yielding the tetracarbomethoxy dimer **11**: mass spectrum *m/e* (rel intensity) 542 (16), 511 (5), 373 (39), 271 (100), 240 (50); NMR δ (CDCl$_3$) 3.80 (s, 3 H), 3.86 (s, 3 H), 3.95 (s, 3 H), 4.00 (s, 3 H), 4.2–4.8 (m, cyclobutanes, 3 H), 6.4 (d, 1 H), 7–8 (m, 9 H, aromatics), 8.22 (s, 1 H). No measurable optical rotation could be obtained for this product.

Isolation and Structure Determination of Products from Racemic 2. Dimers obtained by irradiation of racemic **2** have been isolated exactly as for (*S*)-(+)-**2**, and have exactly the same NMR, IR, and mass spectrum as **7**.

References and Notes

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(6) (a) M. Lahav, E. Gati, L. Roitman, and L. Leiserowitz, in preparation; (b) S. Ariel, M. Lahav, and L. Leiserowitz, in preparation.

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(11) L. Leiserowitz, *Acta Crystallogr., Sect. B*, **32**, 775 (1976).

(12) (a) H. Nakanishi, K. Ueno, M. Hasegawa, Y. Sasada, and T. Yurugi, preprint for the Symposium on Light Induced Polymerization Reactions, Philadelphia, Pa., July 1975; (b) Y. Bernstein, M. D. Cohen, and L. Leiserowitz in "The Chemistry of Quinonoid Compounds", S. Patai, Ed., Wiley, New York, N.Y., 1974, p 37.

(13) As 99% optically pure (*R*)-(−)-*sec*-butyl alcohol is not commercially available, the symmetric behavior of the enantiomers was tested in monomers in which the enantiomeric excess is only 90%.

(14) Prolonged exposure to light of the reaction mixture causes some cis–trans isomerization around terminal double bonds; no evidence, however, has been found for cis–trans isomerization prior to reaction, as no cis isomer was detected either in the recovered monomer or in the products of reaction after short irradiation periods.

(15) Z. Berkovitch-Yellin, private communication.

(16) L. Addadi, E. Gati, M. Lahav, and L. Leiserowitz, *Isr. J. Chem.*, **15**, 116 (1977).

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(18) R. H. Wiley and P. H. Hobson, *J. Am. Chem. Soc.*, **71**, 2429 (1949).

(19) Racemic **1** has two forms when crystallized from the melt: the stable form has mp 90.5 °C and the metastable mp ~87 °C. This point will be dealt with in detail in a further communication.

Chemistry of the Sulfur–Nitrogen Bond. 14.[1,2]
Arenesulfenic Acids from *N*-Alkylidenearenesulfinamides (Sulfinimines)

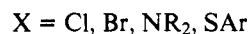### Franklin A. Davis,* Arthur J. Friedman, and Upender K. Nadir

Contribution from the Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104. Received August 31, 1977

Abstract: The synthesis of a novel class of reactive organosulfur–nitrogen compounds, *N*-alkylidenearenesulfinamides (sulfinimines), **1**, prepared by oxidation of the corresponding sulfenimines, **2**, is described. Thermally, these compounds rearrange via a concerted or nearly concerted mechanism to afford nitrile and arenesulfenic acid (ArSOH). The electronic effect of substituents on the rate of this reaction is negligible while steric factors are somewhat more important. The intermediate sulfenic acids were trapped with methyl propiolate and ethyl acrylate to afford **9** and **10** in good yield. Arenesulfenic acids prepared in this fashion decompose to yield disulfide and thiolsulfonate as major products. The corresponding sulfinic acids are obtained when the sulfenic acid contains electron-attracting groups. Possible reaction pathways for the formation of these products are discussed. In the presence of dimethyl sulfate **3g** affords a variety of methylated products, **15–18**, arising from the intermediate 3-nitrobenzenesulfenic acid.

