4-Chlorobenzenesulfenanilide (5c) *via* the Silver Nitrate Method.[10]—In a 500 ml three-necked flask equipped with magnetic stir bar and nitrogen inlet was dissolved 0.59 g (0.0035 mol) of silver nitrate in 150 ml of absolute ethyl alcohol. To the reaction mixture was added 1.0 g (0.0035 mol) of bis(4-chlorophenyl) disulfide (Columbia Organic Chemicals Co.) in 150 ml of absolute ethyl alcohol. The reaction mixture was allowed to stirr for about 5 min, and 1.3 g (0.014 mol) of aniline was added, and the reaction mixture was allowed to stir under nitrogen for 48 hr. The precipitated salts were filtered from the gray solution, solvent was removed, and the residue was dissolved in ether and filtered. The ether solution was washed twice with 100-ml portions of water and dried over $MgSO_4$. Removal of the solvent gave a solid, which when crystallized from ether–pentane gave 0.46 g (60%) of **5c** as white needles: mp 86–88° (lit.[22] mp 84°); ir 3380 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.1 (m, 9) and 5.05 (broad s, 2, NH_2).

(22) H. Tielecke and A. Jumer, East German Patent 17,675 (1959); *Chem. Abstr.*, **55**, P892i (1961).

Registry No.—**5a**, 14933-92-7; **5b**, 14933-91-6; **5c**, 14933-94-9; **5d**, 32338-03-7; **5e**, 27332-21-4; **5f**, 5147-60-4; **8a**, 16452-09-8; **8c**, 37750-29-1; **8d**, 3169-86-6; **9a**, 22865-52-7; **9c**, 32631-29-1; **9d**, 37750-33-7; 4-methyl-2′-nitrodiphenyl sulfide, 20912-17-8; 4-methyl-4′-nitrodiphenyl sulfide, 22865-48-1; 4-chloro-2′-nitrodiphenyl sulfide, 6764-10-9; 4-chloro-4′-nitrodiphenyl sulfide, 21969-11-9; 4-bromo-2′-nitrodiphenyl sulfide, 37750-38-2; 4-bromo-4′-nitrodiphenyl sulfide, 21969-12-0; bis(4-chlorophenyl) sulfide, 5181-10-2.

Acknowledgment.—We thank John R. Ertel for preparing **9d**.

Chemistry of the Sulfur–Nitrogen Bond.[1,2] V. Evidence for an Intermolecular Rearrangement in the Rearrangement of Arenesulfenanilides to *o*- and *p*-Aminodiphenyl Sulfides

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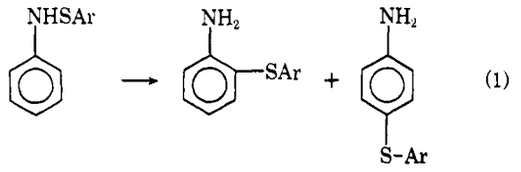
The acid-catalyzed arenesulfenanilide rearrangement has been investigated to determine whether the rearrangement is inter- or intramolecular. The failure of trapping experiments and high ortho/para ratios suggest that the rearrangement is intramolecular. Crossover experiments had little meaning, since sulfenamides exchange with amines. A π-complex or caged radical mechanism, but not a caged ion mechanism, are consistent with these results.

The thermal rearrangement of arenesulfenanilides to 2- and 4-aminodiphenyl sulfides (eq 1) has been established to be quite general.[1] The rearrangement was acid catalyzed and accelerated by electron-donating groups attached to sulfur. Substitution at the para position generally predominated over ortho substitution.



(1)

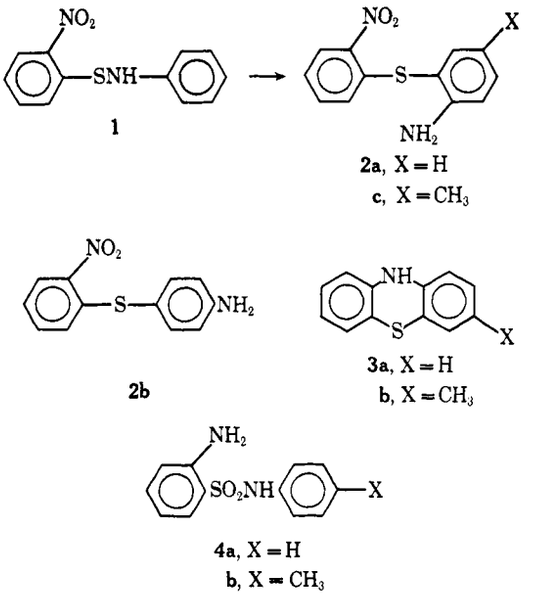
This rearrangement (eq 1) is a member of an important class of N-substituted aminoaromatic rearrangements which include the benzidine, quinamine, and nitramine rearrangements, among others.[4] The benzidine,[5] quinamine,[6] and nitramine[7] rearrangements are specific acid catalyzed and intramolecular.

