,2]

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2-Nitrobenzenesulfenanilides undergo an unusual thermal rearrangement to give *o*- and *p*-amino-2-nitrodiphenyl sulfides, phenothiazines, and 2-aminobenzenesulfonanilides. 3-Nitrobenzenesulfenanilide when heated gave only *o*- and *p*-amino-3-nitrodiphenyl sulfides.

Compounds which contain the sulfur–nitrogen bond are of considerable importance both from a practical as well as theoretical standpoint. Compounds which contain this bond have been reported to be useful as antiradiation drugs, antioxidants, and accelerators in the vulcanization of rubber. Factors which may contribute to the sulfur–nitrogen bond's activity, such as steric interactions, coulombic repulsion between nitrogen and sulfur lone-pair electrons, and p–d π bonding, have only recently been investigated in connection with studies of rotation about the S–N bond.[4]

Moore and Johnson investigated the thermal reactions of arylsulfenanilides.[5] They reported that when 2-nitrobenzenesulfenanilide (**1a**) was heated at 160° in aniline for 6 hr a 70% yield of 4′-amino-2-nitrodiphenylsulfide (**2a**) was obtained.[5a] Similar results were obtained with 2-nitrobenzenesulfen-*p*-toluide (**1b**) which gave 2′-amino-5′-methyl-2-nitrobenzene sulfide (**2b**) on heating in *p*-toluidine.[5a] When **1a** was heated in *p*-to-

(1) Reported in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

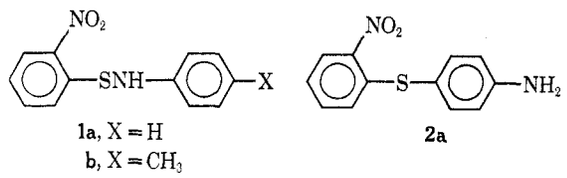
(2) For a preliminary communication, see F. A. Davis, R. B. Wetzel, T. J. Devon, and J. F. Stackhouse, *Chem. Commun.*, 678 (1970).

(3) National Science Foundation Ungergraduate Research Participant, 1968.

(4) (a) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968); (b) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969); (c) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *ibid.*, **91**, 6677 (1969).

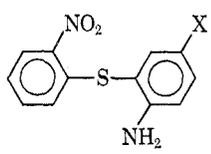
(5) (a) M. L. Moore and T. B. Johnson, *ibid.*, **57**, 1517 (1935); (b) *ibid.*, **57**, 2234 (1935); (c) *ibid.*, **58**, 1091 (1936); (d) *ibid.*, **58**, 1960 (1936).

luidine, **2b** was obtained, and **1b** in aniline gave **2a**.[5a] Products were isolated by treating the reaction mixture with dilute hydrochloric acid, dissolving the resulting precipitate in ethanol, and neutralizing to give the aminonitrodiphenyl sulfide.[5a]



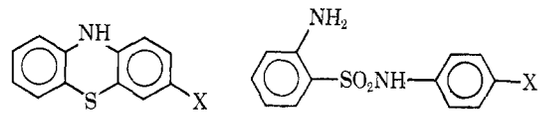
1a, X = H
b, X = CH_3

2a



2b, X = CH_3
c, X = H

In a reinvestigation of this thermal rearrangement, we observed quite different results. Heating **1a** in a sealed tube with an excess of aniline for 15 hr at 195° gave, in addition to a 12% yield of **2a**,[6] phenothiazine (**3a**),[7] 3%, 2′-amino-2-nitrodiphenyl sulfide (**2c**),[8] 5%, and 2-aminobenzenesulfonanilide (**4a**),[9] 37%. Sulfenamide **1b** in *p*-toluidine gave **2b**, 18%, 3-methylphenothiazine (**3b**),[10] 14%, and 2-aminobenzenesulfon-*p*-toluidine (**4b**),[11] 55%. Sulfenamide **1a** in *p*-toluidine gave **2b**, **3b**, and **4b**. Sulfenamide **1b** in aniline gave **1a**, **2a**, **2c**, **3a**, and **4a**. No products from the original sulfenamides were isolated. Products were separated by column chromatography and identified by comparison with authentic samples. At lower temperatures the reaction failed to precede to any significant degree. These results are summarized in Table I.