Sulfenic acids (RSOH) have been proposed as key intermediates in a number of important chemical reactions including biological transformation.[3–7] Despite numerous attempts to isolate these species only a very few special examples are known. Four are derivatives of 1-anthraquinonesulfenic acid, first prepared in 1912 by Fries.[8] A stable azetidinone-(*β*-lactam) sulfenic acid was reported by Chou[4b] in 1974 and *tert*-butanesulfenic acid has been prepared in solution.[3b,c]

While 2-nitrobenzenesulfenic acid has been the subject of numerous investigations,[9] relatively few studies of simple arenesulfenic acids (ArSOH) have been reported.[10] Two methods are available to prepare arenesulfenic acids: the pyrolysis of sulfoxides (eq 1) and the hydrolysis of a sulfenyl derivative (eq 2). Neither of these methods affords isolable arenesulfenic acids.

$$Ar\text{-}S(O)CR_2CHR_2 \rightarrow ArSOH + R_2C{=}CR_2 \quad (1)$$

$$Ar\text{-}S\text{-}X + H_2O \rightarrow ArSOH + HX \quad (2)$$

$$X = Cl, Br, NR_2, SAr$$

The mechanism proposed for the pyrolysis of sulfoxides, which generally takes place in the temperature range 100–200 °C, is believed to involve a stereospecific cis elimination.[11] However, Hammett ρ values observed for the pyrolysis of aryl *tert*-butyl sulfoxides (ρ = 0.65)[3b] and aryl *n*-propyl sulfoxides (ρ = 0.51)[11b] suggest that the transition state for sulfoxide

Table II. Properties of *N*-Alkylidenearenesulfinamides

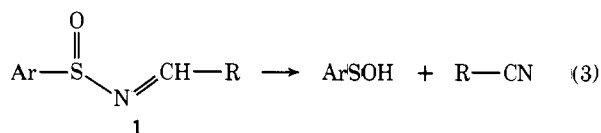| Compd	Yield, %	Mp, °C	Anal. Calcd C	H	Found C	H	NMR δ (CDCl$_3$), ppm
3b	82	73–75	67.50	5.66	67.78	5.74	2.35 (s, 3 H, Me), 7.25–7.9 (m, 9 H), 8.75 (s, 1 H)
3c	68	*a*	M$^+$, *m/e* 243 (17)				2.33 (s, 3 H, Me), 7.2–7.95 (m, 9 H), 8.76 (s, 1 H)
3d	96	80–81	68.09	4.84	67.73	4.74	7.35–7.9 (m, 10 H), 8.76 (s, 1 H)
3e	90	106–108	M$^+$ 307 (32)				7.27–7.9 (m, 10 H), 8.76 (s, 1 H)
3g	74	96–98	56.92	3.67	56.77	3.60	7.26–8.3 (m, 9 H), 8.72 (s, 1 H)
3h	93	135–136	56.92	3.67	57.20	3.79	7.25–8.3 (m, 9 H), 8,79 (s, 1 H)
4d	93	*a*	M$^+$, *m/e* 167 (1.4)				2.2 (d, *J* = 5 Hz, 3 H, Me), 8.25 (q, 1 H)
4e	60	*a*					2.21 (d, *J* = 5 Hz, 3 H, Me), 7.35–7.4 (m, 3 H),
4f	68	*a*	51.75	4.34	51.37	4.37	8.24 (g, 1 H)
4h	95	103–105	45.28	3.80	45.02	3.89	2.20 (d, *J* = 5 Hz, 3 H, Me), 7.35–7.75 (m, 4 H), 8.25 (g, 1 H)
5a	74^b	154–155	55.26	3.97	35.03	4.02	2.23 (d, *J* = 5 Hz, 3 H, Me), 8.23 (g, 1 H), 7.9–8.5 (m, 4 H)
5g	83^b	144–145	48.90	2.84	48.74	2.72	3.8 (s, 3 H, MeO), 7.55–8.7 (m, 8 H), 8.8 (s, 1 H) 6.53–8.73 (m, 8 H), 8.63 (s, 1 H)
5h	68^b	149–150	48.90	2.84	49.19	2.70	6.55–8.3 (m, 8 H), 8.62 (s, 1 H)
6a	98	85–86	45.28	3.80	45.53	3.61	1.95 (d, *J* = 5 Hz, 3 H, Me), 7.75 (m, 4 H), 8.25 (s, 1 H)
6b	90	*a*	M$^+$, *m/e* 226 (100)				1.17 (t, 3 H, Me), 2.58 (q, 2 H, CH$_2$), 7.4–8.5 (m, 4 H), 8.65 (t, 1 H)
6c	89	*a*	M$^+$, *m/e* 240 (7.5)				0.9 (h, 6 H, Me), 2.3 (m, 1 H), 6.95–8.05 (m, 3 H), 8.25 (d, 1 H), 8.5 (t, 1 H)
6d	85	*a*	M$^+$, *m/e* 254 (2)				1.15 (s, 9 H), 7.16 (s, 1 H), 7.5–8.1 (m, 4 H)