In this paper we report the results of an investigation to determine whether the rearrangement is inter- or intramolecular. As we shall see, this has not been an easy task.

(1) Part IV: F. A. Davis, E. R. Fretz, and C. J. Horner, *J. Org. Chem.*, **38**, 690 (1973).
(2) Presented in part at the 7th MARM, Philadelphia, Pa., Feb 1972.
(3) (a) National Science Foundation Undergraduate Research Participant, 1971; (b) Undergraduate Research Participant, 1970.
(4) H. J. Shine, "Aromatic Rearrangements," Vol. 6, Elsevier, New York, N. Y., 1967, Chapter 3.
(5) D. H. Smith, J. A. Schwartz, and G. W. Wheland, *J. Amer. Chem. Soc.*, **74**, 2282 (1952).
(6) B. Miller, *ibid.*, **86**, 1127 (1964).
(7) D. V. Banthrope, E. D. Huges, and D. L. H. Williams, *J. Chem. Soc.*, 5349 (1964).

Results and Discussion

In an earlier paper in this series we reported that 2-nitrobenzenesulfenanilide (**1**), when heated in a sealed tube at 190° in aniline, gave aminodiphenyl sulfides **2a** and **2b**, phenothiazine (**3a**), and 2-aminobenzenesulfonanilide (**4a**).[8] With *p*-toluidine as the



solvent **1** gave crossover products **2c**, **3b**, and **4b**.[8] No products from the original sulfenanilide were isolated. Subsequently it was established that phenothiazines

(8) F. A. Davis, R. B. Wetzel, T. J. Devon, and J. F. Stackhouse, *J. Org. Chem.* **36**, 799 (1971).

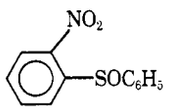
3a,b were formed *via* a thermal Smiles rearrangement of **2a,c**[9] and the sulfonamides, **4a,b**, were formed *via* an intramolecular oxidation–reduction of the 2-nitrobenzenesulfenyl radical formed in homolytic cleavage of the S–N bond.[10,11]

The crossover products isolated when sulfenanilide **1** was heated in *p*-toluidine would appear to be consistent with an intermolecular rearrangement. One possible intermediate would be a sulfenium ion (ArS^+) or ion pair formed by heterolytic cleavage of the S–N bond. The existence of sulfenium ions has been discussed,[12] and they are believed to be intermediates in the formation of diphenyl sulfides from aryl sulfenyl chlorides and aromatic compounds.[13] Since the presence of aniline hydrochloride was found to be necessary for the rearrangement,[1] a sulfenyl chloride, **5**, may also be an intermediate.

$$ArSNHC_6H_5 + C_6H_5NH_3Cl \longrightarrow \underset{\mathbf{5}}{ArSCl} + 2C_6H_5NH_2$$

A sulfenyl radical is a third possibility, since dienesulfenanilides are well known to undergo homolytic cleavage under these conditions.[10,11] Furthermore, the photolysis of phenyl disulfide gave 2- and 4-mercaptodiphenyl sulfides.[14] A sulfenyl radical is an unlikely intermediate, since under the reaction conditions aryl disulfides in the presence of aromatic amines failed to give significant amounts of 2- and 4-aminodiphenyl sulfides.[11,15]

A widely accepted criterion for an intermolecular mechanism is the ability to trap electrophilic intermediates by scavengers such as benzene or anisole. The related thermal rearrangement of phenyl-2-nitrobenzenesulfenate (**6**) to 2- and 4-hydroxy-2′-nitrodiphenyl sulfides (**7a,b**) has been shown to be intermolecular by trapping the intermediate 2-nitrobenzenesulfenium ion with benzene to give **7c**.[16] The trapping of a sulfenium ion by a suitable scavanger in the arenesulfenanilide rearrangement would be evidence for an intermolecular rearrangement.



