Chemistry of the Sulfur–Nitrogen Bond. II.[1] A Mechanistic Study of the Rearrangement of 2-Nitrobenzenesulfenanilides to 2-Aminobenzenesulfonanilides

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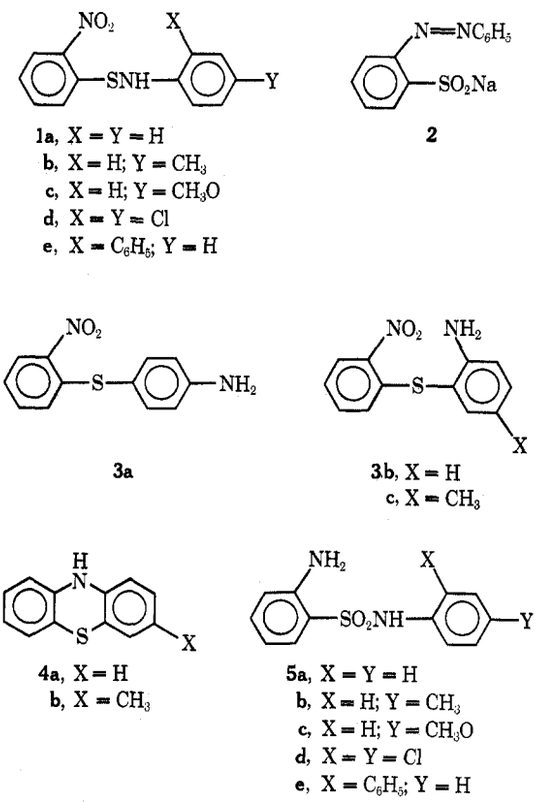
2-Nitrobenzenesulfenanilides thermally rearranged to give, among other products, 2-aminobenzenesulfonanilides. A mechanistic scheme is proposed which involves homolytic cleavage of the sulfur–nitrogen bond and transfer of a hydrogen atom from the solvent.

The ability of an *o*-nitro group to transfer its oxygens to an adjacent group is well known and has been reviewed.[3] There are a number of examples in the literature in which an *o*-nitro group transfers its oxygens to an adjacent sulfur. In this oxidation–reduction the sulfur is oxidized and the nitro group reduced. For example, *o*-nitrothiophenol, when heated in the presence of base, gave 2-azobenzenesulfinic acid;[4] methyl 2,4-dinitrobenzenesulfenate in hydrochloric acid gave 2-amino-4-nitrobenzenesulfonic acid;[5] 2-nitrobenzenesulfenyl chloride in hydrofluoric acid gave bis(2,2′-fluorosulfonyl)azobenzene;[6] and 2-nitrobenzenesulfenanilide (**1a**) with sodium hydroxide gave 2-azobenzenesulfenate (**2**).[7] More recently, the pyrolysis of *tert*-butyl 2-nitrobenzenesulfenate gave, among other products, aniline.[8] Photolysis of 2,4-dinitrobenzenesulfen-*N*-methylanilide gave 2-amino-4-nitrobenzenesulfon-*N*-methylanilide[9] and the photolysis of 2-nitrodiphenyl sulfoxide gave 2-nitrosodiphenyl sulfone.[10] With the exception of Brown's detailed investigation of the mechanism of rearrangement of sulfenamide **1a** to 2-azobenzenesulfenate (**2**),[11] no attempt has been made to elucidate the mechanism of these unusual oxidation–reduction reactions.

In the course of an investigation of the chemistry of the sulfur–nitrogen bond we observed that when 2-nitrobenzenesulfenanilide (**1a**) and 2-nitrobenzenesulfen-*p*-toluide (**1b**) were heated in their corresponding amine solvents they rearranged to give aminonitrodiphenyl sulfides **3a–c**, phenothiazine **4a,b**, and the major products, 2-aminobenzenesulfonanilide (**5a**) and 2-aminobenzenesulfon-*p*-toluide (**5b**).[1] We report here the results of our investigation into the mechanism of rearrangement of 2-nitrobenzenesulfenanilides to 2-aminobenzenesulfonanilides.



1a, X = Y = H
b, X = H; Y = CH_3
c, X = H; Y = CH_3O
d, X = Y = Cl
e, X = C_6H_5; Y = H

2

3a

3b, X = H
c, X = CH_3

4a, X = H
b, X = CH_3

5a, X = Y = H
b, X = H; Y = CH_3
c, X = H; Y = CH_3O
d, X = Y = Cl
e, X = C_6H_5; Y = H

Results

To determine the scope of the rearrangement we investigated the thermal rearrangements of 2-nitrobenzenesulfen-*p*-anisidine (**1c**),[12] 2-nitrobenzenesulfen-2,4-dichloroanilide (**1d**),[13] 2-nitrobenzenesulfen (2-phenyl)anilide (**1e**),[13] and 2-nitrobenzenesulfen-*N*-methylanilide (**6**).[12] The general rearrangement procedure involved heating the sulfenamide in a sealed tube with an excess of the corresponding amine solvent at 195° for 15.5 hr. The excess solvent was removed, and the dark residue was dissolved in methylene chloride, filtered, and chromatographed on Florisil. Products were identified when possible with authentic samples. These results are summarized in Table I.

Sulfenamide **1c** in *p*-anisidine gave two products: *p*-methoxyazobenzene (**7**)[14] and 2-aminobenzenesulfon-*p*-anisidine (**5c**). Structural proof of **5c** is supported by elemental analysis, infrared spectrum, and nmr spectrum. Sulfonamide **5c** was prepared independently by condensation of 2-nitrobenzenesulfonyl chloride with 2-aminobiphenyl. Reduction of the resulting 2-nitrobenzenesulfon-*p*-anisidine gave **5c** in greater than 70% yield.