3a, X = H
b, X = CH_3

4a, X = H
b, X = CH_3

TABLE I
THERMAL REACTIONS OF SULFENAMIDES

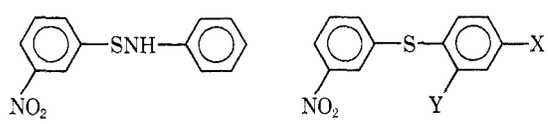
Sulfenamide	Solvent	Temp, C°	Time, hr	Products (% yield)
1a	Aniline	195	15.6	**1a** (34), **2a** (12), **2c** (5), **3a** (3), **4a** (37)
	p-Toluidine	195	15.2	**2b** (20), **3b** (12), **4b** (53)
	p-Toluidine	110	12	**1b** (90)
1b	*p*-Toluidine	195	15.2	**2b** (18), **3b** (14), **4b** (55)
	Aniline	195	15.6	**1a** (36), **2a** (14), **2c** (7), **3a** (3), **4a** (35)
	Aniline	110	12	**1a** (88), **1b** (10)
1b[a]	*p*-Toluidine	195	16	**2b** (21), **3b** (8), **4b** (60)
5	Aniline	195	15	**6a** (22), **6b** (60)

[a] Degassed.

(6) H. H. Hodgson and W. Rosenberg, *J. Chem. Soc.*, 181 (1930).
(7) A. Bernthsen, *Ber.*, **16**, 2896 (1883).
(8) A. Levi, L. A. Warren, and S. Smiles, *J. Chem. Soc.*, 1492 (1933).
(9) F. Ullmann and C. Gross, *Ber.*, **43**, 2694 (1910).
(10) H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, **66**, 888 (1944).
(11) J. H. Freeman and E. C. Wagner, *J. Org. Chem.*, **16**, 815 (1951).

Moore and Johnson reported the melting point of sulfide **2b** as 108°,[5a] whereas the compound isolated by us had mp 87°. The structure of sulfide **2b** is supported by elemental analysis, its infrared spectrum, nmr spectrum, and independent synthesis. The infrared spectrum of **2b** showed doublet absorption centered at 3400 cm^{-1} (primary amine) and strong absorption at 812, 802, and 740 cm^{-1} characteristic of 1,2- and 1,2,5-substituted benzene.[12] The proton nmr spectrum showed absorption at δ 2.25 (singlet), 4.2 (broad singlet), and 7.0 and 8.25 (relative areas 3:2:6:1) in agreement with proposed structure. Sulfide **2b** was prepared independently by condensation of the sodium salt of 2-amino-5-methylbenzenethiol, prepared by zinc reduction of 2-nitro-5-methylphenyl disulfide, with 2-chloronitrobenzene to give a greater than 70% yield of **2b**.

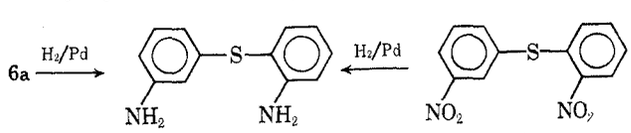
3-Nitrobenzenesulfenanilide (**5**), prepared from 3-nitrobenzenesulfenyl chloride[13] and aniline, when heated in aniline gave only rearrangement products 2′-amino-3-nitrodiphenyl sulfide (**6a**) and 4′-amino-3-nitrodiphenyl sulfide (**6b**). The structure of sulfenamide **5** was supported by elemental analysis, its infrared spectrum, and nmr spectrum. The infrared spectrum of **5** showed absorption at 3350 cm^{-1} (secondary amine) and a medium band at 908 cm^{-1}. This absorption was present in all of the sulfenamides investigated and is presumably the S–N stretching vibration. This absorption was not present in the sulfides. The proton nmr spectrum of **5** showed absorption at δ 5.25, 7.1, and 7.95 (relative areas 1:7:2) in agreement with the proposed structure.



5

6a, X = H; Y = NH_2
b, X = NH_2; Y = H

The structure of **6a** is supported by elemental analysis, infrared spectrum, and reduction to 2,3′-diaminodiphenyl sulfide (**7**). Diamine **7** was prepared independently by reduction of 2,3′-dinitrodiphenyl sulfide (**8**).



7 **8**

The infrared spectrum of **6a** showed doublet absorption centered at 3420 cm^{-1} (primary amine) and strong absorption at 875, 755, 750, and 730 cm^{-1}, characteristic of 1,3- and 1,2-disubstituted benzenes.[12]

Structural proof of **6b** was based upon elemental analysis, infrared and proton nmr spectra, and conversion with iodomethane to 4-*N*,*N*-dimethylamino-3′-nitrodiphenyl sulfide.[13] The infrared spectrum of **6b** showed doublet absorption centered at 3410 cm^{-1} (primary amine) and at 875, 825, 800, and 735 cm^{-1}, characteristic of 1,3- and 1,4-disubstituted benzenes.[12] The nmr spectrum of **6b** showed absorption at δ 3.8, 6.6, 7.3, and 7.8 (relative areas 2:2:4:2).

