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

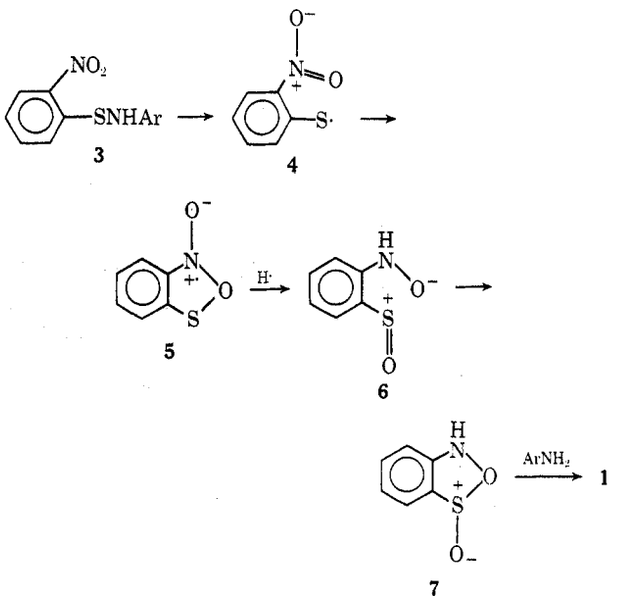
2

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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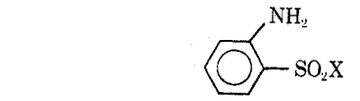
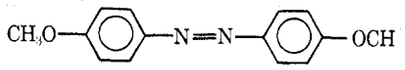
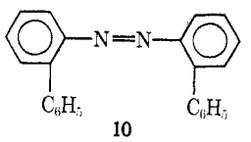


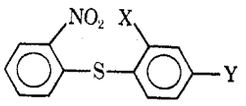
8a, X = $N(CH_3)C_6H_5$
c, X = $N[CH_2CH(CH_3)_2]_2$



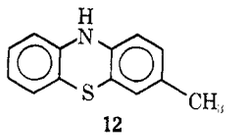
9



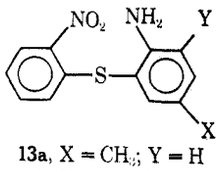
10



11a, X = NH_2; Y = H
b, X = H; Y = NH_2



12



13a, X = CH_3; Y = H
b, X = Y = Cl

isolated. The solid is presumably the hydrosulfate of the amine, since the infrared of both samples showed strong absorption at 1100 cm^{-1} [6] and precipitated barium sulfate from barium chloride solution.

The rearrangement conditions involved heating disulfide **2** with an excess of amine in a sealed tube for 15.5 hr at 195°. The solvent was removed and the dark residue was chromatographed. Products were identified by comparison with authentic samples. These results are summarized in Table I.

TABLE I

REARRANGEMENT OF BIS(2-NITROPHENYL) DISULFIDE IN AMINE SOLVENTS AT 195° FOR 15.5 HR

Solvent	Registry no.	Products (yield, %)
Aniline	62-53-3	**11a** (3),[a] **11b** (7),[a] **1a** (65)[b]
p-Toluidine	106-49-0	**12** (5),[a] **13a** (6),[a] **1b** (77)[b]
p-Anisidine	104-94-9	**9** (21),[c] **1c** (81)[b]
2,4-Dichloroaniline	554-00-7	**13b** (6),[a] **1d** (23),[b] **2** (67)
2-Aminobiphenyl	90-41-5	**10** (16),[c] **1e** (51),[b] **2** (22)
n-Decylamine	2016-57-1	**1f** (63)[b]
N-Methylaniline	100-61-8	**8a** (78)[b]
Diisobutylamine	110-96-3	**8b** (74)[b]

[a] One mole of disulfide yields 1 mol of diphenyl sulfide. [b] One mole of disulfide yields 2 mol of sulfonamide. [c] One mole of disulfide yields 0.5 mol of azobenzene.