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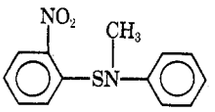
TABLE I
THERMAL REACTIONS OF 2-NITROBENZENESULFENANILIDES AT 195° FOR 15.5 HR

Sulfenamide	Solvent	Products (yield, %)
1a	Aniline[a]	**1a** (34), **3a** (12), **3b** (5), **4a** (3), **5a** (37)
	Anisole	**3a** (4), **3b** (6), **4a** (trace), **5a** (22), **15** (12)
	Decalin	**3a** (5), **3b** (4), **4a** (trace), **5a** (20), **15** (21)
	Neat	**3a** (3), **3b** (4), **5a** (21), **15** (10)
1b	*p*-Toluidine[a]	**3c** (18), **4b** (14), **5b** (55)
1c	*p*-Anisidine	**7** (27)[b], **5c** (56)
	p-Anisidine[c]	**7** (24)[b], **5c** (57)
	Decalin	**5c** (17), **15** (37)
1d	2,4-Dichloroaniline	**3d** (61), **5d** (28)
1e	2-Aminobiphenyl	**1e** (61), **8** (18),[b] **5e** (25)
6	*N*-Methylaniline	**9** (1), **10a** (5), **10b** (5), **11** (57)
	Decalin	**9** (10), **10a** (16), **10b** (30), **11** (8)

[a] Reference 1. [b] Yield calculated assuming that 1 mol of sulfenamide yields 0.5 mol of azobenzene. [c] Degassed.



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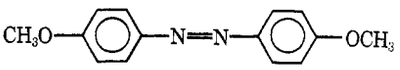

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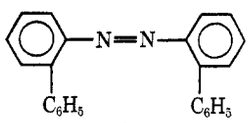
Sulfenamide **1d** in 2,4-dichloroaniline gave 2-amino-3,5-dichloro-2′-nitrodiphenyl sulfide (**3d**)[15] and 2-aminobenzenesulfon-2,4-dichloroaniline (**5d**).[16]



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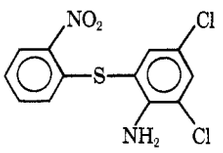
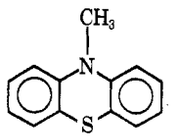


3d

Sulfenamide **1e** in 2-aminobiphenyl gave two products, 2-azobiphenyl (**8**)[17] and 2-aminobenzenesulfon(2-phenyl)anilide (**5e**). Structural proof of sulfonamide **5e** was based upon elemental analysis, infrared spectrum, proton nmr spectrum, and independent synthesis. The proton nmr spectrum of **5e** showed absorption at δ 4.8 (amine) and at δ 6.5 and 7.2 (relatively areas 2:2:12) in agreement with the proposed structure.

Sulfonamide **5e** was prepared independently by condensation of 2-nitrobenzenesulfonyl chloride with 2-aminobiphenyl. Reduction of the 2-nitrobenzenesulfon(2-phenyl)anilide gave **5e** in 7% overall yield.

Sulfenamide **6** in *N*-methylaniline gave four products, *N*-methylphenothiazine (**9**),[18] 2-nitro-2′-(*N*-methyl)-aminodiphenyl sulfide (**10a**),[19] 2-nitro-4′-(*N*-methyl)-aminodiphenyl sulfide (**10b**), and 2-aminobenzenesulfon(*N*-methyl)anilide (**11**).[20] The structure of sulfide **10b** is supported by elemental analysis, infrared spectrum, nmr spectrum, and independent synthesis. The proton nmr spectrum showed absorption at δ 3.80 (broad singlet, amine) and complex absorption at δ 7.05 and 8.24 (relative areas 3:1:7:1) in agreement with the proposed structure. Diphenyl sulfide **10b** was prepared by methylation of sulfide **3b** using *p*-toluenesulfonyl chloride and dimethyl sulfate.



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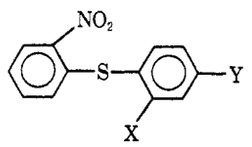
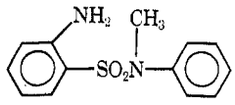


10a, X = $NHCH_3$; Y = H
b, X = H; Y = $NHCH_3$



11

Ullmann and Gross reported that sulfonamide **11** was a white solid, mp 63°.[21] The product that we isolated from the thermal rearrangement of sulfenamide **6** in *N*-methylaniline was an oil which failed to solidify after purification by column chromatography, sublimation, or preparative glc. We prepared sulfonamide **11** according to the method of Ullmann and Gross and isolated an oil which was identical in all aspects with **11**. The structure of sulfonamide **11** is supported by elemental analysis, infrared spectrum, and proton nmr spectrum. The proton nmr spectrum showed absorption at δ 6.62, 7.26, and 7.33 (relative areas 3:2:2:5:2) in agreement with the proposed structure.

Discussion

Previously we reported that 3-nitrobenzenesulfenanilide gave none of the corresponding sulfonamide when treated under the reaction conditions and that the presence or absence of oxygen had little effect on the formation of the 2-aminobenzenesulfonanilides[1] (*i.e.*, **1a**,**c** in degassed solutions gave nearly the same yields of sulfonamides **5a**,**c**, respectively). Brown has recently shown using ^{18}O that the oxygens of the nitro group are transferred intramolecularly in the rearrangement of **1a** to **2**.[11] These results suggest that the oxygens of the nitro group in 2-nitrobenzenesulfenanilides are transferred intramolecularly to the sulfur in the formation of the 2-aminobenzenesulfonanilides. The reported close proximity of the oxygens of the nitro group to the sulfur in 2-nitrobenzenesulfenic acid further supports this conclusion.[21]

Questions as yet unanswered are what is the origin of the hydrogen of the amino group, and does anything happen to the S–N bond during the rearrangement?