Phenothiazines **3a** and **3b** apparently formed from rearrangement products **2c** and **2b**, respectively. Under

(12) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, 1966, Chapter 5.
(13) H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955).

the reaction conditions sulfide **2c** in aniline gave a 25–30% yield of **3a**, and **2b** in *p*-toluidine gave a 42% yield of **3b**. Products were separated by column chromatography and identified by comparison with authentic samples. These results are summarized in Table II.

TABLE II
REARRANGEMENT OF 2,2′-AMINONITRODIPHENYL SULFIDES AT 195° FOR 15 HR

Diphenyl sulfide	Solvent	Products (% yield)
2c	Aniline	**3a** (29), **2c** (61)
2b	*p*-Toluidine	**3b** (42), **2b** (45)

Substitutions on the S–N bond in sulfenamides by the solvent take place under relatively mild conditions. At 110°, **1a** in *p*-toluidine gave a greater than 90% yield of **1b**, and **1b** in aniline gave an 88% yield of **1a**. Furthermore, at 195° when **1b** was heated in aniline, a 36% yield of **1a** was isolated (see Table I).

Discussion

Apparently three reactions take place when 2-nitrobenzenesulfenanilides are heated in primary aromatic amine solvents. They rearrange to give *o*- and *p*-amino-2-nitrodiphenyl sulfides, with the para isomer predominating. They undergo an unusual oxidation–reduction in which the nitro group is reduced and the sulfur oxidized, and they undergo facile exchange with the solvent.

Recently we have established that **2c** rearranges to phenothiazine (**3a**) *via* a thermal Smiles rearrangement,[14] and this mechanism undoubtedly applies to the arrangement of **2b** to **3b**.

The rearrangement of nitrobenzenesulfenanilides to *o*- and *p*-aminonitrodiphenyl sulfides may be inter- or intramolecular. The photolysis of 2,4-dinitrobenzenesulfenyl acetate in benzene to give 2,4-dinitrodiphenyl sulfide[15] and the thermal rearrangement of aryl 2-nitrobenzenesulfenates to give the corresponding hydroxy diphenyl sulfides[16] have both been shown to be intermolecular.

On the basis of present information, no definitive answer as to the inter- or intramolecularity of the rearrangement of sulfenamides can be made because exchange may occur prior to rearrangement.

The ability of an *o*-nitro group to transfer its oxygens to an adjacent group is well known and has been reviewed.[17] The pyrolysis of *tert*-butyl 2-nitrobenzenesulfenate gave, among other products, aniline.[18] The photolysis of 2,4-dinitrobenzenesulfen-*N*-methylaniline gave 2-amino-4-nitrobenzenesulfonyl-*N*-methylaniline, but **1a** under the same conditions gave azobenzene.[15] Brown has recently demonstrated the intramolecular transfer of oxygens in the base-catalyzed rearrangement of **1a** to 2-azobenzenesulfenate.[19]

Formation of 2-aminobenzenesulfonamides **4a** and **4b** probably proceeds in several steps, but attempts to isolate intermediates have thus far failed. However, the lack of sulfonamide formation for sulfenamide **5** and the fact that the absence of molecular oxygen has no effect on the formation of **4b** strongly suggest that the oxygens are transferred by an intramolecular process from the nitro group to the sulfur.

(14) F. A. Davis and R. B. Wetzel, *Tetrahedron Lett.*, 4483 (1969).
(15) D. H. R. Barton, T. Nakano, and P. G. Sammes, *J. Chem. Soc. C*, 322 (1968).
(16) D. R. Hogg, J. H. Smith, and P. W. Vipond, *ibid.*, 2713 (1968).
(17) J. D. Loudon and G. Tennant, *Quart. Rev.*, **18**, 389 (1964).
(18) D. R. Hogg and P. W. Vipond, *J. Chem. Soc. C*, 60 (1970).
(19) C. Brown, *J. Amer. Chem. Soc.*, **91**, 5832 (1969).

Experimental Section

Sulfenamide **1a**[5a] and **1b**[5a] were prepared according to procedures given in the literature. Solvents were purified by standard methods. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Proton nmr spectra were measured on a Varian A-60A instrument, and infrared spectra were measured on a Perkin-Elmer 457 spectrometer.

General Procedure for Thermal Rearrangement of Sulfenamides.—Sulfenamides were heated in an oil bath with an excess of amine in a sealed tube for 12–16 hr. Excess solvent was removed under vacuum (oil pump) and the dark residue chromatographed on Florisil. Samples isolated from the column were washed with pentane or methanol and dried under high vacuum for at least 12 hr.

