ethoxide, other conditions being the same as the general procedure. After evaporation of the solvent from the benzene extract, bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)phenylmethane (6) was obtained as white crystals, yield 1.63 g (65%), mp 161–162° (lit.[3] mp 161–163°).

When potassium hydroxide was used as a base, 1.49 g (60%) of 6 was obtained.

Reaction of 2,6-Dialkylphenols 7 and 8 with Aryl Disulfide.—The reaction was conducted in the same manner as the general procedure using 2,6-di-*tert*-butylphenol. The base used in the reaction was sodium ethoxide. The separation and purification was achieved by column chromatography on silica gel and preparative glpc. The yields of the products, 4-arylthio-2,6-dialkylphenols (9 and 10), are summarized in Table I.[24]

Procedure of Kinetic Runs. A. Reaction of 1 with 2.—In a typical experiment, an ethanol solution (25 ml) of 1 (1.25 mmol) and 2 (0.50 mmol) in a stoppered ampoule was flushed with argon and placed in a constant-temperature bath at 50.0°. An ethanolic sodium ethoxide solution (0.50 *N*, 25 ml) at the same temperature was added to the above solution. A 1-ml aliquot of the resulting solution was pipetted out at definite intervals and poured into a mixture of benzene (2 ml) and 1 *N* hydrochloric acid (5 ml). The amount of 3 in the benzene layer was determined by glpc. The initial rate was determined graphically from the yield of 3 *vs.* time. This rate was confirmed to be the same as that of the consumption of 2 within experimental error (5%).

B. Reaction of 2 with Potassium Hydroxide.—An ethanol solution (25 ml) of 2 (0.50 mmol) and an ethanolic potassium hydroxide solution (0.50 *N*, 25 ml) were treated in the same manner as described above. In this reaction, the rate was determined from the consumption of 2: $-d[2]/dt = k[2][KOH]$.

Registry No.—1, 128-39-2; 2a, 5335-87-5; 2b, 103-19-5; 2c, 882-33-7; 2d, 1142-19-4; 2e, 5335-84-2; 2f, 6386-58-9; 3a, 32551-11-4; 3b, 32551-15-8; 3c, 32551-12-5; 3d, 32551-13-6; 3e, 32551-14-7; 3f, 4673-51-2; 7, 2219-82-1; 8, 2078-54-8; 9a, 37610-74-5; 9c, 37610-75-6; 9e, 37610-76-7; 10a, 37610-77-8; 10c, 37610-78-9; 10e, 37610-79-0; bis(*p*-nitrophenyl) disulfide, 100-32-3.

Acknowledgment.—We are grateful to the Kawakami Memorial Foundation for partial support of this research.

Chemistry of the Sulfur–Nitrogen Bond. IV.[1,2] The Effects of Nuclear Substitution, Solvent, Temperature, and Time on the Rearrangement of Arenesulfenanilides to *o*- and *p*-Aminodiphenyl Sulfides

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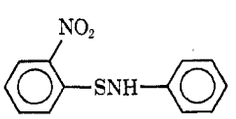
The scope and limitations of the thermal rearrangement of arenesulfenanilides to 2- and 4-aminodiphenyl sulfides has been investigated. Arenesulfenanilides undergo two thermal reactions: disproportionation to give aryl disulfides and azobenzenes and rearrangement to 2- and 4-aminodiphenyl sulfides. Electron-withdrawing groups favor rearrangement as does the addition of aniline hydrochloride. Electron-donating groups accelerate the rate of rearrangement. The effects of nuclear substitution, solvent, temperature, and time on the composition of the reaction products are discussed.

Compounds containing the sulfur–nitrogen bond are of considerable importance both from a practical as well as a theoretical standpoint. An understanding of the chemistry of sulfenamides is important in elucidating the various types of interaction possible between adjacent sulfur and nitrogen. At least three types of interactions may be considered: lone-pair interactions resulting from the presence of lone pairs of electrons on sulfur and nitrogen; bond polarization resulting from the difference in electronegativity between sulfur and nitrogen; and the donation of electrons from nitrogen to sulfur (p–d π bonding).

There is considerable evidence in support of some sort of electron donation from nitrogen to sulfur in the ground state of arenesulfenanilides which affects both torsional barriers[4] and displacement reactions at the S–N bond.[5] However, the extent to which this effect, as well as the other effects, determine reactions of sulfenamides is less well understood.