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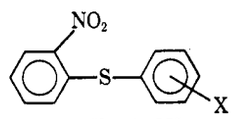


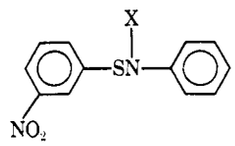
7a, X = 2-OH
b, X = 4-OH
c, X = H

Previous results have shown that the arenesulfenanilide rearrangement (eq 1) is favored in primary and secondary aromatic amine solvents.[1] 3-Nitrobenzenesulfenanilide (**8a**) in aniline gave 27 and 69% yields of aminodiphenyl sulfides **9a** and **10a**, respectively.[1] In *N,N*-diethylaniline or anisole the major product was bis(3-nitrophenyl) disulfide (**11**). These results are summarized in Table I. In anisole 3-nitro-4′-methoxydiphenyl sulfide (**12**), prepared from the corresponding sulfenyl chloride,[17] was not detected by gas chromatography.

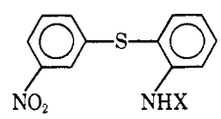
TABLE I
THERMAL REARRANGEMENT OF ARENESULFENANILIDES AT 195° FOR 15.5 HR

Entry	Sulfenanilide[a]	Solvent[b]	Products (yield, %)
1	**8a**[c]	Aniline	**9a** (27), **10a** (69)
2	**8a**	Anisole	**9a** (1), **10a** (4), **11** (74)
3	**8a**	Anisole + $C_6H_5NH_3Cl$[d]	**9a** (32), **10a** (20), **11** (26)
4	**8a**	Anisole + HCl[e]	**9a** (12), **10a** (1), **11** (13), **12** (15)
5	**8a**	*N,N*-Diethylaniline	**10a** (15), **11** (60)
6	**8a**	3-Nitroaniline	**10a** (58)[f]
7	**8a**	2,4-Dichloroaniline	**9a** (~5),[f] **10a** (70)[f]
8	**8a**	*N*-Methylaniline[g]	**10a** (1), **9b** (24), **10b** (75)
9	**8b**	*N*-Methylaniline	**9b** (32), **10b** (53)
10	**8b**	Aniline[h]	**9a** (21), **10a** (42), **9b** (5), **10b** (10)
11	**13a**	Anisole + HCl[e]	**15a** (33), **15a** (27)
12	**13b**	Anisole + HCl[e]	**14b** (23),[c] **15a** (30), **16** (1)
13	**17**	Aniline	**18** (13), **19** (57), **20a** (13), **20b** (29)
14	**17**	Aniline $C_6H_5NH_3Cl$[d]	**20a** (33), **20b** (62)

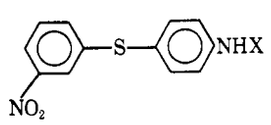
[a] Prepared from the corresponding sulfenyl chloride. [b] Mole ratio of sulfenanilide to solvent, 1:15. [c] Reference 1. [d] Mole ratio of sulfenanilide to aniline hydrochloride, 1:7. [e] See Experimental Section. [f] Isolated yields. [g] Mole ratio of sulfenanilide to *N*-methylaniline, 1:24. [h] Mole ratio of sulfenanilide to aniline, 1:39.



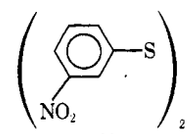
8a, X = H
b, X = CH_3



9a, X = H
b, X = CH_3



10a, X = H
b, X = CH_3



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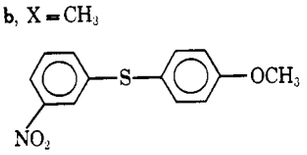


12

The failure to achieve significant rearrangement or to trap intermediates in these solvents may have resulted from a lack of acid catalysis. A molar ratio of sulfenanilide to aniline hydrochloride of 1:7 in anisole substantially increased the yield of rearrangement for sulfenanilide **8a**, but **12** was not formed. It would appear that these results are not consistent with an intermolecular mechanism involving a sulfenium ion, ion pair, or sulfenyl chloride as intermediates.

(9) F. A. Davis and R. B. Wetzel, *Tetrahedron Lett.*, 4483 (1969).
(10) F. A. Davis and R. P. Johnston, II, *J. Org. Chem.*, **37**, 854 (1972).
(11) F. A. Davis and R. P. Johnston, II, *ibid.*, **37**, 859 (1972).
(12) N. Hkarasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 32; see also G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Amer. Chem. Soc.*, **90**, 1635 (1968).
(13) C. M. Buess and N. Kharasch, *J. Amer. Chem. Soc.*, **72**, 3529 (1950); N. Kharasch, *J. Chem. Educ.*, **37**, 585 (1956).
(14) Y. Schaffsma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, **10**, 76 (1960).
(15) E. R. Fretz, unpublished results.
(16) D. R. Hogg, J. H. Smith, and P. W. Vipond, *J. Chem. Soc. C*, 273 (1970).
(17) H. Z. Lecher and F. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955).