2-Nitrobenzenesulfenanilide (**1a**).—Sulfenamide **1a** (0.1553 g, 0.00063 mol) in aniline gave, on elution with pentane–benzene (1:1), 0.0038 g (3%) of a white solid, mp 183° (lit.[7] mp 180°), identified as **phenothiazine** (**3a**) by comparison of its properties with an authentic sample. Elution with pentane–benzene (2:3) gave 0.0529 g (34%) of a red solid, mp 94° (lit.[20] mp 94.5°), identified as sulfenamide **1a** by comparison of its properties with an authentic sample. The proton nmr spectrum of **1a** ($CDCl_3$) showed absorption at δ 5.1 (s, 1 H), 7.2 (m, 8 H), and 8.2 (d, 1 H). Elution with benzene–chloroform (4:1) gave 0.0078 g (5%) of a yellow solid, mp 86° (lit.[8] mp 85°), identified as **2′-amino-2-nitrodiphenyl sulfide** (**2c**) by comparison of its properties with an authentic sample. Diphenyl sulfide **2c** had the following properties: infrared (KBr) 3450 (s), 3330 (s), 3060 (w), 1610 (s), 1590 (s), 1560 (m), 1500 (s), 1480 (s), 1450 (m), 1330 (s), 1300 (s), 1250 (w–m), 1150 (w), 1100 (m), 1055 (m), 1050 (m), 1040 (m), 1020 (m–w), 850 (m), 780 (m), 765 (s), 730 (s), 710 (m), 680 (w), and 500 cm^{-1} (m); nmr ($CDCl_3$) δ 4.2 (s, 2 H), 6.8 (complex d, 3 H), 7.3 (m, 4 H), and 8.2 (d, 1 H). Further elution with benzene–chloroform (1:1) gave 0.0188 g (12%) of a brown-yellow solid, mp 102° (lit.[6] mp 102–103°), identified as **4′-amino-2-nitrodiphenyl sulfide** (**2a**) by comparison of its properties with an authentic sample. Diphenyl sulfide **2a** had the following properties: infrared spectrum (KBr) 3400 (m–w), 3320 (m), 3210 (w), 1645 (w), 1595 (s), 1560 (m), 1510 (s), 1450 (w–m), 1340 (s), 1305 (s), 1290 (m), 1250 (m–w), 1180 (m), 1100 (m), 1040 (w), 840 (m–w), 786 (w–m), and 730 cm^{-1} (s); nmr ($CDCl_3$) δ 4.05 (s, 2 H), 6.8 (m, 3 H), 7.25 (m, 4 H), and 8.2 (d, 1 H). Elution with chloroform gave a brown oil which was alternately washed with 5% sodium hydroxide solution and water (three 50-ml portions). The aqueous washings were carefully neutralized with 5% hydrochloric acid solution and on cooling overnight gave 0.0542 g (37%) of white crystals, mp 119–120° (lit.[9] mp 119°), identified as **2-aminobenzenesulfonanilide** (**4a**) by comparison of its properties with an authentic sample. Sulfonamide **4a** had the following properties: infrared (KBr) 3470 (s), 3380 (s), 3310 (s), 1630 (s), 1610 (s), 1490 (s), 1460 (m), 1420 (m), 1330 (m), 1290 (m), 1290 (s), 1230 (m), 1155 (s), 1100 (m), 1070 (m–w), 1040 (m–w), 930 (s), 820 (w), 760 (s), 730 (m) 700 (s), 630 (w), and 600 cm^{-1} (s); nmr ($CDCl_3$) δ 4.7 (s, 2 H), 6.7 (t, 2 H), (s, 7 H), and 7.5 (m, 1 H).

2-Nitrobenzenesulfen-*p*-toluidine (**1b**).[5a]—Sulfenamide **1b** had the following properties: infrared (KBr) 3450 (m), 1600 (m), 1510 (s), 1340 (s), 1300 (m–s), 1290 (m), 1240 (m), 1100 (w), 1030 (w), 910 (m), 960 (w), 815 (s), 790 (m), and 735 cm^{-1} (s); nmr ($CDCl_3$) δ 2.25 (s, 3 H), 6.8 (m, 3 H), 7.2 (m, 3 H), and 8.2 (m, 1 H). Sulfenamide **1b** (0.1448 g, 0.00056 mol) in *p*-toluidine gave, on elution with pentane–benzene (4:1), 0.0172 g (14%) of white crystals, mp 167–168 (lit.[10] mp 168°), identified as **3-methylphenothiazine** (**3b**) by comparison of its properties with an authentic sample. Compound **3a** had the following properties: infrared (KBr) 3340 (m), 1600 (w), 1470 (s), 1430 (m), 1310 (m), 1300 (m–w), 1260 (m), 920 (w), 810 (s), 740 (s), and 640 cm^{-1} (w); nmr (acetone-d_6) δ 2.18 (s, 3 H), 6.8 (t, 7 H), and 7.6 (s, 1 H). Elution with benzene–chloroform (4:1) gave

(20) M. P. Cava and C. E. Blake, *ibid.*, **78**, 5444 (1956).