Recently, we reported an unusual thermal reaction for 2-nitrobenzene sulfenanilide (1).[6] When heated in aniline at 200°, 1 gave 2- and 4-aminodiphenyl sulfides (2a–b), phenothiazine (3), and 2-aminobenzenesulfonanilide (4). It was inferred at that time that arenesulfenanilides undergo two types of reactions: rearrangement to 2- and 4-aminodiphenyl sulfides and disproportionation to give amino and sulfenyl radicals.[6]



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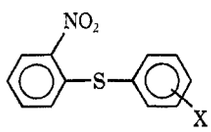
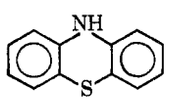


2a, X = 2-NH_2
b, X = 4-NH_2



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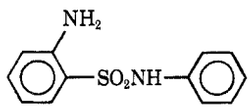

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Subsequently it was shown that the 2-nitrobenzenesulfenyl radical resulting from the disproportionation reaction underwent an intramolecular oxidation–reduc-

(1) Part III: F. A. Davis and R. P. Johnston II, *J. Org. Chem.*, **37**, 859 (1972).

(2) Presented in part at the 7th MARM, Philadelphia, Pa., Feb 1972.

(3) National Science Foundation Undergraduate Research Participant, 1971.

(4) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 2692 (1971).

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

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

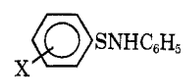
tion to give **4**.[7] Phenothiazine (**3**) resulted from a thermal Smiles rearrangement of **2a**.[8] It was also established that aminodiphenyl sulfides **2a, b** were not formed in the disproportionation reaction.[1]

An understanding of the arenesulfenanilide rearrangement mechanism is important in determining the contributions of the various types of interaction between sulfur and nitrogen to the chemistry of sulfenamides. Furthermore, this rearrangement is a member of an important class of N-substituted aminoaromatic rearrangements which include the benzidine, quinamine, and nitramine rearrangements, among others.[9]

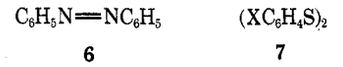
An understanding of this rearrangement must first be based upon a knowledge of the scope and limitations of the rearrangement. In this paper we have explored the effect of nuclear substitution, solvent, temperature, and time on the rearrangement.

Results

Effect of Nuclear Substitution.—To determine the scope of the arenesulfenanilide rearrangement, sulfenanilides **5a–f** were heated at 195° in purified commercial aniline for 15.5 hr. The composition of the reaction products was determined by glc analysis by comparison with authentic samples. Four types of products were identified: azobenzene (**6**), aryl disulfides (**7**), 2-aminodiphenyl sulfides (**8**), and 4-aminodiphenyl sulfides (**9**). These results are summarized in Table I.



5a, X = 4-CH_3
b, X = H
c, X = 4-Cl
d, X = 4-Br
e, X = 3-NO_2
f, X = 4-NO_2



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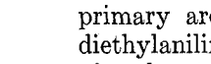

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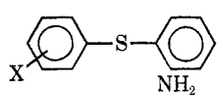

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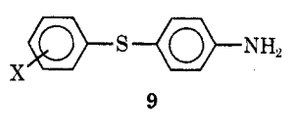

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The results summarized in Table I indicate that the rearrangement of arenesulfenanilides to 2- and 4-aminodiphneyl sulfides is quite general. Electron-donating groups favor dispropoportionation (disulfide and azobenzene formation), whereas electron-withdrawing groups favor rearrangement. With the exception of **5e**, the ortho/para ratios for **5a–f** are nearly identical, suggesting a similar mechanism. The method of synthesis of the sulfenanilide also appears to have an effect on the composition of the reaction products. Sulfenanilide **5c** (entry 3, Table I), prepared from the corresponding sulfenyl chloride, gave a higher yield of rearrangement than did **5c** prepared *via* the silver nitrate method.[10] We will come back to this in a later section.

Azobenzene (**6**) isolated in the thermal rearrangement of sulfenanilides **5a–c**, is formed by thermal disproportionation of hydrazobenzene.[11] The hydrazobenzene is formed by dimerization of two amino radicals resulting from homolytic cleavage of the S–N bond.[7] Under the reaction conditions hydrazobenzene in aniline gave a nearly quantitative yield of azobenzene.[12]

$$ArNH\cdot \longrightarrow ArNH\text{–}NHAr \longrightarrow ArNH_2 + ArN{=}NAr$$

Solvents Effects.—The solvent used in the arenesulfenanilide rearrangement is critical in determining the composition of the reaction products. Table II summarizes the effects of various solvents on the reaction products obtained from sulfenanilides **5c** and **5e**. Rearrangement is favored only in secondary[7] and primary aromatic amine solvents. In anisole, *N,N*-diethylaniline, dimethylacetamide, or in the absence of solvent disproportionation was favored giving disulfide.