^{a} Unstable liquid. ^{b} NMR in C$_6$D$_6$.

pyrolysis (eq 1) is not completely concerted, but involves some C–S bond breaking prior to C–H bond breaking.[3a]

The acidity of the migrating proton also has some influence on the rate of sulfoxide pyrolysis. Consequently a 15 000-fold increase in pyrolysis rate for alkyl sulfinylpropionates with respect to that of di-*n*-propyl sulfoxide has been observed.[3b] In addition, the increased rate of isomerization of thiazine sulfoxides containing acidic migrating hydrogens has been noted.[12] The reversibility of the reactions sulfoxide ⇌ sulfenic acid and alkene (eq 1) has been demonstrated.[3b,c,11c]
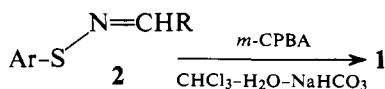
Although the hydrolysis of sulfenyl derivatives (sulfenyl halides, disulfides, sulfenamides) is believed to involve the initial formation of a sulfenic acid (eq 2), these species have never been isolated or even detected using this procedure.[10,13] The products most often isolated are disulfides (ArSSAr), thiolsulfonates (ArSO$_2$SAr), and sulfinic (ArSO$_2$H) and sulfonic acids (ArSO$_3$H),[13] purportedly arising via secondary reactions of the initially formed sulfenic acid.

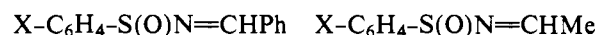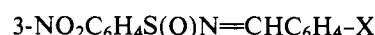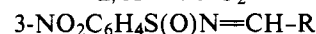Recently we reported that the thermolysis of *N*-alkylidenearenesulfinamides (1) affords the corresponding arene-

$$\underset{\textbf{1}}{\text{Ar--}\overset{\overset{\text{O}}{\|}}{\text{S}}\diagdown_{\text{N}}\diagup\text{CH--R}} \longrightarrow \text{Ar'SOH} + \text{R--CN} \quad (3)$$

sulfenic acid and nitrile (eq 3) under mild nonaqueous conditions.[14] In this paper we report on the chemistry of 1 and the use of these compounds to prepare and study simple arenesulfenic acids.

Synthesis and Properties of *N*-Alkylidenearenesulfinamides (1). *N*-Alkylidenearenesulfinamides (sulfinimines) 1, a new class of reactive sulfur–nitrogen compounds, are prepared by oxidation of the corresponding *N*-alkylidenearenesulfenamide (2) with 1 equiv of *m*-chloroperbenzoic acid (*m*-CPBA). Compounds 2 were prepared from the corresponding disulfide and aldehyde using the metal-assisted procedure previously described.[15] The properties of 2 are listed in Table I.[16]

$$\underset{\textbf{2}}{\text{Ar--S}\diagup^{\text{N}=\text{CHR}}} \xrightarrow[\text{CHCl}_3-\text{H}_2\text{O}-\text{NaHCO}_3]{m\text{-CPBA}} \textbf{1}$$

A special two-phase oxidation procedure is necessary for the oxidation of 2 to 1 and involves the dropwise addition of *m*-