0.026 g (18%) of red crystals, mp 87°, identified as **2'-amino-5'-methyl-2-nitrodiphenyl sulfide** (**2b**) by comparison of its properties with an authentic sample (see below). Elution with chloroform gave a brown oil which was alternately washed with 5% sodium hydroxide solution and water (three 50-ml portions). The aqueous washings were carefully neutralized with 5% hydrochloric acid solution and on cooling overnight gave 0.0795 g (55%) of white crystals, mp 124–126° (lit.[11] mp 124°), identified as **2-aminobenzenesulfon-*p*-toluidide** (**4b**) by comparison of its properties with an authentic sample. Sulfonamide **4b** had the following properties: infrared (KBr) 3460 (m), 3380 (m), 3250 (m), 1625 (m–s), 1600 (m), 1560 (w), 1510 (m–s), 1480 (s), 1450 (m), 1390 (m–w), 1320 (m), 1300 (m), 1225 (m), 1135 (s), 915 (m), 850 (m), 810 (m), 760 (s), 730 (m), 700 (m), and 600 cm^{-1} (s); nmr ($CDCl_3$) δ 2.25 (s, 3 H), 4.82 (s, 2 H), 6.7 (t, 2 H), 6.95 (s, 5 H, and 7.3 (m, 2 H).

2'-Amino-5'-methyl-2-nitrodiphenyl Sulfide (**2b**).—3-Chloro-4-nitrotoluene (20.5 g, 0.12 mol) in 100 ml of alcohol was added dropwise to a solution of sodium disulfide (prepared from 23 g of sodium sulfide 9-hydrate and 3.75 g of sulfur) in 150 ml of alcohol in a 500-ml three-necked flask equipped with reflux condenser, dropping funnel and mechanical stirrer. After addition, the reaction mixture was refluxed for 6 hr and cooled, and the precipitated salt and disulfide were removed by filtration. The solid was washed with alcohol (two 50-ml portions) and with water (two 50-ml portions). After air drying, 9.0 g (45%) of the crude disulfide was obtained and used without further purification. The crude disulfide, 4.0 g, was dissolved in 350 ml of glacial acetic acid in a 500-ml three-necked flask equipped with magnetic stirring bar, reflux condenser, and thermometer. The reaction mixture was warmed to 100°, 20.0 g of zinc dust added over 0.5 hr, and the reaction mixture refluxed for 1 hr. The solution was filtered while hot and the residue washed with hot acetic acid (two 50-ml portions) and hot water (100 ml). Hot water (800 ml) was added to the filtrate and on cooling gave 1.3 g of the zinc salt of 2-amino-5-methylbenzenethiol. The zinc salt (1.3 g, 0.00382 mol) was placed in 100 ml of absolute ethanol in a 250-ml three-necked flask equipped with mechanical stirrer and reflux condenser. Metallic sodium (0.175 g, 0.0076 g-atom) was slowly added to the reaction mixture, the solution was refluxed for 0.5 hr at which time 1-chloro-2-nitrobenzene (1.16 g, 0.0076 mol) was added, and the reaction mixture was refluxed for 10 hr. The solution was cooled and filtered, and the solvent was removed to give a dark oil which was redissolved in ether, washed with 5% sodium hydroxide solution (two 50-ml portions), treated with charcoal (Norit A), and dried over anhydrous magnesium sulfate. Removal of solvent under vacuum gave a yellow oil which solidified under high vacuum. Crystallization from ether–pentane gave 1.4 g (71%) of bright red-orange plates, mp 87°.

Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65. Found: C, 60.29; H, 4.52.

Diphenyl sulfide **2b** had the following properties: infrared (KBr) 3440 (s), 3360 (s), 3100 (w), 3030 (w), 3010 (w), 1630 (m), 1610 (m), 1525 (s), 1495 (s), 1460 (m), 1435 (m), 1415 (w), 1350 (s), 1310 (m–w), 1270 (s), 1210 (s), 1180 (w), 1125 (w), 1035 (s), 875 (m), 800 (m–w), 745 (s), 730 (s,) and 665 cm^{-1} (m); nmr ($CDCl_3$) δ 2.25 (s, 3 H), 4.2 (broad s, 2 H), 6.8 (t, 2 H), 7.3 (m, 6 H), and 8.2 (m, 1 H).