The type of aniline used as the solvent is also important. Commercial aniline (aniline I) favors rearrangement. Aniline prepared by hydrogenation of nitrobenzene (aniline II) favors disproportionation (entries 1, 12, and 3, 13, Table II). Both anilines were purified by distillation from potassium hydroxide. Commercial aniline is prepared by metal–hydrochloric acid reduction of nitrobenzene. A trace impurity that may not have been removed in the purification steps is aniline hydrochloride. This impurity would not be present in aniline prepared by hydrogenation of nitrobenzene.

Addition of a small amount of aniline hydrochloride to aniline II resulted in 99 and 100% yields of rearrangement for sulfenanilides **5c** and **5e**, respectively (entries 2 and 14, Table II). Addition of aniline hydrochloride to **5c** in anisole, or in the absence of solvent, was also observed to increase the percentage of rearrangement (entries 6 and 11, Table II). These results support the above interpretation as well as inferring that the arenesulfenanilide rearrangement is acid catalyzed.

The lower yield of rearrangement obtained from **5c** prepared *via* the silver nitrate method compared with the higher yield of rearrangement obtained from **5c** prepared from the sulfenyl chloride (compare entries 3 and 4, Table I) is readily explained in terms of acid

TABLE I

REARRANGEMENT OF SULFENANILIDES **5a–f** AT 195° IN ANILINE[a] FOR 15.5 HR (PER CENT YIELD)

Entry	Sulfenanilide[b]	Azobenzene (**6**)	Disulfide (**7**)	Aminodiphenyl sulfide ortho (**8**)	Aminodiphenyl sulfide para (**9**)	Total rearrangement	Ortho/para
1	**5a**	20	69	5	10	15	0.5
2	**5b**	34	43	9[c]	17[d]	26	0.53
3	**5c**		28	24	46	70	0.5
4	**5c**[e]	13	48	14	28	43	0.5
5	**5d**		29	21	39	60	0.54
6	**5e**			27[f]	69[f]	96	0.4
7	**5f**			33[g]	67[g]	100	0.49

[a] Purified commercial aniline; mole ratio of sulfenanilide to aniline, 1:15. [b] Prepared from the corresponding sulfenyl chloride unless otherwise noted. [c] Reference 19. [d] Reference 20. [e] Prepared *via* the silver nitrate method; ref 10. [f] Reference 6. [g] Reference 21.

(7) F. A. Davis and R. P. Johnston, II, *J. Org. Chem.*, **37**, 854 (1972).
(8) F. A. Davis and R. B. Wetzel, *Tetrahedron Lett.*, 4483 (1969).
(9) (a) H. J. Shine, "Aromatic Rearrangements," Vol. 6, Elsevier, New York, N. Y., 1967, Chapter 3; (b) M. J. S. Dewar in "Molecular Rearrangement," P. De Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 5.
(10) M. D. Bentley, I. B. Douglass, J. A. Lacadie, D. C. Weaver, F. A. Davis, and S. J. Eitelman, *Chem. Commun.*, 1625 (1971).
(11) P. Walker and W. A. Water, *J. Chem. Soc.*, 1632 (1962); L. G. Korolik and V. O. Lukaghevich, *Dokl. Chem.*, 649 (1961).
(12) It is interesting to note that benzidine was not detected. The thermal benzidine rearrangement is known to give, among other products, benzidine and azobenzene. See ref 9a, p 171.

TABLE II

EFFECTS OF SOLVENT ON THE REARRANGEMENT OF ARENESULFENANILIDES AT 195° FOR 15.5 HR (PER CENT YIELD)

Entry	Sulfenanilide[a]	Solvent[b]	Disulfide (7)	Aminodiphenyl sulfides ortho (8)	Aminodiphenyl sulfides para (9)	Total rearrangement
1	5c	Aniline I[c]	28	24	46	70
2	5c	Aniline I + $C_6H_5NH_3Cl$[d]		44	48	92
3	5c	Aniline III[e]	44			0
4	5c	Aniline II + $C_6H_5NH_3Cl$[d]		45	51	96
5	5c	Anisole	91	6	2	8
6	5c	Anisole + $C_6H_5NH_3Cl$[d]	45	19	6	25
7	5c	*N*,*N*-Diethylaniline	31			0
8	5c	Phenol	57	Trace		
9	5c	Dimethylacetamide	55	1	4	5
10	5c	None	62	2	4	6
11	5c	$C_6H_5NH_3Cl$[f]		27	25	52
12	5e	Aniline I[c]		27	69	96
13	5e	Aniline II[e]	42	7	12	19
14	5e	Aniline II + $C_6H_5NH_3Cl$[d]		34	65	99

[a] Prepared from the corresponding sulfenyl chloride. [b] Mole ratio of sulfenanilide to solvent, 1:15. [c] Purified commercial aniline. [d] Mole ratio of aniline hydrochloride to sulfenanilide, 1:11. [e] Purified aniline prepared by hydrogenation of nitrobenzene. [f] Mole ratio of sulfenanilide to aniline hydrochloride, 4.4:1.