The hydrogen of the amino group may be transferred either from the solvent or by some intramolecular process from the sulfenamide nitrogen. This latter process may be ruled out as a major pathway for the

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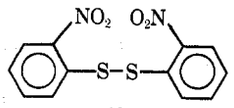
formation of the sulfonamide by a consideration of the rearrangement of sulfenamide **6**. Sulfenamide **6**, which has no sulfenamide hydrogen, gave a greater than 57% yield of sulfonamide **11**. In this example the hydrogen must be transferred from the solvent.

Sulfenamide **1a** in anisole, decalin, or in the absence of solvent gave 20–22% of sulfonamide **5a**, and **1c** in decalin gave 17% of **5c**. The hydrogen is therefore transferred from the sulfenamide nitrogen because the reaction proceeded to the same extent without solvent as in anisole or decalin. The transfer of the hydrogen is probably not intramolecular, since sulfenamide **6** in decalin gave 8% sulfonamide **11**. In all probability the hydrogen is transferred after cleavage of the S–N bond, since in all cases bis(2-nitrophenyl) disulfide (**12**) was isolated in substantial amounts (Table I).



12

There is compelling evidence that the sulfur–nitrogen bond in sulfenamides is labile under thermal conditions. At 109° aryl sulfenanilides undergo a facile exchange with aryl amines.[1,22] Homolytic cleavage of the S–N bond in benzothiazole-2-alkylsulfenamides to give thiyl and amino radicals has been suggested to account for their activity as accelerators in the vulcanization of rubber.[23] Heating *N*-cyclohexylbenzothiazole-2-sulfenamide at 143° gave strong esr signals.[24]

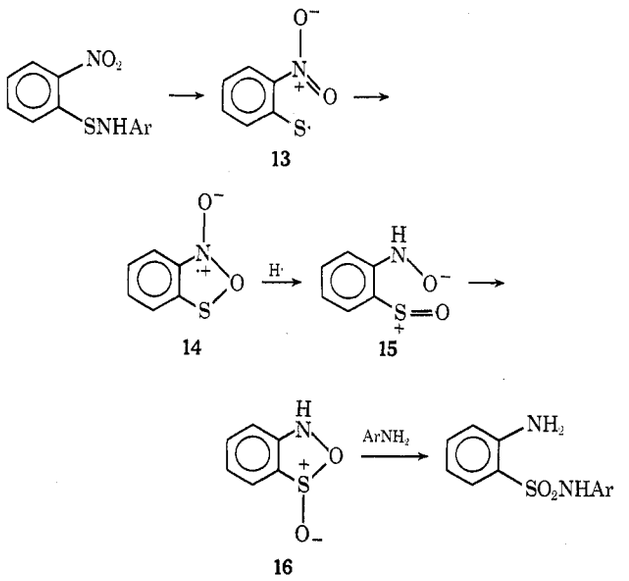
Heterolytic cleavage of the sulfur–nitrogen bond must also be considered. Heating *tert*-butyl 2-nitrobenzenesulfonate is reported to give sulfenium ions,[8] and alkyl sulfenyl esters thermally decompose by a cyclic mechanism.[25] Field and coworkers have shown that unsymmetrical disulfides, at moderate temperatures (*ca.* 68–89°), cleave heterolytically.[26,27]

Scheme I suggests a mechanistic pathway for the formation of the 2-aminobenzenesulfonanilides and involves cleavage of the S–N bond prior to transfer of the hydrogen. This scheme involves homolytic cleavage of the S–N bond to give the 2-nitrobenzenesulfenyl radical (**13**), which may be stabilized by interaction with the oxygens of the nitro group (**14**). Structures similar to **13** have been suggested to account for the "abnormal" chlorination of 2-nitrobenzenesulfenyl chloride[28] and the stabilization of the 2,4-dinitrobenzenesulfenium ion.[29]

Addition of a hydrogen atom from the amine solvent gave **15**, which cyclizes to **16**. Attack of the amine solvent on **16** gave the sulfonamides.

Although mechanistic schemes involving heterolytic cleavage of the sulfur–nitrogen bond have been considered,[30] the present data are most in agreement with a mechanistic scheme which involves homolytic cleavage of the S–N bond to produce a sulfenyl radical **13** and an aryl amino radical (ArNH·). Support for this interpretation is obtained from the reactions of bis(2-nitrophenyl) disulfide (**12**) and aryl amines, substituent electronic effects, the isolation of bis(2-nitrophenyl) disulfide (**12**), and the formation of azobenzenes **7** and **8**.

SCHEME I



13 **14** **15** **16**

Support for the formation of sulfenyl radical **13** is obtained from the reactions of disulfide **12** and aryl amines. When treated under the reaction conditions with aryl amines, **12** gave high yields (51–81%) of the corresponding 2-aminobenzenesulfonanilides (**5**).[31]

Neglecting possible steric effects and assuming that the rate-determining step is either cleavage of the S–N bond or transfer of the hydrogen atom from the solvent, then the substituent electronic effects of groups attached to the aryl amine support the formation of an amino radical. Increased formation of the sulfonamides were observed in the order $2,4\text{-}Cl_2 \leq 2\text{-}C_6H_5 < H < 4\text{-}CH_3 \leq 4\text{-}CH_3O \leq NCH_3$. The formation of the sulfonamides is not very sensitive to the substituents as expected for a radical. However, electron-donating groups stabilize the radical, and electron-withdrawing groups destabilize the radical. These substituent effects are in approximate agreement with those reported for homolytic cleavage of unsymmetrical disulfides[26] and the thermal decomposition of bis(*N*-arylimidoyl) disulfides.[32]

When the rearrangement of sulfenamides **1a,c** and **6** was carried out in solvents less likely to transfer a hydrogen atom than aryl amines, bis(2-nitrophenyl) disulfide (**12**) was isolated. Disulfide **12** is presumably formed by dimerization of two sulfenyl radicals, **13**.