CPBA in CHCl$_3$ to a rapidly stirring solution of 2 in CHCl$_3$–10% of aqueous NaHCO$_3$. Single-phase oxidation of 2 resulted in low yields and complex reaction mixtures. The acid sensitivity of the S–N bond in sulfenamides may explain these results.[17] The properties of sulfinimines 3–6 prepared in this way are listed in Table II.
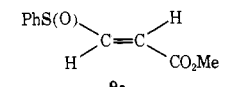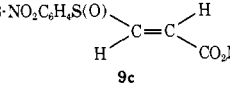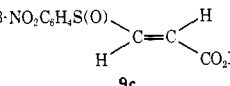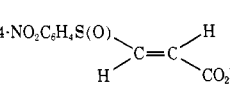
$$\text{X--C}_6\text{H}_4\text{--S(O)N}{=}\text{CHPh} \quad \text{X--C}_6\text{H}_4\text{--S(O)N}{=}\text{CHMe}$$

<div align="center">

3   **4**

3-NO$_2$C$_6$H$_4$S(O)N=CHC$_6$H$_4$-X

5a, X = 4-MeO
b, X = 4-Me
c, X = 2-Me
d, X = H
e, X = 4-Br
f, X = 4-Cl
g, X = 3-NO$_2$
h, X = 4-NO$_2$

3-NO$_2$C$_6$H$_4$S(O)N=CH-R

6a, R = Me
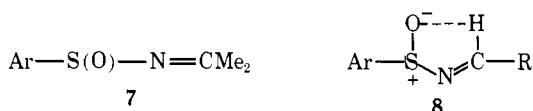**b**, R = Et
c, R = *i*-Pr
d, R = *t*-Bu

</div>

Structural proof of sulfinimines 3–6 is based on elemental analysis (stability permitting), mass spectra, infrared, and ^{1}H NMR spectra. The infrared spectra of 3–6 are characterized by strong absorption in the region 1060–1092 cm^{-1}, absent in the corresponding sulfenimine. We attribute this absorption to the S–O stretching vibration.

N-Alkylidenearenesulfenamides (2) can exist as mixtures of *E* and *Z* isomers.[15a] Both isomers were observed for 2 prepared from aliphatic aldehydes (2, R = alkyl), with a single isomer observed for 2 prepared from aryl aldehydes. The NMR spectra of 2 corresponding to 4 and 6a (R = Me) indicated the presence of approximately equal amounts of the *E* and *Z* forms. As the size of R in 6 was changed from methyl to ethyl to isopropyl a regular decrease in one of the isomers was observed. When R in 2 was *tert*-butyl (as in 6d) a single isomer was isolated (Table I).[16]

Oxidation of 2 to 1 yields one isomer. The chemical shift of the imidoyl proton in these compounds appears in the region δ 8.25–8.88 and is approximately 0.4 ppm to lower field than

Table III. Sulfoxides from 1 and Methyl Propionate or Ethyl Acylate

Sulfen- imine	Alkyne/ alkene	Products	(% yield)
3d	HC≡CCO₂Me	9a	(70)[a]
3d	CH₂=CH- CO₂Et	PhS(O)CH₂CH₂CO₂Et 10a	(60)
3g	HC≡CCO₂Me	9c	(71)
3g	CH₂=CH- CO₂Et	3-NO₂C₆H₄S(O)CH₂- CH₂CO₂Et 10c	(56)
6a	CH₂=CH- CO₂Et	3-NO₂C₆H₄S(O)CH₂- CH₂CO₂Et 10c	(60)
6a	HC≡CCO₂Me	9c	(72)
3f	CH₂=CH- CO₂Et	4-ClC₆H₄S(O)CH₂CH₂- CO₂Et 10b	(77)
3h	HC≡CCO₂Me	9d	(82)

[a] Reference 3c.