An intramolecular rearrangement must therefore be considered. In order to explain the crossover products obtained when **1** was heated in *p*-toluidine[8] an intramolecular rearrangement requires a displacement on the S–N bond by the amine solvent prior to rearrangement (Scheme I). For sulfenanilide **1** in p-toluidine, therefore, $k_1 > k_2$.

SCHEME I

$$\mathrm{ArSNHAr'} + \mathrm{Ar''NH_2} \xrightarrow{K_2} \text{products}$$

$$k_1 \downarrow\uparrow k_{-1}$$

$$\mathrm{ArSNHAr''} + \mathrm{Ar'NH_2} \xrightarrow{K_3} \text{products}$$

Arene sulfenanilides have been shown to undergo a facile exchange with aromatic amine solvents under relatively mild conditions.[18] Electron-withdrawing groups attached to sulfur[18] and electron-donating groups attached to the sulfenamide nitrogen[19] were observed to slow the exchange. Rearrangement was favored by electron-donating groups on sulfur.[1]

A test of the hypothesis that arenesulfenanilides exchange with the solvent and rearrange *via* an intramolecular mechanism according to Scheme I would be the isolation of noncrossover products and mixtures of crossover and noncrossover products when K_3 and/or k_1 are slowed. This may be achieved by proper choice of sulfenanilide and arylamine solvent.

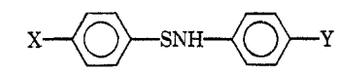
3-Nitrobenzenesulfen-*N*-methylaniline (**8b**), prepared from the corresponding sulfenyl chloride[18] and *N*-methylaniline, rearranges in *N*-methylaniline to give aminodiphenyl sulfides **9b** and **10b** in 32 and 53% yields. In aniline, at a mole ratio of **8b** to aniline of 1:39, sulfenanilide **8b** gave four products: crossover products **9a** and **10a** in 21 and 42% yield and the noncrossover products **9b** and **10b** in 5 and 10% yields (entry 10, Table I). If the rearrangement had been intermolecular, under these conditions only a total of 2.5% of the noncrossover products should have been isolated. It can be argued, however, that the high yield of noncrossover products resulted from the slightly greater nucleophilicity of the *N*-methylaniline compared to aniline. More conclusive evidence for Scheme I was obtained when **8a** was rearranged in *N*-methylaniline. At a molar ratio of 1:24 (sulfenamide to *N*-methylaniline), if the rearrangement were intermolecular, about 4% of the noncrossover products would be expected. Less than 1% of noncrossover products were detected (entry 8, Table I). In 2,4-dichloroaniline or 3-nitroaniline sulfenamide **8a** gave only noncrossover products **9a** and **10a** (entries 6 and 7, Table I).

These results are readily explained in terms of Scheme I. The *N*-methyl group in **8b** slows exchange and may accelerate rearrangement. The rate of exchange is accelerated when *N*-methylaniline is the solvent. With 2,4-dichloroaniline, which is known to exchange with **8a**,[18] or 3-nitroaniline as the solvent the rate of exchange is slowed and $K_2 > K_3$.

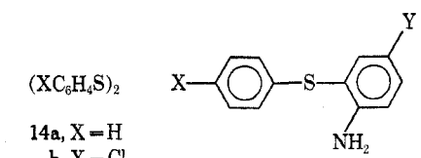
A second generally used method for determining the inter- or intramolecularity of a rearrangement is the use of crossover experiments. Two closely related reactants are rearranged together. If crossover products are obtained the rearrangement is said to be intermolecular.

The arenesulfenanilide rearrangement is favored in aryl amine solvents. However, the use of such solvents for crossover experiments would have little meaning, since sulfenamides exchange with aryl amines.[18] A similar objection applies to the use of anisole and amine hydrochlorides as a solvent system.