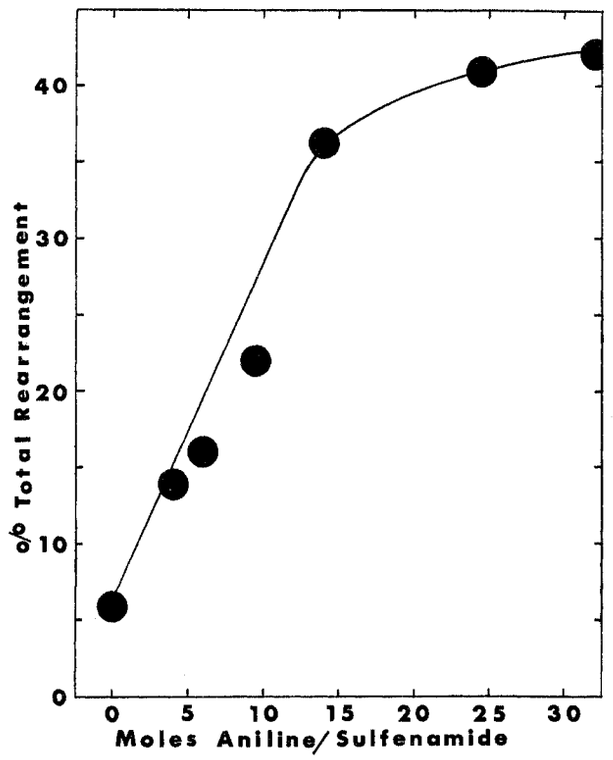


Figure 1.—Per cent total rearrangement *vs.* the mole ratio of aniline to sulfenanilide **5c**.

catalysis by aniline hydrochloride. A by-product in the synthesis of sulfenanilides from the sulfenyl chloride is aniline hydrochloride. Aniline hydronitrate is the corresponding by-product in the preparation of sulfenanilides *via* the silver nitrate method.[10] The latter impurity is apparently more easily removed than the aniline hydrochloride in the purification of the 4-chlorobenzenesulfenanilide (**5c**).

The concentration of the aniline solvent is also important in determining the composition of the reaction products. Figure 1 shows a plot of the per cent yield of total rearrangement *vs.* the mole ratio of aniline to sulfenanilide **5c**. At low concentrations of aniline little rearrangement is observed. As the concentration of aniline increases, the per cent rearrangement increases to a maximum of 42%. Figure 1 may also be interpreted in terms of acid catalysis by the impurity aniline hydrochloride. As the concentration of aniline increases the aniline hydrochloride impurity also increases and rearrangement is favored. It may have been anticipated that rearrangement should have increased as the concentration of aniline increased, since the concentration of the impurities should also be increasing. It may be that at these higher concentrations the sulfenanilide has to compete with aniline for the acid.

Effects of Temperature and Time.—The effects of temperature and time on the composition of the reaction products were determined for sulfenanilides **5b, 5c** and **5f**. These sulfenanilides were heated in aniline and aniline containing aniline hydrochloride at appropriate temperatures and time intervals. The products were analyzed by glc. In the absence of complete rearrangement only the yield of the *p*-aminodiphenyl sulfides could be determined.[13] To minimize problems resulting from trace impurities, experiments were performed with the same batch of sulfenanilide and solvent. These results are summarized in Table III.

In the absence of aniline hydrochloride (entries 1–4, Table III) a lower temperature slows the rate of reaction. A reaction time of 96 hr (monitoring the disappearance of the NH proton in the nmr) was required for complete reaction of sulfenamide **5c** at 110°. However, at 190 or 150° the reaction was complete after 16 hr. When the reaction was allowed to go to completion the lower temperature favored rearrangement (entries 2 and 4, Table III). Addition of aniline hydrochloride (entries 5–23, Table III), in all cases, accelerated the rate of rearrangement and favored it over disproportionation. Sulfenanilide **5b** in the absence of added aniline hydrochloride give only 10% rearrangement after 2 hr, whereas, with added aniline hydrochloride, rearrangement was complete after 0.5 hr (compare entries 1 and 5, Table III).