Table IV. Kinetic Parameters for the Thermolysis of N-Alkylidenearenesulfinamides at 77.0 °C

Entry	Sulfinimine (X)	k_r,[a] $M^{-1} s^{-1}$ $\times 10^5$	$t_{1/2}$, h	Rel rate	$\Delta G^{\ddagger}$, kcal/mol
	XC₆H₄S(O)N=CHPh (3)				
1	b (4-Me)	1.5	12.7	0.9	28.3
2	c (2-Me)	3.0	6.4	1.8	27.8
3	d (H)	1.7	11.4	1.0	28.3
4	e (4-Br)	1.9	10.3	1.1	28.2
5	g (3-NO₂) (1.0 M)	2.1	9.7	1.3	28.1
6	(0.5 M)	2.0	9.6		
7	(0.1 M)	1.9	10.4		
8	h (4-NO₂)	2.3	8.5	1.4	28.0
	ρ = 0.17, R = 0.985 (3c omitted for Hammett plot)				
	XC₆H₄S(O)N=CHMe (4)				
9	d (H)	8.6	2.3	1.0	27.1
10	e (4-Br)	9.6	2.0	1.1	27.0
11	f (4-Cl)	9.5	2.0	1.1	27.0
12	6a (3-NO₂)	12.4	1.6	1.4	26.9
13	h (4-NO₂)	14.3	1.3	1.7	26.8
	ρ = 0.270, R = 0.967				
	3-NO₂C₆H₄S(O)N=CHC₆H₄X (5)				
14	a (4-MeO)	1.2	15.8	0.6	28.5
15	3g (H)	2.1	9.7	1.0	28.1
16	g (3-NO₂)	2.9	6.7	1.4	27.9
17	h (4-NO₂)	3.1	6.3	1.5	27.8
	ρ = 0.341, R = 0.887				
	3-NO₂C₆H₄S(O)N=CHR (6)				
18	a (Me) (77 °C)	12.4	1.6	1.0	26.9
19	a (Me) (67 °C)	5.6			26.6
20	a (Me) (57 °C)	2.2			26.4
21	b (Et)	12.9	1.5	1.0	26.8
22	c (i-Pr)	29.0	0.7	2.3	26.3
23	d (t-Br)	33.5	0.6	2.7	26.2
	Steric ρ* = −0.3, R = 0.947 (vs. E_s);[b]				
	ρ* = 0.67, R = −1.407 (vs. σ*)				

[a] Concentration 1.0 M unless otherwise noted. [b] Reference 22.

Ar—S(O)—N=CMe₂

7   8

the corresponding sulfenimine. The free energy of activation ($\Delta G^{\ddagger}$) for inversion at nitrogen in N-isopropylidinearenesulfinamides (7) is 17 kcal/mol.[18a] This is approximately 3 kcal/mol lower than the barriers in the corresponding N-isopropylidenearenesulfenamides.[18b]
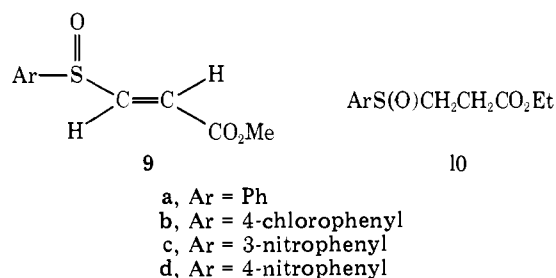
The possibility of an attractive interaction between the imidoyl proton and the sulfinyl oxygen, as depicted in 8, may suggest that 1 has the E configuration and would explain the isolation of a single isomer for 1. Dreiding models suggest that there is a close proximity between the imidoyl proton and the sulfinyl oxygen when 1 has the E configuration. The transition state leading from 1 to sulfenic acid and nitrile (eq 3) must be very close to 8.

In general sulfinimines prepared from aromatic aldehydes are crystalline solids whereas sulfinimines prepared from aliphatic aldehydes are liquids (Table II). The latter compounds were readily hydrolyzed by moist air or aqueous solvents to the corresponding sulfinamide (ArS(O)NH₂) and carbonyl compound. Conjugative stabilization of the C–N double bond in 3 and 5 by the aryl group apparently inhibits hydrolysis of these compounds.