The high yields of sulfonamides formed in the reactions of disulfide **2** with amines is consistent with homolytic cleavage of the S–N bond to form two sulfenyl radicals **4**, both of which can rearrange to the sulfonamide. The isolation of azobenzenes **9** and **10** further supports the radical mechanism and the transfer of a hydrogen atom from the amine solvent with the formation of an amino radical.

Disproportionation of hydrazobenzenes (ArNHNHAr) to give amine and azobenzene[7-9] was previously suggested to account for the formation of **9** and **10** in the thermal rearrangement of the corresponding 2-nitrobenzensulfenanilides.[1] The hydrazobenzenes would be formed by dimerization of two aryl amino radicals (ArNH·) formed in the transfer of a hydrogen atom from the amine solvent to **5** (Scheme I). If it is assumed that 1 mol of disulfide **2** results in 0.5 mol of azobenzene, then the yield of **9** (21%) and **10** (16%) are, within experimental error, similar to the yields of **9** and **10** isolated in the rearrangement of the corresponding sulfenamides (*i.e.*, 27 and 18%, respectively[1]).[10]

Displacements at sulfenyl sulfur are well known,[11] and displacements on alkyl sulfenylthiocyanates[12] and disulfides[13] to give sulfenamides have been reported.

$$ArS\text{–}SAr + Ar'NH_2 \longrightarrow ArS\text{–}NHAr' + ArSH$$

Unboubtedly some displacement by the amine solvent on the S–S bond to form the corresponding sulfenamide does take place, since the only plausible way to rationalize the formation of diphenyl sulfides **11a,b** and **13a,b** is *via* the sulfenamide. Phenothiazine **12** is formed by a Smiles rearrangement of **13a**.[14]

However, it is unlikely that the major pathway for the formation of the sulfonamides is *via* the sulfenamide. This becomes quite clear when the ratio of the yields of phenothiazine and nitroaminodiphenyl sulfides to sulfonamide are compared for the rearrangement of disulfide **2** and the corresponding sulfenamide. These results are summarized in Table II. As can be seen from this table, the ratios for the disulfide rearrangement are much less than those obtained for the corresponding sulfenamide.[1] These results indicate that the major pathway for formation of the sulfonamides is not *via* the sulfenamides.

TABLE II

RATIOS OF THE YIELDS OF PHENOTHIAZINE AND NITROAMINODIPHENYL SULFIDES TO SULFONAMIDES

Solvent	Sulfenamide[a]	Disulfide
Aniline	0.54	0.15 (**11a** + **11b**/**1a**)
p-Toluidine	0.58	0.14 (**12** + **13a**/**1b**)
2,4-Dichloroaniline	2.18	0.26
N-Methylaniline	0.19	*b*

[a] From ref 1. [b] Phenothiazine and nitroaminodiphenyl sulfide not isolated.

Finally, the rearrangement of **2** with alkyl and aryl primary and secondary amines to give high yields of 2-aminobenzenesulfonamides appears to have some synthetic utility. The alternate route to these sulfonamides is *via* a two-step synthesis: condensation of 2-nitrobenzenesulfonyl chloride with the amine to give the nitrobenzenesulfonamide followed by reduction of the nitro group.

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(7) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).
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(9) H. Wieland and E. Schamberg, *Ber.*, **53**, 1329 (1920).
(10) The sulfenamide may form aryl amino radicals in two ways: (i) homolytic cleavage of the S–N bond; (ii) transfer of a hydrogen atom from the amine solvent to **5**.
(11) For a review see E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).
(12) R. T. Major and L. H. Peterson, *J. Amer. Chem. Soc.*, **78**, 6181 (1956).
(13) M. Busch, *Ber.*, **29**, 2127 (1896).
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The yields are often low *via* the latter synthetic route. For example, the synthesis of sulfonamide **1e** *via* this route was only 7%.[1] The reaction of **2** with 2-aminobiphenyl, however, gave **1e** in greater than 51% yield.

Experimental Section

Solvents were purified according to procedures given in the literature. Melting points were obtained on a Fisher-Johns melting point apparatus. Proton nmr spectra were measured on a Varian A-60A instrument. Infared spectra were measured on a Perkin-Elmer 457 spectrometer.