2-Nitrobenzenesulfen-*p*-toluidine (**1b**).—**1b** (0.1603 g, 0.000627 mol) in aniline gave, on elution with pentane–benzene (1:1), 0.0040 g (3%) of **3a**; elution with pentane–benzene (2:3) gave 0.0555 g (36%) of **1a**; elution with benzene–chloroform (4:1) gave 0.0108 g (7%) of **2c**; elution with benzene–chloroform (4:1) gave 0.0219 g (14%) of **2a**; elution with chloroform gave an oil which when treated with 5% sodium hydroxide followed by neutralization and cooling gave 0.0578 g (38%) of **4a**.

3-Nitrobenzenesulfenanilide (**5**).—3-Nitrobenzenesulfenyl chloride,[12] prepared from 3-nitrophenyl disulfide (Aldrich Chemical Co.) (52.6 g, 0.171 mol) and dry chlorine gas in 100 ml of dry chloroform, was added dropwise over 0.5 hr to aniline (62.2 g, 0.680 mol) in 100 ml of dry ether cooled to −78° in a Dry Ice–acetone bath in a 1000-ml three-necked flask equipped with dropping funnel, mechanical stirrer, and nitrogen inlet tube. After addition, the yellow reaction mixture was stirred for an additional 0.5 hr at −78° at which time 700 ml of dry pentane, cooled to −78°, was added followed by 50 ml of water, and the reaction mixture was allowed to warm to room temperature. The yellow sulfenamide which had precipitated out was collected by filtration, dissolved in ether, washed with water (three 50-ml portions) and 5% sodium hydroxide solution (two 50-ml portions), and dried over anhydrous magnesium sulfate. Removal of solvent under vacuum gave a yellow solid which was crystallized from pentane–ether at −50° to give 34 g (40%) of yellow needles, mp 93–94°.

Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.4; S, 13.0. Found: C, 58.79; H, 3.97; N, 11.57; S, 13.17.

Sulfenamide **5** had the following properties: infrared (KBr) 3400 (m), 1600 (s), 1510 (s), 1490 (s), 1400 (m), 1320 (s), 1300 (m), 1290 (m), 1220 (m), 1110 (m), 1060 (w), 1010 (w), 995 (w), 910 (m–s), 870 (s), 830 (w–m), 800 (m), 745 (s), 720 (s), and 690 cm^{-1} (s); nmr ($CDCl_3$) δ 5.25 (broad s, 1 H), 7.1 (m, 7 H), and 7.95 (m, 2 H). Sulfenamide **5** (0.1650 g, 0.00067 mol) in aniline gave, on elution with pentane–ether, an oil which on sublimation at 40° (0.5 mm) gave 0.0363 g (22%) of yellow needles, mp 63–64°, identified as **2'-amino-3-nitrodiphenyl sulfide** (**6a**) by reduction to **7**.

Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09. Found: C, 58.51; H, 4.39.

Diphenyl sulfide **6a** had the following properties: infrared (KBr) 3465 (m), 3370 (m), 1615 (s), 1525 (s), 1480 (m), 1460 (w), 1445 (w), 1350 (s), 1310 (w), 1275 (w), 1250 (w), 1155 (w), 1120 (w), 1070 (w), 1020 (w), 885 (w–m), 875 (m), 850 (w), 800 (m), 755 (s), 750 (s), 730 (s), and 668 cm^{-1} (m); nmr ($CDCl_3$) δ 4.2 (s, 2 H), 6.8 (t, J = 8 Hz, 2 H), 7.4 (m, 4 H), and 8.0 (s, 2 H). Further elution with pentane–ether gave 0.099 g (60%) of yellow plates, mp 130–131°, identified as **4-amino-3-nitrodiphenyl sulfide** (**6b**) by conversion with iodomethane to 4-*N*,*N*-dimethylamino-3'-nitrodiphenyl sulfide.[13]

Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.06; N, 11.4; S, 13.0. Found: C, 58.46; H, 4.11; H, 11.29; S, 12.80.

Diphenyl sulfide **6b** had the following properties: infrared (KBr) 3450 (m), 3370 (m), 1625 (m), 1595 (m), 1510 (m–s), 1490 (m–s), 1450 (w), 1420 (w), 1345 (s), 1300 (m), 1270 (m), 1190 (m), 1110 (w–m), 1100 (w), 875 (m), 825 (m), 810 (w), 800 (m), 745 (m), 735 cm^{-1} (s), nmr ($CDCl_3$) δ 3.8 (broad s, 2 H), 6.6 (d, J = 8 Hz, 2 H), 7.3 (m, 4 H), and 7.8 (m, 2 H).

Reduction of 6a with Hydrogen.—Compound **6a** (0.1199 g, 0.00049 mol) in 50 ml of absolute ethanol at 40 psi over 100 mg of 10% palladium on charcoal for 6 hr gave a oil which was sublimed at 110° (0.1 mm). The resulting clear oil, 0.074 g (70%), was identified as **2,3'-diaminodiphenyl sulfide** (**7**) by comparison of its properties with an authentic sample (see following discussion).