Arenesulfenic Acids from Sulfinimines (1). When heated for 24 h at 80–115 °C in methyl propiolate or ethyl acrylate as solvents, 1 affords methyl *trans*-areneacrylates (9) and ethyl arenesulfinylpropionates (10). Sulfenic acids are known to be trapped by activated alkenes and alkynes,[3a–c] and the isolation of 9 and 10 in the thermolysis of 1 is consistent with the rearrangement of these compounds to the sulfenic acids and nitrile

9   10

a, Ar = Ph
b, Ar = 4-chlorophenyl
c, Ar = 3-nitrophenyl
d, Ar = 4-nitrophenyl

(eq 3). Short of isolating a stable sulfenic acid the best method for demonstrating its presence is trapping with an alkene or alkyne.

Some representative examples of 9 and 10 prepared by thermolysis of 1 are listed in Table III. Structural proof for 9 and 10 is based on elemental analysis, infrared, and NMR spectra. Propionates 10a and 10b proved to be thermally unstable liquids for which satisfactory elemental analyses could not be obtained. Compound 10a was prepared independently by oxidation of ethyl phenylmercaptopropionate with *m*-CPBA. The coupling constant of 14–15 Hz observed for the olefinic protons of 9 indicates that arenesulfenic acids derived from 1 add in a syn manner to methyl propynoate. Similar results have been reported for alkane- and benzenesulfenic acids.[3a–c]

A study of the thermolysis of 3–6 was undertaken in order to ascertain the mechanism and factors that influence the rate of formation of arenesulfenic acids from 1. The rate of thermolysis of 3–6 was determined by monitoring the rate of dis-

Table V. Synthesis of Arenesulfenic Acids from Sulfoxides and *N*-Alkylidenearenesulfinamides (1)

Entry	Compd	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Temp, °C	Ref
1	PhS(O)CH$_2$CH$_2$CH$_3$		25.9	−15.1	170–185	11a
2	ArS(O)CH$_2$CH$_2$CH$_3$	32–33			180	11a
3	ArS(O)CMe$_3$	28			101.3	3b
4	3-NO$_2$C$_6$H$_4$S(O)CMe$_3$	27.7			101.3	3b
5	ArS(O)N=CHPh (3)	27–28			77.0	This work
6	ArS(O)N=CHMe (4)	27			77.0	This work
7	3-NO$_2$C$_6$H$_4$S(O)N=CHC$_6$H$_4$Y (5)	28			77.0	This work
8	3-NO$_2$C$_6$H$_4$S(O)N=CHR (6)	26–27			77.0	This work
9	3-NO$_2$C$_6$H$_4$S(O)N=CHCMe$_3$ (6d)	26			77.0	This work
10	3-NO$_2$C$_6$H$_4$S(O)N=CHMe (6a)	26.9	19.1[a]	−22.2[a]	57–77	This work

[a] Calculated at 77 °C.

appearance of the imidoyl proton in **3, 5**, and **6** and the methyl proton in **4** by NMR relative to an internal standard. The thermal instability of **3–6** precluded rate measurements by GLC.

First-order rate constants (K_r) for the thermolysis of **3–6** are listed in Table IV. Excellent first-order plots were observed for all compounds. No change in the value of K_r was observed over a concentration range of 0.1–1.0 M for *N*-benzylidene-3-nitrobenzenesulfinamide (**3g**); see Table IV, entries 5–7. Activation parameters for *N*-ethylidene-3-nitrobenzenesulfinamide (**6a**) were obtained by measuring the change in rate over a temperature range of 57–77 °C (Table V, entry 10; Table IV, entries 18–20).

The error range for the rate constants (Table IV) was determined through calculation of standard deviations for each plot. They were invariably within 10% of the calculated rate constant. Kasler has estimated that the error in the NMR technique using a Varian A-60A, as was used in the present study, is 2%.[19] However, error estimates as large as 10% have been attributed to the NMR technique.[19]

Hammett ρ values of 0.17 and 0.27 were calculated for sulfinimines **3** and **4** (Table II) and indicate that substituent electronic effects have little influence on the rate of sulfenic acid formation from **1**. The acidity of the imidoyl proton (migrating proton) in **5** ($\rho = 0.25$) also has a negligible effect on the rate of eq 3.[21] All attempts to prepare **1** where R was a trichloro- or trifluoromethyl group failed.