General Procedure for Thermal Rearrangement of Bis(2-nitrophenyl) Disulfide (2) with Amines.—Disulfide **2** was heated with an excess of the primary or secondary alkyl or aryl amine in a sealed tube at 195° in an oil bath for 15.5 hr. Excess solvent was removed either by distillation (vacuum pump) or sublimation and the resulting dark residue was dissolved in chloroform and filtered. The filtrate was chromatographed on Florisil unless otherwise noted. Samples isolated from the column were washed with pentane or methanol and dried for at least 12 hr at high vacuum. Products were identified by comparison of their properties with those of authentic samples.

Aniline.—Disulfide **2** (0.174 g, 0.000565 mol) in aniline gave on elution with pentane–benzene (3:2) 0.004 g (3%) of a yellow solid, mp 86° (lit.[15] mp 85°), identified as **2-amino-2′-nitrodiphenyl sulfide (11a)**. Further elution with pentane–benzene (3:2) gave 0.01 g (7%) of a yellow solid, mp 102° (lit.[16] mp 102–103°), identified as **4-amino-2′-nitrodiphenyl sulfide (11b)**. 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 0.181 g (65%) of white crystals, mp 119° (lit.[17] mp 119°), identified as **2-aminobenzenesulfonanilide (1a)**.

***p*-Toluidine.**—Disulfide **2** (0.174 g, 0.000654 mol) in *p*-toluidine gave on elution with pentane–benzene (3:2) 0.007 g (6%) of a white solid, mp 167–168° (lit.[18] mp 168°), identified as **3-methylphenothiazine (12)**. Further elution with pentane–benzene (3:2) gave 0.008 g (5%) of red crystals, mp 87° (lit.[1] mp 87°), identified as **2-amino-5-methyldipenyl sulfide (13a)**. Elution with chloroform gave a brown oil which, when treated with sodium hydroxide solution followed by neutralization and cooling, gave 0.227 (77%) of white crystals, mp 124–125° (lit.[19] mp 124°), identified as **2-aminobenzenesulfon-*p*-toluidide (1b)**.

***p*-Anidisine.**—Disulfide **2** (0.205 g, 0.000664 mol) in *p*-anisidine gave on elution with pentane–benzene (3:2) 0.017 g (21%) of a yellow solid, mp 164–165° (lit.[20] mp 164°), identified as ***p*-methoxyazobenzene (9)**. Elution with chloroform gave a brown oil, which was treated with potassium hydroxide solution and water, and the aqueous solution was extracted with ether. The aqueous washings were carefully neutralized with 5% hydrochloric acid solution and on cooling overnight gave 0.297 g (81%) of white crystals, mp 123–124° (lit.[1] mp 123°), identified as **2-aminobenzenesulfon-*p*-anisidine (1c)**.

2,4-Dichloroaniline.—Disulfide **2** (0.168 g, 0.00054 mol) in 2,4-dichloroaniline gave on elution with pentane–benzene (1:1) 0.1122 g (67%) of a yellow solid, mp 193° (lit.[21] mp 193°), identified as **bis(2-nitrophenyl) disulfide (2)**. Elution with pentane–benzene (1:1) gave 0.01 g (6%) of a yellow solid, mp 198° (lit.[1,22] mp 198°), identified as **2-amino-3,5-dichloro-2′-nitrodiphenyl sulfide (13b)**. Elution with chloroform gave a brown oil which was sublimed at 120° (0.1 mm) to give 0.0785 g (23%) of white needles, mp 106° (lit.[23] mp 108°), identified as **2-aminobenzenesulfon-2,4-dichloroanilide (1d)**.