(13) The 2-aminodiphenyl sulfides and the sulfenanilide could not be satisfactorily separated by glc. Sulfenanilides **5e** and **5f** may rearrange on the glc column to the corresponding 2-aminodiphenyl sulfides. No evidence was obtained for rearrangement of any of the sulfenanilides to the 4-aminodiphenyl sulfides in the glc. It is possible that the mechanism for rearrangement to the 2- and 4-aminodiphenyl sulfides may be different, and there is some evidence which suggests this. See following paper.[14]

(14) F. A. Davis, C. J. Horner, E. R. Fretz, and J. F. Stackhouse, *J. Org. Chem.*, **38**, 695 (1973).

TABLE III

THE EFFECT OF TEMPERATURE AND TIME ON THE REARRANGEMENT OF ARENESULFENANILIDES IN ANILINE[a] (PER CENT YIELD)

Entry	Sulfenanilide[b]	Time, hr	Temp, °C	Disulfide (7)	Aminodiphenyl sulfide o- (8)	Aminodiphenyl sulfide p- (9)	Total rearrangement
1	5b	2	190	c		10	10
2	5c	16	190	28	14	46	70
3	5c	16	150	10	31	53	84
4	5c	96	110	11	33	55	88
		Aniline Hydrochloride Added[d]					
5	5a	0.5	190		40	53	93
6	5b	2.0	190		39	59	98
7	5b	16	190		42	50	92
8	5b	0.5	100			7	
9	5b	1.0	100			9	
10	5b	1.5	100			25	
11	5b	2.0	100			32	
12	5b	3.0	100			39	
13	5b	5.0	100			54	
14	5f	0.5	190		35	52	87
15	5f	2.0	190		34	54	88
16	5f	16	190		34	59	93
17	5f	2.0	100			5	
18	5f	3.0	100			11	
19	5f	5.0	100			13	
20	5f	12.0	100			23	
21	5f	16.0	100			39	
22	5f	21.5	100			47	
23	5f	41.3	100			70	

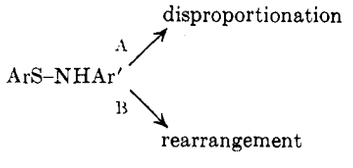
[a] Purified commercial aniline; mole ratio of sulfenanilide to aniline, 1:15. [b] Sulfenanilide prepared from the corresponding sulfenyl chloride. [c] Not detected. [d] Mole ratio of sulfenanilide to aniline hydrochloride, 1:5.1.

Lowering the temperature to 100° slows the rate of rearrangement for **5b** and **5f** sufficiently in the presence of aniline hydrochloride to permit a semiquantitative comparison of the rate of rearrangement for the two sulfenanilides. Figure 2 shows a plot of the per cent yield of sulfides **9b** and **9f** obtained from the thermal rearrangement of sulfenanides **5b** and **5f**, respectively, *vs.* time (entries 8–23, Table III). As is evident from Figure 2, the rate of rearrangement of 4-nitrobenzenesulfenanilide (**5f**) is substantially slower than that of benzenesulfenanilide (**5b**). Electron-donating groups; therefore, facilitate the rate of rearrangement, suggesting that in the transition state for rearrangement sulfur is electron deficient.

The concentration of the added aniline hydrochloride also affects the rate of rearrangement. Figure 3 summarizes this data and shows that as the mole per cent of aniline hydrochloride increases the percentage of **9b** increases.

Discussion

The experimental evidence obtained in this paper confirms our earlier observations that two thermal reactions are characteristic of arenesulfenanilides.[6] The first reaction involves disproportionation of the S–N bond to give sulfenyl and amino radicals (pathway A) which lead to aryl disulfides and azobenzene. The second reaction involves rearrangement (pathway B) leading to 2- and 4-aminodiphenyl sulfides.