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(29) N. Kharasch, C. M. Buess, and W. King, *ibid.*, **75**, 6035 (1953).

(30) A detailed discussion of the various mechanistic possibilities for the rearrangement of o-nitrobenzenesulfonanilides to 2-aminobenzenesulfonanilides will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(31) F. A. Davis and R. P. Johnston II, *J. Org. Chem.*, **37**, 859 (1972).

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This result further supports homolytic cleavage of the S–N bond and transfer of a hydrogen atom from the aryl amine solvent.

Finally, the formation of azobenzenes **7** and **8** support homolytic cleavage of the sulfur–nitrogen bond.

Azobenzenes.—A rationalization for the formation of azobenzenes **7** and **8** is derived from thermal dismutation of the corresponding hydrazobenzenes. Hydrazobenzenes are known to thermally rearrange to give azobenzenes and aryl amines.[33,34] Hydrazobenzenes would be formed by dimerization of two aryl amino radicals formed by cleavage of the S–N bond or by

$$2ArNH\cdot \longrightarrow ArNHNHAr \longrightarrow ArN{=}NAr + ArNH_2$$

transfer of a hydrogen atom from the amine solvent. The yields of **6** and **8** are calculated based on this assumption (Table I).

Azobenzenes were isolated in only two cases: the rearrangements of sulfenamides **1c** and **1e**. In each of these examples a phenyl amino radical may be substantially stabilized by resonance with the substituent group. A fairly long lifetime for the amino radical may be necessary for two aryl amino radicals to dimerize to form the hydrazobenzenes. A more reactive radical may react with the solvent to give the tars that were isolated in all of these reactions.

Conclusions

A radical mechanism appears to be consistent with the present experimental data for the rearrangement of 2-nitrobenzenesulfenanilides to 2-aminobenzenesulfonanilides. Attempts to isolate or trap intermediates or to inhibit the rearrangement by use of radical scavengers have thus far proved disappointing. Undoubtedly, this is in part due to the temperature and solvent which is necessary for the rearrangement. Mass spectral and esr studies may shed further light on the mechanism.

Experimental Section

Sulfenamides **1c**,[12] **1d**,[13] **1e**,[13] and **6**[12] were prepared according to procedures given in the literature. Melting points were obtained on a Fisher-John apparatus. Proton nmr spectra were measured on a Varian A-60A instrument. Infrared spectra were measured on a Perkin-Elmer 457 spectrometer. Solvents were purified according to literature procedures.

General Procedure for Thermal Rearrangement of Sulfenamides.—Sulfenamides were heated in an oil bath with an excess of solvent in a sealed tube for 15.5 hr. Excess solvent was removed either by distillation (vacuum pump) or sublimation and the dark residue was dissolved in methylene chloride and filtered. The filtrate was chromatographed on Florisil unless otherwise noted. 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** (0.234 g, 0.00095 mol) in anisole gave, on elution with pentane–benzene (4:1), 0.01 g (1%) of a white solid, mp 183° (lit.[35] mp 192°), identified as **phenothiazine (4a)** by comparison of its properties with those of an authentic sample. Elution with pentane–benzene (1:1) gave 0.018 g (12%) of a yellow solid, mp 193–194° (lit.[36] mp 192°), identified as **bis(2-nitrophenyl) disulfide (12)** by comparison of its properties with those of an authentic sample. Elution with pentane–benzene (1:2) gave 0.013 g (6%) of a yellow solid, mp 86° (lit.[37] mp 85°), identified as **2-amino-2′-nitrodiphenyl sulfide (3b)** by comparison of its properties with those of an authentic sample. Further elution with pentane–benzene (1:2) gave 0.01 g (4%) of a yellow-brown solid, mp 102° (lit.[38] mp 102–103°), identified as **4′-amino-2-nitrodiphenyl sulfide (3a)** by comparison of its properties with those of an authentic sample. 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 0.051 g (22%) of white crystals, mp 119–120° (lit.[20] mp 119°), identified as **2-aminobenzenesulfonanilide (5a)** by comparison of its properties with those of an authentic sample.

Sulfenamide **1a** (0.204 g, 0.00084 mol) in decalin gave, on elution with pentane–benzene (1:1), 0.027 g (21%) of **12**; elution with pentane–benzene (1:2) gave 0.0082 g (4%) of **3b** and 0.01 g (5%) of **3a**; elution with chloroform gave an oil which, when treated with 5% sodium hydroxide solution followed by neutralization and cooling, gave 0.041 g (20%) of **5a**.

Sulfenamide **1a** (0.222 g, 0.0009 mol) in the absence of solvent gave, on elution with pentane–benzene (1:1), 0.01 g (7%) of **12**; elution with pentane–benzene (1:2) gave 0.007 g (3%) of **3b** and 0.0087 g (4%) of **3a**; elution with chloroform gave an oil which when treated with sodium hydroxide followed by neutralization and cooling gave 0.047 g (21%) of **5a**.