2-Aminobiphenyl.—Disulfide **2** (0.2258 g, 0.000733 mol) in 2-aminobiphenyl was chromatographed on neutral alumina. Elution with pentane gave an orange solid which was sublimed (80° 0.1 mm) to give 0.020 g (16%) of an orange-red solid, mp 137–138° (lit.[24] mp 136–139°), identified as **2-phenylazobenzene (10)**. Elution with pentane–benzene (1:1) gave 0.05 g (27%) of a yellow solid, mp 193 (lit.[21] mp 198°), identified as disulfide **2**. Elution with chloroform gave a brown oil which was alternately washed with 10% 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 an oil which was extracted into ether. The ether solution was dried over $MgSO_4$ and on removal gave 0.240 g (51%) of an oil which was identified as **2-aminobenzenesulfon(2-phenyl)anilide (1e)**.[1]

***n*-Decylamine.**—Disulfide **2** (0.218 g, 0.00071 mol) in *n*-decylamine gave on elution with pentane–benzene two minor fractions isolated as an oil which were not identified. Elution with chloroform gave a brown oil which was sublimed at 120° (0.1 mm) to give white crystals, mp 48–49°, identified as **2-aminobenzenesulfon-*n*-decylamide (1f)**.

2-Aminobenzenesulfon-*n*-decylamide (1f).—Compound **1f** was prepared by reduction of the corresponding 2-nitrobenzenesulfonamide as previously described.[1] The crude sulfonamide (5.0 g, 0.0146 mol) in ethanol gave 4.1 g (90%) of a white solid which was crystallized from pentane–ether to give white needles, mp 48°.

Anal. Calcd for $C_{16}H_{28}N_2O_2S$: C, 61.54; H, 8.97. Found: C, 61.77; H, 9.12.

Sulfonamide **1f** has the following properties: infrared (KBr) 3500 (m), 3400 (m), 3290 (s), 2930 (s), 2860 (m), 1615 (s), 1540 (w), 1480 (s), 1430 (m-w), 1380 (w), 1320 (s), 1145 (s), 1070 (s), 1020 (m-w), 890 (m), 860 (w), 845 (w), 755 (s), 720 (w), 700 (m), 610 (m), 575 (w), and 525 cm^{-1} (m); nmr ($CDCl_3$) δ 0.9 (m, 3 H), 1.2 (s, 16 H), 2.9 (q, 2 H), 4.7 (broad s, 2 H), 6.7–7.5 (m, 4 H), and 7.7 (m, 1 H).

***N*-Methylaniline.**—Disulfide **2** (0.50 g 0.00163 mol) in *N*-methylaniline was chromatographed on basic alumina. Elution with chloroform gave a pale brown oil which was purified by molecular distillation at 50° (0.05 mm) to give 0.670 g (78%) of a colorless oil identified as **2-aminobenzenesulfon-*N*-methylanilide (8a)**.

Diisobutylamine.—Disulfide **2** (0.350 g, 0.0011 mol) in diisobutylamine gave on elution with pentane–benzene two minor fractions isolated as oils which were not identified. Elution with chloroform gave a brown oil which was purified by molecular distillation at 110° (0.5 mm) to give 0.48 g (74%) of a colorless oil identified as **2-aminobenzenesulfondiisobutylamide (8b)**.

2-Aminobenzenesulfondiisobutylamide (8b).—Compound **8b** was prepared as previously described by reduction of the corresponding 2-nitrobenzenesulfonamide.[1] The crude sulfonamide (5.0 g, 0.016 mol) in ethanol gave an oil which was purified by molecular distillation at 110° (0.5 mm).

Anal. Calcd for $C_{14}H_{24}N_2O_2S$: C, 59.15; H, 8.45. Found: C, 58.97; H, 8.33.

Sulfonamide **8b** had the following properties: infrared (thin film) 3480 (s), 3380 (s), 3200 (w), 2960 (s), 1610 (s), 1470 (s), 1390 (m), 1320 (s), 1140 (s), 1090 (m), 1005 (s), 960 (w), 940 (w), 920 (w), 870 (m), 840 (m), 815 (w), 750 (s), and 690 cm^{-1} (m); nmr ($CDCl_3$) δ 0.9 (d, 12 H), 1.9 (m, 2 H), 3.0 (d, 4 H), 5.1 (broad s, 2 H), and 6.6 to 7.7 (m, 4 H).

Registry No.—**1f**, 33214-32-3; **2**, 1155-00-6; **8b**, 33214-34-5.

Acknowledgment.—We thank Mr. E. W. Kluger for the synthesis of **8b**.

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