Anisole containing gaseous hydrogen chloride suggests that it may be a useful solvent for effecting the arenesulfenanilide rearrangement. Sulfenanilide **8a** in anisole HCl gave, in addition to disulfide **11**, 2-aminodiphenyl sulfide (**9a**) and 3-nitro-4′-methoxydiphenyl sulfide (**12**) as major products. Less than 1% of the 4-aminodiphenyl sulfide **10a** was detected (entry 4, Table I). Similar results were obtained for sulfenanilides **13a,b** which gave disulfides, (**14a,b**), 2-aminodiphenyl sulfides (**15a,b**), and 4-chloro-4′-methoxydiphenyl sulfide (**16**).

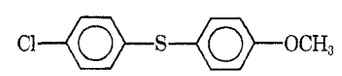


13a, X = H; Y = CH_3
b, X = Cl; Y = H



14a, X = H
b, X = Cl

15a, X = H; Y = CH_3
b, X = Cl; Y = H



16

Sulfenamides are cleaved by hydrogen chloride to the sulfenyl chloride and amine.[20] Apparently the anisole HCl solvent cleaves the S–N bond in the sulfenanilide to give the corresponding sulfenyl chloride. The sulfenyl chlorides attack the solvent to give **12** and **16**, and react with the amine to give a sulfenamide which rearranges or attacks the amine directly to give the 2- and 4-aminodiphenyl sulfides. It is evident from these results that anisole HCl is also unsatisfactory for crossover experiments.[21]

The fact that sulfenanilides **8a** and **13b** and crossover experiments[21] gave almost exclusively the 2-aminodiphenyl sulfides in anisole HCl supports an intramolecular rearrangement under these conditions. A sulfenyl chloride (or sulfenium ion) would be expected to produce more of the 4-aminodiphenyl sulfide if the rearrangement had been intermolecular. The exclusive formation of 3-nitro- and 4-chloro-4′-methoxydiphenyl sulfides (**12** and **16**) tends to support this conclusion. High ortho to para ratios have also been used as evidence for intramolecular rearrangements.[7,23] The observation that the ortho/para ratio increased on addition of aniline hydrochloride to aniline[1] and anisole

(18) F. A. Davis, S. Divald, and A. H. Confer, *Chem. Commun.*, 678 (1971).

(19) F. A. Davis and J. M. Kaminski, manuscript in preparation.

(20) For a recent review see A. Fontana and E. Scoffone, *Mech. React. Sulfur Compounds*, **4**, 14 (1969).

(21) A crossover experiment with sulfenanilides **13a,b** and anisole HCl gave a complex mixture of products which could not be quantitatively analyzed by glc. As expected, crossover 2-aminodiphenyl sulfides were identified in the reaction mixture. However, the 4-aminodiphenyl sulfides were apparently not formed.

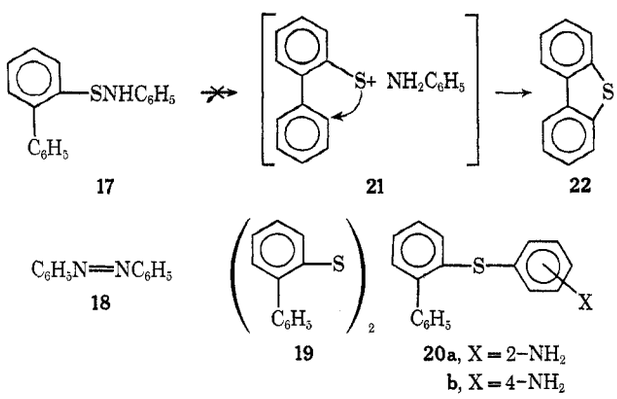
(entry 3, Table I) and the lack of solvent crossover products also supports an intramolecular rearrangement under these conditions.

Despite our inability to obtain more conventional tests for an intramolecular arenesulfenanilide rearrangement the experimental results are in agreement with an intramolecular rearrangement. Assuming then that the rearrangement is intramolecular, it is possible to speculate as to possible mechanisms and to eliminate one possibility.

Previous results suggested that the conjugate acid of the sulfenamide was involved in the transition state for rearrangement and that sulfur was electron deficient.[1] It was not possible to specify whether or not the rearrangement was specific or general acid catalyzed.[1]

At least two types of mechanisms are consistent with the experimental results: the caged radical or caged ion mechanisms and the π-complex mechanism.[22] The first mechanism involves either homolytic or heterolytic cleavage of the conjugate acid of the sulfenanilide to form a radical ($ArS\cdot + H_2NAr$) or ion ($ArS^+ H_2NAr$) in the solvent cage. Recombination of the sulfenyl radical or sulfenium ion in the solvent cage at the positions of highest electron density of the amine fragment would result in the formation of the observed products intramolecularity.