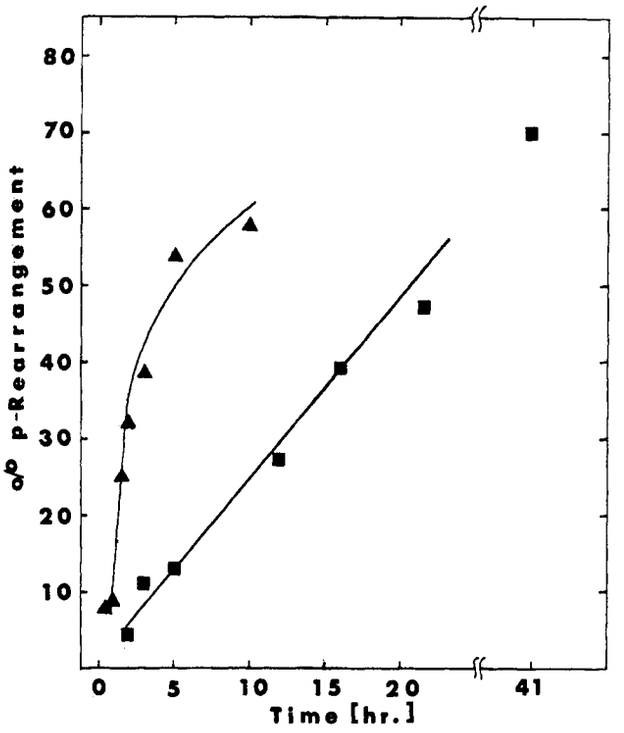


Figure 2.—Per cent yields of 4-aminodiphenyl sulfides **9b** (▲) and **9f** (■) from sulfenanilides **5b** and **5f** at 100° *vs.* time.

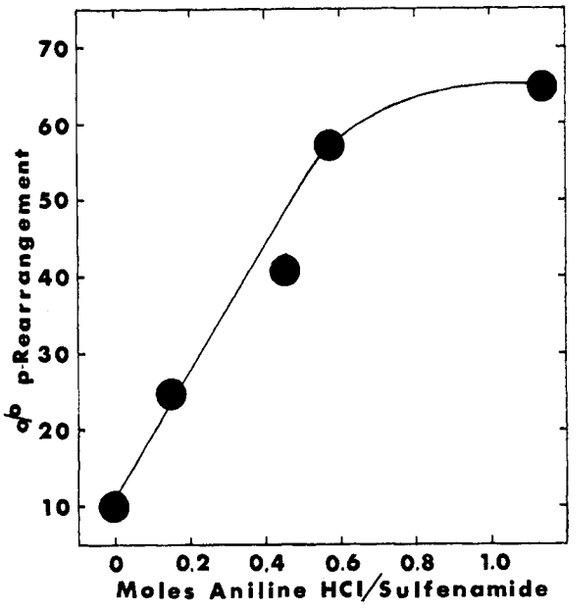


Figure 3.—Per cent yield of 4-aminodiphenyl sulfide **9b** from **5b** at 100° after 1.5 hr *vs.* mole ratio of aniline hydrochloride to sulfenanilide **5b**.

Electron-donating groups favor disproportionation (pathway A) and electron-withdrawing groups favor rearrangement (pathway B). The favoring of pathway A by electron-donating groups is readily explained in terms of stabilization of the resulting sulfenyl radical or lone-pair repulsion which destabilizes the S–N bond.

Rearrangement is favored by addition of aniline hydrochloride. As a consequence of this acid catalysis, both the purity of the solvent and the method of preparation of the sulfenamide have a dramatic effect on the composition of the reaction products. Sulfenanilides, prepared from the corresponding sulfenyl chlorides in which aniline hydrochloride is a by-product, consistently gave higher yields of rearrangement.

Rearrangement was favored only in primary and secondary aromatic amine solvent, and this may in part reflect the lack of acid to catalyze the rearrangement.

Semiquantitative rate studies of sulfenanilides **5b** and **5f** are perhaps the most enlightening as far as a mechanism is concerned. Electron-donating groups accelerated the rate of rearrangement, suggesting that sulfur may be electron deficient in the transition state for rearrangement.

The concentration of added aniline hydrochloride also had an important effect on the rate of rearrangement. Rearrangement increases linearly as the concentration of the aniline hydrochloride increases, which strongly implies that the conjugate acid of the sulfenanilide (**10**) is involved in the rate-determining step. Equations 1 and 2 summarize these results.

$$\mathrm{ArSNHAr' + Ar'NH_3^+Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{10}}{ArS\overset{+}{N}H_2Ar'\,Cl^-} + Ar'NH_2} \quad (1)$$

$$\mathrm{ArS\overset{+}{N}H_2Ar' \xrightarrow{k_2} \text{rearrangement products}} \quad (2)$$

There is considerable evidence that canonical forms such as **11** make important contributions to the ground-state stabilization of sulfenanilides toward torsion[4] and displacement reactions at the S–N bond.[5] As the

$$\mathrm{ArSNHAr \longleftrightarrow \underset{\mathbf{11}}{Ar\bar{S}{=}\overset{+}{N}HAr}}$$

electronegativity of substituents attached to sulfur increased the importance of **11** increased.[4,5] The decrease in electron density on nitrogen as the electronegativity of groups attached to sulfur increase will result in a lower concentration of the conjugate acid **10** (eq 1). Whether or not eq 1 or 2 is rate determining, if **10** is involved in the transition state electron-withdrawing groups will slow the rate.