Treatment of 6b with Iodomethane.—In a 100-ml one-necked flask equipped with an efficient reflux condenser was placed sulfide **6b** (0.2612 g, 0.00106 mol) in 50 ml of absolute methanol and 1.0 g of iodomethane. The reaction mixture was refluxed for 48 hr, solvent removed under vacuum, and the resulting oil dissolved in benzene. The benzene solution was washed with 5% potassium hydroxide (two 50-ml portions) and dried over anhydrous magnesium sulfate. The solvent was removed after drying. The oil dissolved in 50 ml of methanol and 1.0 g of iodomethane, and the reaction mixture refluxed for 24 hr. The solvent was removed, and the dark oil was dissolved in xylene and heated at 138° for 4 hr in an oil bath. Removal of solvent under vacuum gave a greenish oil which when chromatographed on Florisil (elution with benzene) gave 0.101 g (34%) of yellow plates, mp 116–118° (lit.[13] mp 115–116°), identified as 4-*N*,*N*-dimethylamino-3'-nitrodiphenyl sulfide[13] by comparison of its properties with an authentic sample. 4-*N*,*N*-Dimethylamino-3'-nitrodiphenyl sulfide had the following properties: infrared (KBr) 3100 (w), 2900 (w), 1595 (s), 1502 (s), 1445 (m), 1365 (m–s), 1350 (s), 1310 (w), 1275 (w–m), 1230 (m), 1200 (s), 1125 (m), 1100 (w), 1070 (m), 1000 (w), 880 (s), 815 (s), 765 (w), 750 (m–s), 735 (s), and 670 cm^{-1} (m); nmr ($CDCl_3$) δ 3.05 (s, 6 H), 6.7 (d, J = 9 Hz, 2 H), 7.3 (m, 4 H), and 7.82 (m, 2 H).

2,3'-Dinitrodiphenyl Sulfide (**8**).—In a 250-ml three-necked flask equipped with mechanical stirrer and reflux condenser was placed 3-nitrodiphenyl disulfide (2.0 g, 0.0065 mol) and sodium (0.312 g, 0.013 g-atom) in 100 ml of absolute ethanol. The reaction mixture was refluxed for 0.5 hr, and 2-chloronitrobenzene (2.054 g, 0.012 mol) was added slowly with stirring. The reaction mixture was heated at reflux for an additional 12 hr and filtered while hot. The solvent was removed under vacuum to give a dark oil which was taken up in ether, filtered, washed with 5% potassium hydroxide (two 50-ml portions) and water (two 50-ml portions), treated with charcoal (Norit A), and dried over anhydrous magnesium sulfate. Removal of the ether solvent gave an orange solid which was crystallized from ethanol to give 2.8 g (85%) of yellow-orange needles, mp 137–138°.

Anal. Calcd for $C_{12}H_8N_2O_4S$: C, 52.17; H, 2.95. Found: C, 52.26; H, 2.95.

Diphenyl sulfide **8** had the following properties: infrared (KBr) 3010 (w), 1590 (m), 1520 (s), 1450 (w), 1325 (s), 1340 (m), 1310 (w), 1260 (w), 1100 (w), 1055 (w), 1040 (w), 915 (w), 880 (w), 810 (w), 790 (m), 750 (w), 735 (s), and 680 cm^{-1} (w); nmr ($CDCl_3$) δ 6.9 (m, 1 H), 7.3 (m, 2 H), 7.8 (m, 2 H), and 8.4 (m, 3 H).

2,3'-Diaminodiphenyl Sulfide (7).—Hydrogenation of sulfide **8**, prepared above (0.20 g, 0.000725 mol) in 100 ml of absolute ethanol at 40 psi over 200 mg of 10% palladium on charcoal for 6 hr, yielded an oil which was distilled at 110° (0.1 mm). The resulting clear oil, 0.102 g (65%), failed to crystallize. An analytical sample of **7** was obtained by preparative glc.

Anal. Calcd for $C_{12}H_{12}N_2S$: C, 66.63; H, 5.59. Found: C, 66.76; H, 5.70.

Aminodiphenyl sulfide **7** had the following infrared and nmr properties: infrared (thin film) 3410 (m), 3320 (m), 2980 (w), 1620 (s), 1590 (s), 1520 (m), 1480 (s), 1450 (w), 1410 (w), 1380 (w), 1330 (w), 1305 (w), 1145 (m), 1070 (w), 1020 (w), 990 (m), 940 (w–m), 855 (w–m), 835 (m), 815 (w–m), 770 (s), 750 (s), 685 cm^{-1} (m–s); nmr ($CDCl_3$) δ 3.6 (broad s, 2 H), 4.25 (s, 2 H), and 6.8 (m, 8 H).