The solvent-caged ion mechanism may, however, be eliminated by the following experimental results. Sulfenanilide **17** prepared from the corresponding sulfenyl chloride and aniline gave, on heating in aniline, four products: azobenzene (**18**), disulfide **19**, and 2- and 4′-aminodiphenyl sulfides, **20a** and **20b**, in 13 and 29% yields, respectively. If a solvent-caged ion, **21**, were involved in the rearrangement of **17** to **20a,b**, some intramolecular combination of this ion to dibenzothiopene (**22**) would have been anticipated. Dibenzothiophene (**22**) was not detected by gas chromatography. Even in the presence of added aniline hydrochloride, which increased rearrangement to nearly 100% **22** was not detected. In a separate experiment 2-phenylbenzenesulfenyl chloride with a trace of anhydrous aluminum chloride gave a greater than 45% yield of **22**.



The π-complex mechanism as advocated by Dewar[22] is also consistent with the experimental results. This mechanism involves the formation of a π-complex between the electron-deficient leaving group (ArS) and the aromatic π system. A series of 1,2 shifts would result in the observed products. One objection to the π-complex mechanism has been the lack of 3-substituted products,[4] and 3-aminodiphenyl sulfides have never been isolated in the arenesulfenanilide rearrangement. As Dewar points out, however, ortho and para substitution are greatly favored by this mechanism over meta substitution.[22]

(22) M. J. S. Dewar in "Molecular Rearrangements," P. De Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 5.

Experimental Section

Sulfenanilides **8a**,[8] **13a**,[19] and **13b**[1] were prepared from the corresponding sulfenyl chloride unless otherwise noted. Melting points were obtained on a Fisher-Johns apparatus. Proton nmr spectra were measured on a Varian A-60A instrument. Infrared spectra were measured on a Perkin-Elmer 457 spectrometer. Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph using a 3% OV-17 on 80/100 mesh Chromosorb W (regular) column. Solvents were purified according to literature procedures.

General Procedure for Thermal Rearrangement of Arenesulfenanilides.—The sulfenanilides (approximately 0.008 mol) were heated in an oil bath with an excess of solvent (mole ratio of sulfenanilide to solvent, 1:15) at 195° in sealed tubes. The reaction mixture was diluted with methylene chloride and filtered, and a known weight of standard was added and analyzed by glc by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice and the values were averaged. Anisole HCl solvent was prepared by bubbling dry HCl at a controlled rate into 5 ml of anisole. After the reaction of the arenesulfenanilide in this solvent had taken place, the reaction mixture was diluted with methylene chloride, washed with 10% sodium hydroxide solution and twice with water, and dried over $MgSO_4$. The dried solution was analyzed as described above.

3-Nitrobenzenesulfen-*N*-methylanilide (8b).—3-Nitrobenzenesulfenyl chloride,[17] prepared from 3-nitrophenyl disulfide (**11**) (10.0 g, 0.032 mol) and dry chlorine gas in 100 ml of dry methylene chloride, was added dropwise over 1 hr to *N*-methylaniline (6.8 g, 0.064 mol) and triethylamine (9.7 g, 0.096 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. After addition the yellow solution was allowed to stir for an additional 0.5 hr at −78°; 100 ml of *n*-pentane was added and the solution was allowed to warm to 0°. After the precipated salts were filtered off the filtrate was washed with water, 2 × 50 ml, and dried over $MgSO_4$. Removal of the solvent gave a yellow oil which was dissolved in ether–pentane and cooled to −78°, and the yellow solid was collected. Crystallization from *n*-pentane give 6.0 g (36%) of yellow plates: mp 48–49°; nmr ($CDCl_3$) δ 3.6 (s, 3, NCH_3), 7.5 (m, 7), and 8.1 (m, 2).

Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 60.00; H, 4.61. Found: C, 60.12; H, 4.74.

Bis(2-phenyl)phenyl Disulfide (19).—2-Mercaptobiphenyl,[23] 10.0 g (0.054 mol), was treated with 10 ml of 10% sodium hydroxide solution and 10 ml of 10% hydrogen peroxide in 100 ml of 1:1 alcohol–water. The white solid was collected and crystallized from ether to give 5.1 g (51%) of white plates: mp 114–116°; nmr ($CDCl_3$) δ 7.2 (m, 3), 7.35 (s, 5), and 7.6 (m, 1).