2-Nitrobenzenesulfen-*p*-anisidine (1c).[12]—Sulfenamide **1c** had the following properties: infrared (KBr) 3325 (s), 3070–2830 (w), 1590 (s), 1565 (s), 1500 (vs), 1460 (s), 1445 (s), 1385 (w), 1340 (s), 1305 (s), 1285 (s), 1260 (m), 1225 (vs), 1175 (m), 1120 (m), 1095 (m), 1035 (s), 900 (s), 850 (m), 820 (s), 790 (m), 780 (s), 730 (s), 710 (m), 565 (m), and 515 cm^{-1} (m); nmr ($CDCl_3$) δ 3.75 (s, 3 H), 5.02 (s, 1 H), 6.87 (m, 4 H), 7.34 (d, 1 H), 7.60 (d, 1 H). Sulfenamide **1c** (0.150 g, 0.00054 mol) in *p*-anisidine gave, on elution with pentane–benzene (3:2), 0.017 g (27%) of a yellow solid, mp 164–165° (lit.[14] mp 165°), identified as **4,4′-dimethoxyazobenzene (7)** by comparison of its properties with those of an authentic sample. Compound **7** had the following properties: infrared (KBr) 3020 (s), 2840 (s), 1600 (s), 1580 (s), 1495 (s), 1455 (m), 1440 (m), 1420 (m), 1315 (m), 1290 (m), 1240 (s), 1180 (m), 1140 (s), 1100 (m), 1020 (s), 840 (s), 820 (w), 745 (m), 640 (w), 550 (m), 540 (m), 505 (w), and 405 cm^{-1} (w); nmr ($CDCl_3$) δ 3.75 (s, 6 H), 7.39 (q, 8 H). Elution with chloroform gave a brown oil which was alternately washed with 20% potassium hydroxide solution and water (three 50-ml portions); the aqueous washings were carefully neutralized with 5% hydrochloric acid solution and on cooling overnight gave 0.087 g (56%) of white crystals, mp 123–124°, identified as **2-aminobenzenesulfon-*p*-anisidide (5c)** by comparison of its properties with those of an authentic sample.

Sulfenamide **1c** (0.184 g, 0.00067 mol) in decalin gave, on elution with pentane–benzene (3:2), 0.038 g (37%) of **12**. Elution with chloroform gave an oil which, when treated with 20% potassium hydroxide solution followed by neutralization and cooling, gave 0.032 g (17%) of **5c**.

2-Aminobenzenesulfon-*p*-anisidide (5c).—2-Nitrobenzenesulfon-*p*-anisidide was prepared by condensation of 2-nitrobenzenesulfonyl chloride with *p*-anisidine in ether.[39] The crude sulfonamide, 0.5 g, in 100 ml of acetic acid at 35 psi of hydrogen over 25 mg of 10% palladium on charcoal for 14 hr gave, after solvent removal, a green oil. The oil was dissolved in 20% potassium hydroxide solution and neutralized with 5% hydrochloric acid solution and, on cooling overnight, gave a brown solid which was crystallized from ethanol to give 0.38 g (72%) of colorless crystals, mp 123–124°.

Anal. Calcd for $C_{13}H_{14}N_2O_3S$: C, 56.09; H, 5.08. Found: C, 56.05; H, 5.22.

Sulfonamide **5c** had the following properties: infrared (KBr) 3480 (s), 3380 (s), 3210 (s), 1630 (s), 1595 (m), 1500 (s), 1480 (s), 1325 (s), 1300 (s), 1240–1220 (s), 1140 (s), 1020 (s), 930 (s), 825 (m), 745 (s), 695 (m), 635 (m), 595–580 (s), and 540–510 cm^{-1} (m); nmr ($CDCl_3$) δ 3.74 (s, 3 H), 4.63 (s, 2 H), 6.66–7.53 (m, 9 H).

2-Nitrobenzenesulfen-2,4-dichloroanilide (1d).[13]—Sulfenamide **1d** had the following properties: infrared (KBr) 3380 (m), 3100 (w), 1595 (m), 1570 (m), 1505 (s), 1480 (s), 1380 (w), 1365 (w), 1340 (s), 1315 (m), 1290 (s), 1170 (w), 1155 (w), 1105 (m), 1050 (doublet, m), 910 (m), 875 (m), 820 (s), 790 (m), 740 (s), 720

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(m-s), 700 (w), 682 (w), 655 (m-w), 560 cm^{-1} (m-w); nmr ($CDCl_3$) δ 5.8 (s, 1 H), 7.2–7.6 (m, 6 H), and 8.3 (d, 1 H). Sulfenamide **1d** (0.153 g, 0.000486 mol) in 2,4-dichloraniline was chromatographed on acidic alumina and on elution with pentane–benzene (1:1) gave 0.093 g (61%) of yellow plates which on sublimation (140°, 0.05 mm), mp 198° (lit.[15] mp 175°), was identified as **2-amino-3,5-dichloro-2′-nitrodiphenyl sulfide (3d)** by comparison of its properties with those of an authentic sample.[40]

Anal. Calcd for $C_{12}H_8Cl_2N_2O_2S$: C, 45.86; H, 2.55. Found: C, 45.92; H, 2.54.

Diphenyl sulfide **3d** had the following properties: infrared (KBr) 3480 (m-w), 3390 (m), 1610 (m), 1590 (m), 1565 (m), 1506 (s), 1450 (s), 1335 (s), 1310 (m), 1280 (w), 1255 (m), 1210 (w-m), 1045 (w), 875 (m), 855 (m), 790 (m), 740 (s), 715 (w), and 655 cm^{-1} (w); nmr ($CDCl_3$) δ 4.8 (s, 2 H), 6.9 (d, 1 H), 7.5 (m, 4 H), and 8.4 (d, 1 H). Elution with chloroform gave a brown oil which was subblimed (120°, 0.1 mm) to give a white, crystalline solid which was crystallized from ether–pentane to give 0.042 g (28%) of white needles, mp 105–106° (lit.[16] mp 108°), identified as **2-aminobenzenesulfon-2,4-dichloroanilide (5d)** by comparison of its properties with those of an authentic sample.