The present experimental evidence does not permit a distinction to be made as to whether the arenesulfenanilide rearrangement is general or specific acid catalyzed, *i.e.*, eq 1 or 2 rate determining. Figure 3 would suggest general acid catalysis, but the benzidine[15] and nitramine[16] rearrangements are specific acid catalyzed.

In the following paper, evidence is presented for an intramolecular arenesulfenanilide rearrangement.[14]

Experimental Section

Sulfenanilides **5a**,[17] **5b**,[17] **5c**,[5] **5d**,[5] **5e**,[6] and **5f**[18] were prepared from the corresponding sulfenyl chloride unless otherwise noted. 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. Gas chromatographic analysis 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. Commercial aniline, aniline I, and aniline prepared by hydrogenation of nitrobenzene over 10% palladium on charcoal in ethanol at 40 psi, aniline II, were distilled twice from potassium hydroxide.

General Procedure for the 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 appropriate temperatures and time intervals in sealed tubes. The reaction mixture was diluted with methylene chloride and filtered, a known weight of standard was added, and the mixture was analyzed by glc by comparison of peak areas with standard solutions of the reactions products. Analysis were performed at least twice and the values were averaged.

General Procedure of Synthesis of 2- and 4-Aminodiphenyl Sulfides (8 and 9).[6]—The 2- and 4-aminodiphenyl sulfides **8** and **9** were prepared by catalytic reduction, over 10% palladium on charcoal in ethanol at 40 psi, of the corresponding crude 2- and 4-nitrodiphenyl sulfides. The 2- and 4-nitrodiphenyl sulfides were prepared by condensation of the sodium salt of the appropriate aryl thiol, prepared by addition of the disulfide or thiol to sodium ethoxide in absolute ethanol, with 2- and 4-chloronitrobenzene. After refluxing for 10 hr the precipitated salts were filtered (solvent removed), dissolved in ether, and filtered. The ether solution was washed twice with 10% sodium hydroxide and twice with water and dried over $MgSO_4$. Removal of the solvent gave the crude nitrodiphenyl sulfide, which was used as described above without purification.

4-Methyl-2′-aminodiphenyl Sulfide (8a).—Reduction of 2.3 g of the nitrodiphenyl sulfide gave after crystallization from pentane 1.5 g (74%) of **8a** as white crystals: mp 47.5–49°; ir (KBr) 3500 and 3390 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.0 (m, 8), 4.1 (s, 2, NH_2) and 2.2 (s, 3, CH_3).

Anal. Calcd for $C_{13}H_{13}NS$: C, 72.56; H, 6.05. Found: C, 72.42; H, 6.02.

4-Methyl-4′-aminodiphenyl Sulfide (9a).—Reduction of 4.0 g of the nitrodiphenyl sulfide gave after crystallization from pentane 2.9 g (85%) of **9a** as white crystals: mp 72–73°; ir (KBr) 3480 and 3375 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.1 (s, 4), 7.4–6.15 (AB q, 4, J = 8 Hz), 3.6 (s, 2, NH_2), and 2.2 (s, 3, CH_3).

Anal. Calcd for $C_{13}H_{13}NS$: C, 72.56; H, 6.05. Found: C, 72.78; H, 6.27.

2-Aminodiphenyl sulfide (8b)[19] had the following properties: ir (KBr) 3410 (NH_2) and 3340 cm^{-1}; nmr ($CDCl_3$) δ 7.0 (m, 9) and 4.1 (s, 2, NH_2).

4-Aminodiphenyl sulfide (9b)[20] had the following properties: ir (KBr) 3460 and 3360 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.2 (s, 5), 7.5–6.7 (AB q, J = 8 Hz), and 3.6 (s, 2, NH_2).

4-Chloro-2′-aminodiphenyl Sulfide (8c).—Reduction of 2.0 g of the nitrophenyl disulfide gave, after molecular distillation (60°, 0.05 mm), 1.4 g (80%) of **8c** as an oil: ir (thin film) 3480 and 3380 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.0 (m, 8) and 4.2 (s, 2, NH_2).

Anal. Calcd for $C_{12}H_{10}ClNS$: C, 61.15; H, 4.25. Found: C, 61.32; H, 4.44.

4-Chloro-4′-aminodiphenyl Sulfide (9c).—Reduction of 1.5 g of the nitrodiphenyl sulfide gave, after crystallization from ether–pentane, 1.2 g (90%) of **9c** as light tan crystals: mp 60–61°; ir 3400 and 3310 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.1 (m, 4), 7.3–6.4 (AB q, 4, J = 9 Hz), and 3.6 (s, 2, NH_2).