General Procedure for Rearrangement of 2,2'-Aminonitrodiphenyl Sulfides.—Sulfides were heated in an oil bath at 195° with an excess of amine in a sealed tube. Excess solvent was removed under vacuum and the dark residue chromatographed on Florisil. Samples isolated from the column were washed with pentane and placed under vacuum for at least 8 hr.

Phenothiazine (3a).—Sulfide **2c** (0.1554 g, 0.000632 mol) in aniline gave, on elution with benzene–pentane (3:2), 0.0357 g (29%) of a white solid, mp 183° (lit.[7] mp 180°), identified as **3a** by comparison of its properties with an authentic sample. Elution with pentane–benzene (1:1) gave 0.0948 g (61%) of a yellow-orange solid, mp 86° (lit.[8] mp 85°), identified as **2c** by comparison of its properties with an authentic sample.

3-Methylphenothiazine (3b).—Sulfide **2b** (0.1596 g, 0.000614 mol) in *p*-toluidine gave, on elution with pentane–benzene (4:1), 0.0557 g (42%) of a white solid, mp 167–168° (lit.[10] mp 168°), identified as **3b** by comparison of its properties with an authentic sample. Elution with benzene gave 0.0723 g (45%) of a red solid, mp 87°, identified as **2b** by comparison of its properties with an authentic sample.

Registry No.—**1a**, 4837-33-6; **1b**, 4837-32-5; **2a**, 1144-81-6; **2b**, 27332-17-8; **2c**, 19284-81-2; **3b**, 3939-47-7; **4a**, 27332-20-3; **4b**, 27384-96-9; **5**, 27332-21-4; **6a**, 27332-22-5; **6b**, 27332-23-6; **7**, 27332-24-7; **8**, 27332-25-8; 4-*N*,*N*-dimethylamino-3'-nitrodiphenyl sulfide, 27332-26-9.

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Reduction of Aromatic Nitro Compounds with Sodium Borohydride in Dimethyl Sulfoxide or Sulfolane. Synthesis of Azo or Azoxy Derivatives

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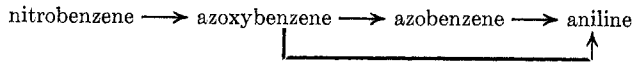
The reduction of aromatic nitro compounds with sodium borohydride in the polar aprotic solvents, DMSO and sulfolane, has been investigated. The reactions involve initial production of azoxy compounds which, in most cases, are subsequently reduced to the corresponding azo derivatives and amines. Other functional groups including cyano and amido are not reduced under the reaction conditions. Electron-withdrawing substituents facilitate both the initial production of azoxy compounds and the further reduction to azobenzenes and anilines. Electron-releasing groups slow the reductions of the azoxy compounds to the extent that these derivatives may be obtained in reasonable yields.

During a recent investigation of the reduction of aliphatic halides and tosylates with sodium borohydride in polar aprotic solvents,[2] we observed that reduction of aromatic nitro groups proceeded slowly at mild temperatures (*i.e.*, 25°) enabling benzylic halides to be selectively removed in their presence; the same results have also been obtained independently by Bell and coworkers.[3] However, at higher temperatures (*i.e.*, 85°) we have observed the ready reduction of aromatic nitro groups by borohydride in dimethyl sulfoxide or sulfolane to initially afford azoxy compounds which may be further reduced to mixtures of the corresponding azo derivatives and amines. As part of our exploratory investigations of the synthetic utility of borohydride in polar aprotic solvents,[2] we wish to report the scope of such reductions as convenient procedures for preparing azoxy and/or azobenzenes.

In order to determine the timing of production of the various observed products and thus aid in obtaining the best experimental procedures, the reduction of nitrobenzene in DMSO was monitored using gas chromatography to simultaneously measure the disappearance of nitrobenzene and appearance of azoxybenzene, azobenzene, and aniline. To conveniently accomplish this, an internal standard was added at the beginning of the reaction. Small aliquots of the reaction mixture were removed at appropriate time intervals, quenched in water, and extracted with chloroform, and the organic solution was analyzed. The results of such studies at 55 and 85° are plotted in Figure 1. Several noteworthy features of the reaction are evident from these plots. First, both cases suggest that the overall reduction occurs in three sequential steps.



This is further evidenced by the borohydride reduction of *p*,*p*'-dichloroazoxybenzene to the corresponding azo and amine derivatives (entry 24, Table I). Furthermore, the rate of formation of azoxybenzene is very much faster than is subsequent reduction at 85°; the

(1) (a) National Science Foundation Undergraduate Research Participant, (b) Undergraduate Research Participant, 1969–present.

(2) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969).

(3) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969).