Sulfonamide **5d** had the following properties: infrared (KBr) 3460 (m), 3380 (m), 3280 (m), 1620 (m), 1600 (w-m), 1570 (w), 1475 (s), 1415 (m), 1380 (m), 1335 (s), 1280 (w), 1220 (w), 1170 (s-m), 1150 (s-m), 1150 (s), 1100 (w-m), 1050 (w-m), 910 (m), 865 (w-m), 840 (m), 815 (w-m), 765 (m), 750 (m), 730 (w), 700 (m), 655 (w), 600 (s), and 580 cm^{-1} (s); nmr ($CDCl_3$) δ 5.0 (s, 2 H), 6.75 (m, 2 H), 7.25 (m, 4 H), and 7.55 (m, 2 H).

2-Nitrobenzenesulfen(2-phenyl)anilide (1e).[18]—Sulfenamide **1e** had the following properties: infrared (KBr) 3380 (s), 1590 (m), 1570 (m), 1500 (s), 1480 (s), 1450 (m), 1440 (m), 1382 (m), 1340 (s), 1310 (s), 1270 (s), 1215 (w), 1160 (w), 1112 (w), 1100 (m), 1055 (w), 1010 (w), 900 (m), 860 (m), 790 (m), 755 (s), 740 (s), 705 (s), 655 (w), and 520 cm^{-1} (m); nmr ($CDCl_3$) δ 5.4 (s, 1 H), 7.2 (m, 4 H), 7.5 (s, 8 H), and 8.3 (d, 1 H). Sulfenamide **1e** (0.181 g, 0.00056 mol) in 2-aminobiphenyl was chromatographed on neutral alumina, and elution with *n*-pentane gave 0.016 g (18%) of a red solid which on sublimation (80°, 0.1 mm), mp 137–138° (lit.[18] mp 136–139°), was identified as **2-phenylazobenzene (8)** by comparison of its properties with those of an authentic sample. Compound **8** had the following properties: infrared (KBr) 3070 (w), 1475 (m), 1460 (w-m), 1435 (w-m), 1280 (w-m), 1280 (w), 1250 (w), 1330 (w), 1195 (w), 1160 (w), 1120 (w), 1080 (w), 1050 (w), 1015 (w), 990 (w), 960 (w), 910 (w), 840 (w), 775 (s), 740 (s), 730 (m-s), 700 (s), 620 (w), 590 (m), 550 (m), 540 (m), and 480 cm^{-1} (m); nmr ($CDCl_3$) δ 7.48 (s, 18 H). Elution with chloroform gave a brown oil which was alternately washed with 10% sodium hydroxide solution and water (three 50-ml potions). The aqueous washings were carefully neutralized with 5% hydrochloric acid solution and on cooling overnight gave an oil which was extracted into ether. The ether solution was dried over $MgSO_4$ and on removal gave 0.045 g (25%) of an oil which was identified as **2-aminobenzenesulfon(2-phenyl)anilide (5e)** by comparison of its properties with those of an authentic sample.

2-Aminobenzenesulfon(2-phenyl)anilide (5e).—2-Nitrobenzenesulfon(2-phenyl)anilide was prepared by condensation of 2-nitrobenzenesulfonyl chloride with 2-aminobiphenyl in tetrahydrofuran.[39] The crude sulfonamide, 10.0 g, in 50 ml of ethanol at 40 psi over 100 mg of 10% palladium on charcoal for 24 hr gave 0.64 g (70%) of an oil which was purified by molecular distillation (120°, 0.1 mm).

Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.67; H, 5.56. Found: C, 66.55; H, 5.41.

Sulfonamide **5e** had the following properties: infrared (thin film) 3485 (s), 3380 (s), 3060 (w), 1620 (s), 1570 (m), 1480 (s), 1455 (m), 1440 (w), 1395 (m-s), 1330 (s), 1260 (m), 1205 (m-w), 1150 (s), 1110 (m), 1055 (m-w), 1030 (w), 1010 (s), 900 (s), 840 (m), 820 (w), 750 (s), 700 (s), 700 (s), and 635 cm^{-1} (m-s); nmr ($CDCl_3$) δ 4.7 (s, 2 H), 6.6 (m, 2 H), and 7.3 (m, 12 H).