Anal. Calcd for $C_{24}H_{18}S_2$: C, 72.84; H, 4.86. Found: C, 72.66; H, 4.91.

2-Phenylbenzenesulfenanilide (17).—Sulfenanilide **17** was prepared by addition of 2-phenylbenzenesulfenyl chloride, prepared from 2.0 g (0.0054 mol) of the disulfide in 50 ml of methylene chloride and chlorine, to 2.0 g (0.021 mol) of aniline in 1:1 ether–DMAC at −78° as described above. The crude sulfenanilide was purified by column chromatography on neutral alumina (elution with pentane) to give a white solid, which was crystallized from pentane to give 0.4 g (13%) of white crystals: mp 86–88°; ir (KBr) 3380 cm^{-1} (s, NH); nmr ($CDCl_3$) δ 7.3 (m, 14) and 4.9 (s, 1, NH).

Anal. Calcd for $C_{18}H_{15}NS$: C, 77.98; H, 5.42. Found: C, 77.83; H, 5.31.

General Procedure for Synthesis of 2- and 4-Aminodiphenyl Sulfides.—The 2- and 4-aminodiphenyl sulfides were prepared

(23) D. D. Emrich and W. E. Truce, *J. Org. Chem.*, **25**, 1103 (1960).

as previously described by reduction of the corresponding 2- and 4-nitrodiphenyl sulfides.[1]

2-Amino-5-methyldiphenyl Sulfide (15a).—Reduction of 5.0 g of the nitrodiphenyl sulfide gave an oil which was distilled, bp 125–128° (0.3 mm), to give 1.5 g (35%) of a clear oil which darkened on standing: ir (thin film) 3360 and 3460 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 2.1 (s, 3, NCH_3), 3.9 (s, 2, NH_2), 6.5 (d, 1), and 7.0 (m, 7).

Anal. Calcd for $C_{13}H_{13}NS$: C, 72.56; H, 6.04. Found: C, 72.80; H, 6.24.

2-Phenyl-2′-aminodiphenyl Sulfide (20a).—DMAC was used in the place of ethanol to prepare the nitrodiphenyl sulfide.[1] Reduction of 2.0 g of the nitrodiphenyl sulfide gave, after molecular distillation at 110° (0.1 mm), 0.8 g (43%) of an oil: ir (thin film) 3380 and 3480 cm^{-1} (s, NH_2); nmr ($CDCl_3$) δ 3.8 (s, 2, NH_2) and 7.2 (m, 13).

Anal. Calcd for $C_{18}H_{15}NS$: C, 77.98; H, 5.42. Found: 77.90; H, 5.53.

2-Phenyl-4′-aminodiphenyl Sulfide (20b).—DMAC was used in the place of ethanol to prepare the nitrodiphenyl sulfide.[1] Reduction of 2.4 g of the nitrodiphenyl sulfide gave, after molecular distillation at 100° (0.1 mm), 0.7 g (33%) of an oil which solidified on standing after several weeks: mp 58–60°; ir (thin film) 3400 and 3480 cm^{-1} (m, NH_2); nmr ($CDCl_3$) δ 3.5 (s, 2, NH_2) and 7.0 (m, 13).

Anal. Calcd for $C_{18}H_{15}NS$: C, 77.98; H, 5.42. Found: C, 77.77; H, 5.48.

3-Nitro-4′-methoxydiphenyl Sulfide (12).—Into a 250-ml three-necked flask equipped with magnetic stir bar and nitrogen inlet was placed 10.0 g (0.032 mol) of 3-nitrophenyl disulfide (11) in 100 ml of dry methylene chloride. Dry chlorine gas was passed through the solution for 10 min, followed by dry nitrogen for 20 min. The sulfenyl chloride was cooled to 0° and 10.0 g of anhydrous aluminum chloride followed by 13.8 g (0.128 mol) of anisole were added. The reaction mixture was allowed to stir overnight under nitrogen; 10 ml of ethyl alcohol was added followed by 100 ml of water. The organic layer was separated and dried over $MgSO_4$. Solvent was removed under vacuum (first water pump and then oil pump) to give a dark oil which was chromatographed on Florisil. Elution with pentane–benzene gave a yellow solid which was crystallized from ether–pentane to give 1.6 g (10%) of yellow plates: mp 56–57°; ir (Nujol) 1250 cm^{-1} (s, ether); nmr ($CDCl_3$) δ 3.8 (s, 3, OCH_3), 6.85 (d, 2, J = 9 Hz), 7.1 (s, 4), and 7.35 (d, 2, J = 9 Hz).

Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 62.39; H, 4.41. Found: C, 62.14; H, 4.53.

Thermal Rearrangement of 3-Nitrobenzenesulfen-*N*-methylanilide (8b).—Sulfenanilide **8b** (0.1968 g, 0.00076 mol) in aniline (1.1 g, 0.011 mol) was heated as previously described in a sealed tube. Excess solvent was removed (oil pump) and the dark residue was chromatographed on Florisil. Elution with pentane–benzene gave 0.039 g (20%) of an oil identified as 3-nitro-2′-*N*-methylaminodiphenyl sulfide (**9b**): glc–mass spectrum M 260; ir (thin film) 3400 cm^{-1} ($NHCH_3$); nmr ($CDCl_3$) δ 2.9 (s, 3, NCH_3), 4.8 (broad s, 1, NH), 7.4 (m, 4), and 7.9 (m, 2). Further elution with pentane–benzene gave a yellow solid, which when crystallized from pentane–ether gave 0.12 g (61%) of a yellow solid, mp 82–84°, identified as 3-nitro-4′-*N*-methylaminodiphenyl sulfide (**10b**): ir (KBr) 3420 cm^{-1} (s, NH); nmr ($CDCl_3$) δ 2.9 (s, 3, NCH_3), 4.0 (broad s, 1, NH), 6.6 (d, 2), 7.3 (m, 4), and 7.9 (m, 2).

Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 60.00; H, 4.61. Found: C, 59.97; H, 4.66.

Thermal Rearrangement of 3-Nitrobenzenesulfenanilide (8a) in 2,4-Dichloroaniline.—Sulfenanilide **8a** (0.2019 g, 0.00082 mol) was heated in 2.0 g (0.0123 mol) of 2,4-dichloroaniline in a sealed tube. The excess solvent was removed by sublimation (40°, 0.05 mm) and the dark residue was chromatographed on Florisil. Elution with pentane gave a yellow solid which was sublimed (40°, 0.5 mm) to give 0.01 g (5%) of yellow needles, mp 62–64° (lit.[8] mp 63–64) identified as **9a**. Further elution with pentane–benzene gave a solid which was washed with *n*-pentane to give 0.14 g (70%) of a yellow solid, mp 130–132° (lit.[8] mp 130–131°), identified as **10a**.

Thermal Rearrangement of 3-Nitrobenzenesulfenanilide in 3-Nitroaniline.—Sulfenanilide **8a** (0.1964 g, 0.0008 mol) in 3-nitroaniline (1.66 g, 0.012 mol) was treated as described above. Solvent was removed by sublimation (55°, 0.05 mm) and the dark residue was chromatographed on Florisil. Elution with pentane–benzene gave a solid which was washed with *n*-pentane to give 0.115 g (58%) of a yellow solid, mp 130–131° (lit.[8] mp 130–131°), identified as **10a**.

Dibenzothiophene (22) from 2-Phenylbenzenesulfenyl Chloride.—Into a 250-ml three-necked flask equipped with magnetic stir bar and nitrogen inlet was placed 0.20 g (0.00054 mol) of bis(2-phenyl)phenyl disulfide (19) in 150 ml of *n*-pentane. Dry chlorine gas was passed through the solution for 10 min followed by dry nitrogen for 10 min. The sulfenyl chloride was cooled to 0° and *ca.* 30 mg of anhydrous aluminum chloride was added; the reaction mixture was refluxed for 48 hr, and 10 ml of ethyl alcohol was added. The reaction mixture was washed twice with water and dried over $MgSO_4$. Removal of the solvent gave an oil which was analyzed by gas chromatography, as described above, to give a 45% yield of dibenzothiophene (22).

Registry No.—**8a**, 37332-21-4; **8b**, 37692-03-8; **9b**, 37692-04-9; **10b**, 37692-05-0; **11**, 37755-03-6; **12**, 37692-06-1; **13a**, 14933-93-8; **13b**, 14933-94-9; **15a**, 37692-09-4; **17**, 37692-10-7; **19**, 19813-97-9; **20a**, 2688-98-4; **20b**, 37692-13-0; 3-nitrobenzenesulfinyl chloride, 37692-14-1; *N*-methylaniline, 100-61-8; 2-mercaptobiphenyl, 2688-96-2; 2-phenylbenzenesulfenyl chloride, 37692-16-3.