Anal. Calcd for $C_{12}H_{10}ClNS$: C, 61.15; H, 4.25. Found: C, 61.22; H, 4.12.

4-Bromo-2′-aminodiphenyl Sulfide (8d).—Reduction of 5.0 g of the nitrophenyl sulfide gave, after crystallization form ether–pentane, 3.4 g (75%) of **8d** as white crystals: mp 41.5–42.5°; ir (KBr) 3500 and 3390 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.1 (m, 8) and 4.2 (broad s, 2, NH_2).

Anal. Calcd for $C_{12}H_{10}BrNS$: C, 51.43; H, 3.57. Found: C, 51.48; H, 3.52.

4-Bromo-4′-aminodiphenyl Sulfide (9d).—Reduction of 3.0 g of the nitrodiphenyl sulfide gave, after crystallization from ether–pentane, 1.6 g (60%) of **9d** as white crystals: mp 69–69.5°; ir (KBr) 3460 and 3380 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 7.1 (m, 8) and 3.8 (broad s, 2, NH_2).

Anal. Calcd for $C_{12}H_{10}BrNS$: C, 51.43; H, 3.57. Found: C, 51.51; H, 3.52.

4-Nitro-2′-aminodiphenyl sulfide (8f)[21] had the following properties: ir (KBr) 3460 and 3360 cm^{-1} (NH_2); nmr (acetone-d_6) δ 8.2 (d, 2) and 7.1 (m, 8).

4-Nitro-4′-aminodiphenyl sulfide (9f)[21] had the following properties: ir (KBr) 3480 and 3280 cm^{-1} (NH_2); nmr (acetone-d_6) δ 8.0 (d, 2), 7.1 (m, 5), and 5.1 (broad s, 2, NH_2).

(15) D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2878 (1964).

(16) D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J. Chem. Soc.*, 5349 (1964); D. V. Banthorpe, J. A. Thomas, and D. L. H. Williams, *ibid.*, 6135 (1965).

(17) H. Lecher, F. Holschneider, K. Koberler, W. Speer, and P. Stocklin, *Ber.*, **58**, 409 (1925).

(18) M. L. Moore and T. B. Johnson, *J. Amer. Chem. Soc.*, **57**, 1517 (1935).

(19) E. Bourgeois and P. Huber, *Recl. Trav. Chim. Pays-Bas*, **31**, 30 (1912).

(20) R. Gillespie and R. Passerini, *J. Chem. Soc.*, 3850 (1956).

(21) H. H. Hodgson and W. Rosenberg, *ibid.*, 180 (1930).

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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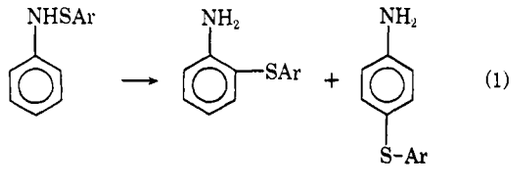
The acid-catalyzed arenesulfenanilide rearrangement has been investigated to determine whether the rearrangement is inter- or intramolecular. The failure of trapping experiments and high ortho/para ratios suggest that the rearrangement is intramolecular. Crossover experiments had little meaning, since 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)

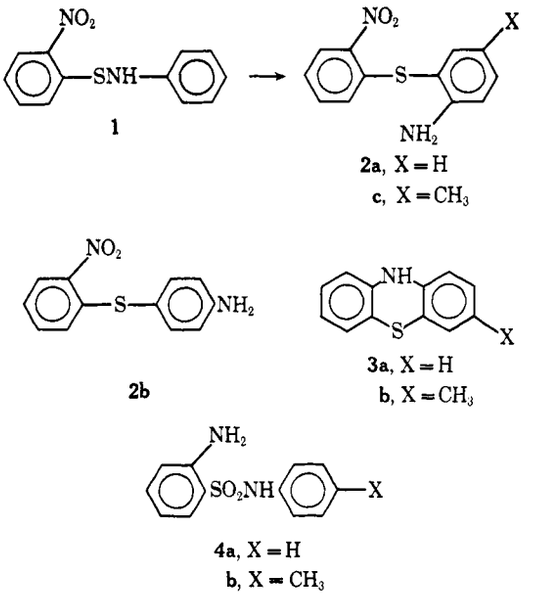
This rearrangement (eq 1) is a member of an important class of N-substituted aminoaromatic rearrangements which include the benzidine, quinamine, and nitramine rearrangements, among others.[4] The benzidine,[5] quinamine,[6] and nitramine[7] rearrangements are specific acid catalyzed and intramolecular.

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).