2-Nitrobenzenesulfen-*N*-methylanilide (6).[12]—Sulfenamide **6** had the following properties: infrared (KBr) 3070–2820 (w), 1600 (s), 1570 (m), 1500 (s), 1450 (m), 1345 (s), 1315 (s), 1290 (s), 1195 (w), 1170 (w), 1100 (m), 1090 (m), 1070 (m), 1040 (m), 1030 (m), 995 (w), 870 (s), 820 (m), 785 (m), 760 (s), 735 (s), 695 (m), 520 (w), 490 (w), and 435 cm^{-1} (w), nmr ($CDCl_3$) δ 3.46 (s, 3 H), 7.3 (m, 8 H), and 8.3 (d, 1 H). Sulfenamide **6** (0.852 g, 0.00325 mol) in *N*-methylphenothiazine was chromatographed on basic alumina. Elution with cyclohexane gave 0.005 g (1%) of white needles, mp 97–99° (lit.[18] mp 99–100°), identified as **3-methylphenothiazine (9)** by comparison of its properties with those of an authentic sample. Phenothiazine **9** had the following properties: infrared (KBr) 1590 (w), 1565 (w), 1460 (s), 1335 (s), 1290 (m), 1260 (s), 1140 (m), 1040 (m), 860 (w), 760 (s), 750 (s), and 730 cm^{-1} (w); nmr ($CDCl_3$) δ 3.3 (s, 3 H) and 6.7–7.2 (m, 8 H). Elution with cyclohexane–benzene (4:1) gave a yellow solid which was crystallized from ethanol to give 0.046 g (5%) of yellow-orange plates, mp 105–106° (lit.[19] mp 110°), identified as **2-nitro-2′-(*N*-methyl)aminodiphenyl sulfide (10a)** by comparison of its properties with those of an authentic sample. Compound **10a** had the following properties: infrared (KBr) 3380 (s), 3070 (w), 2810 (w), 1595 (s), 1570 (s), 1500 (s), 1450 (m), 1340 (s), 1300 (s), 1170 (m), 1100 (m), 1040 (m), 860 (m), 785 (m), 740 (s), and 715 cm^{-1} (m); nmr ($CDCl_3$) δ 2.8 (s, 3 H), 4.8 (s, 1 H), 6.8 (m, 3 H), 7.4 (m, 4 H), and 8.3 (m, 1 H). Elution with cyclohexane–benzene (4:1) gave a red solid which was recrystallized from 95% ethanol to give 0.041 g (5%) of orange crystals, mp 84.5–85.5°, identified as **2-nitro-4′-(*N*-methyl)aminodiphenyl sulfide (10b)** by comparison of its properties with those of an authentic sample (*vide infra*). Elution with chloroform gave a pale brown oil which was purified by molecular distillation at 0.05 mm (50°) to give 0.491 g (57%) of a colorless oil identified as **2-aminobenzenesulfon-*N*-methylanilide (11)** by comparison of its properties with those of an authentic sample (*vide infra*).

2-Nitro-4′-(*N*-methyl)aminodiphenyl Sulfide (10b).—Diphenyl sulfide **3b** (7.0 g, 0.0285 mol) was dissolved in 11.7 ml of pyridine in a 100-ml flask fitted with a reflux condenser and the flask was cooled to 0°. *p*-Toluenesulfonyl chloride (Matheson Coleman and Bell) (5.41 g, 0.0284 mol) was dissolved separately in 11.7 ml of pyridine, cooled, and added slowly to the reaction flask through the condenser with constant swirling and cooling. When the exothermic reaction had subsided the reaction mixture was heated on the steam bath for 3 hr, cooled, and washed into a 100-ml separatory funnel with 10% hydrochloric acid solution (300 ml) and chloroform (300 ml). The aqueous layer was discarded and the organic layer was washed with 10% hydrochloric acid solution (two 200-ml portions) and water (two 200-ml portions) and dried over $MgSO_4$. Solvent removal under vacuum gave 10.5 g of an orange solid, which was added without further purification to a 250-ml flask containing 6.6 ml of 4 *N* sodium hydroxide. The reaction mixture was heated to reflux and cooled to 0°, and 6.6 ml of 4 *N* sodium hydroxide and 2.4 ml of dimethyl sulfate were added. The dark residue was heated in 200 ml of 0.75 *N* sodium hydroxide for 15 min, the reaction mixture was cooled, and the aqueous portion was decanted. The residue was dissolved in 200 ml of chloroform, washed with 3% sodium hydroxide solution and water, and dried over $MgSO_4$. Removal of the solvent gave a yellow solid. The solid was added to 10.0 g of phenol and 75 ml of 48% hydrobromic acid and the reaction mixture was heated at reflux for 1.5 hr. To the cooled solution 150 ml of water was added and the aqueous solution was extracted with ether. The aqueous solution was neutralized with 20% sodium hydroxide to pH 6 and then extracted with chloroform (three 100-ml portions). The chloroform extracts were dried over anhydrous magnesium sulfate and the solvent was removed under vacuum to give an orange solid, which on crystallization from 95% ethanol gave 1.74 g (23%) of orange needles, mp 84.5–85.5°.

Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.96; H, 4.65. Found: C, 59.86; H, 4.74.

Diphenyl sulfide **10b** had the following properties: infrared (KBr) 3420 (m), 3100–2820 (w), 1595 (s), 1565 (m), 1500 (s), 1450 (m), 1335 (s), 1310 (s), 1265 (w), 1250 (w), 1185 (s), 1155 (w), 1110 (m), 1060 (w), 1055 (w), 850 (w), 820 (m), 785 (w), and 740 cm^{-1} (m); proton nmr ($CDCl_3$) δ 2.9 (s, 3 H), 3.8 (s, 1 H), 7.1 (m, 7 H), and 8.3 (m, 1 H).

2-Aminobenzenesulfon-*N*-methylanilide (11).—The compound was prepared according to the method of Ullmann and Gross[20] and purified by molecular distillation (50°, 0.05 mm) to yield a colorless oil.

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.50; H, 5.39. Found: C, 59.46; H, 5.48.

Sulfonamide **11** had the following properties: infared (thin film) 3500 (s), 3390 (s), 3070–2880 (w), 1620 (s), 1600 (s), 1565 (m), 1490 (s), 1455 (s), 1350 (s), 1325 (s), 1260 (m), 1175 (s),

(40) An authentic sample of **3d** was prepared by the method of Farrington and Warburton[16] and on sublimation had a melting point and mixture melting point identical with those of **3d**.

1145 (s), 1070 (s), 1030 (s), 920 (w), 870 (s), 760 (s), 735 (s), 700 (s) and 680 cm^{-1} (m); nmr ($CDCl_3$) δ 3.3 (s, 3 H), 4.5 (s, 2 H), 6.6 (m, 2 H), 7.3 (s, 5 H), and 7.3 (m, 2 H).

Sulfenamide **6** (0.2183 g, 0.00084 mol) in decalin gave on elution with pentane–benzene (4:1) 0.017 g (10%) of **9**; elution with pentane–benzene (3:2) gave 0.035 g (16%) of **10a**; elution with benzene–methylene chloride (2:3) gave 0.018 g (8%) of **11**.

Registry No.—**1a**, 4837-33-6; **1b**, 4837-32-5; **1c**, 4997-95-9; **1d**, 33224-41-8; **1e**, 33224-42-9; **3d**, 33224-43-0; **5c**, 33224-44-1; **5d**, 33224-45-2; **5e**, 33224-46-3; **6**, 33224-04-3; **7**, 501-58-6; **8**, 13701-27-5; **9**, 1207-72-3; **10a**, 33224-08-7; **10b**, 33224-09-8; **11**, 33224-10-1.

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Chemistry of the Sulfur–Nitrogen Bond. III.[1] The Reactions of Bis(2-nitrophenyl) Disulfide with Amines

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The thermal rearrangement of bis(2-nitrophenyl) disulfide with primary or secondary alkyl or aryl amines to give the corresponding 2-aminobenzenesulfonamides is described. A radical mechanism is proposed.

We wish to report a new and facile synthesis of 2-aminobenzenesulfonamides (**1**) from bis(2-nitrophenyl) disulfide (**2**) and primary or secondary alkyl

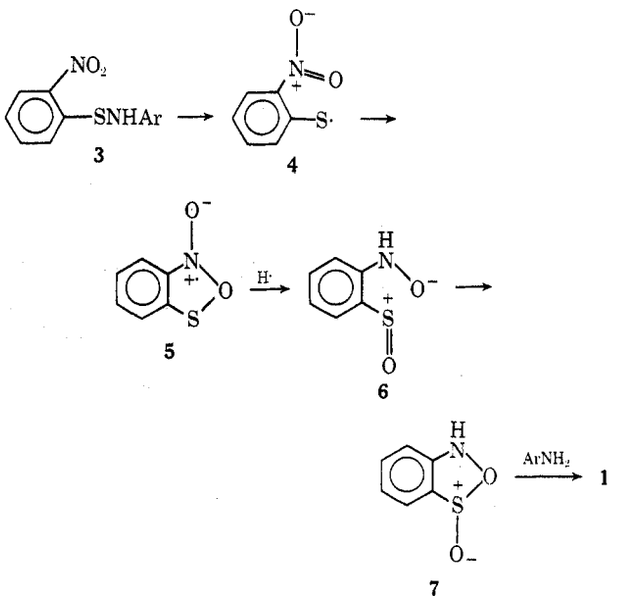
2

1a, Ar = C_6H_5
b, Ar = 4-$CH_3C_6H_4$
c, Ar = 4-$CH_3OC_6H_4$
d, Ar = 2,4-$Cl_2C_6H_3$
e, Ar = 2-$C_6H_5C_6H_4$
f, R = $CH_3(CH_2)_8CH_2$

or aryl amines. This reaction lends support to the mechanism recently proposed for the thermal rearrangement of 2-nitrobenzenesulfenanilides (**3**) to 2-aminobenzenesulfonanilides **1**.[1] The mechanism involved homolytic cleavage of the sulfur–nitrogen bond in **3** to give the 2-nitrobenzenesulfenyl radical **4**, which was stabilized by interaction with one of the *o*-nitro group oxygens (**5**). Transfer of a hydrogen atom from the amine solvent gave **6**, which cyclized to **7**. Attack of the amine solvent on **7** gave **1** (Scheme I). This mechanistic sequence was supported by several results, including the substantial amount of disulfide **2**, isolated when the thermal rearrangements of the sulfenamides were carried out in solvents less likely to transfer a hydrogen atom than the amine solvent. Disulfide **2** is presumably formed by dimerization of two sulfenyl radicals (**4**).

There appears to be a considerable amount of evidence which suggests that disulfides dissociate homolytically at elevated temperatures.[3-5] Therefore, to test whether or not sulfenyl radical **4** was an intermediate in the rearrangement of **3** to **1** we investigated the reactions of disulfide **2** with the primary aryl amines, aniline,

SCHEME I



p-toluidine, *p*-anisidine, 2,4-dichloroaniline, and 2-aminobiphenyl, and with a secondary aryl amine, *N*-methylaniline. With the exception of 2,4-dichloroaniline, yields of the corresponding 2-aminobenzenesulfonamides **1a–c**, **1e**, and **8a** were 51–81% (1 mol of **2** yields 2 mol of **1**).

The reaction also works with primary and secondary alkyl amines; *N*-decylamine gave 63% **1f** and diisobutylamine gave 74% **8b**.

In addition to the sulfonamides, several other products were isolated. Disulfide **2** with *p*-anisidine and 2-aminobiphenyl gave azobenzenes **9** and **10**, respectively. Disulfide **2** with aniline gave diphenyl sulfides **11a,b**; in *p*-toluidine **2** gave 3-methylphenothiazine (**12**) and diphenyl sulfide **13a**; and in 2,4-dichloroaniline **2** gave diphenyl sulfide **13b**.

Several minor fractions were isolated as oils from the reaction of **2** with *n*-decylamine and diisobutylamine. They were not identified. In both reactions a small amount (*ca.* 10–30 mg) of a white solid, insoluble in organic solvents but soluble in water, was

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