A change of R in **1** from aryl to alkyl resulted in a 8- to 20-fold increase in the rate of sulfenic acid formation (Table IV). This effect appears to be steric in nature since a plot of Taft E_s values[22] vs. log k/k_0 results in a value for $\rho^* = -0.3$ ($R = 0.947$). No correlation was observed in a similar plot using σ^* values (Table IV, entries 18–23).

The negative entropy, the free energies of activation, and the effect of substituents on the thermolysis rate of **1** (eq 3) suggests a mechanism for sulfenic acid formation similar to that proposed for sulfoxide pyrolysis,[3b,c,11] namely, a cis or syn elimination via a transition state where bond breaking is nearly synchronous. Substituent effects observed for **1** suggest that the transition state leading to sulfenic acid and nitrile (eq 3) is somewhat more concentrated than sulfoxide pyrolysis.[3b,c,11]

Steric effects have the most influence on the rate of sulfenic acid formation from **1** (Table IV, entries 18, 21–23), although the effect is small. It is likely that this steric acceleration results from a repulsive interaction between R in **1** and the nitrogen lone pair of electrons and/or the C–N π system in the ground state relative to the transition state. Shelton and Davis have noted an increase in the rate of sulfoxide pyrolysis on replacing an *n*-alkyl group by a *tert*-butyl group.[3b,c] Their rate acceleration, however, appears to result from both steric and electronic factors.

As a synthesis of simple arenesulfenic acids the thermolysis of **1** is better than the pyrolysis of aryl *n*-alkyl sulfoxides (Table V; compare entries 2 with 5 and 6) and comparable with the pyrolysis of aryl *tert*-butyl sulfoxides (Table V; compare entries 3 with 6 and 7). The choice of a bulky R group in **1** (isopropyl or *tert*-butyl) permits the synthesis of simple arenesulfenic acids under even milder conditions (Table V; compare entries 8 and 9 with 3 and 4) than the pyrolysis of aryl *tert*-butyl sulfoxides.

Reactions and Properties of Arenesulfenic Acids. The reactions proposed for sulfenic acids are many and varied. Most have never been proven because of the elusive nature of this species. Information concerning their properties has, for the most part, been obtained indirectly from studies of thiosulfinates (ArS(O)SAr)[3a,23] and the hydrolysis of sulfenyl derivatives[13] in an effort to rationalize end reaction products. Recently, more direct evidence for the chemistry of these compounds has been obtained from studies of the stable azetidinonesulfenic acid.[4] Whether these same properties hold for the simple unstable sulfenic acid remains to be determined.

The reaction most characteristic of alkanesulfenic acids is thiolsulfinate (RS(O)SR) formation (eq 4),[3,4] and demon-

$$2ArSOH \rightarrow ArS(O)SAr + H_2O \qquad (4)$$

strates the ability of sulfenic acids to function as both S-electrophiles and S-nucleophiles. Arenesulfenic acids are also believed to form aryl arenethiolsulfinates (ArS(O)SAr), but these compounds are almost never observed.[10] One reason is that aryl arenethiolsulfinates thermally disproportionate to thiolsulfonates (ArSO$_2$SAr) and disulfide (eq 5).[10,24,25] The

$$2ArS(O)SAr \rightarrow ArSSAr + ArSO_2SAr \qquad (5)$$

mechanism for this reaction has been studied by Fava[24] and others[25] and appears to involve homolytic cleavage of the S–S bond of the thiolsulfinate to form sulfinyl (ArSO·) and thiyl (ArS·) radicals.

Although eq 5 predicts equal amounts of disulfide and thiolsulfonate, the ratio of disulfide to thiolsulfonate is greater than unity. For example, phenyl benzenethiolsulfinate (PhS(O)SPh) disproportionates to phenyl disulfide (58%) and phenyl benzenethiolsulfonate (40%). A sulfonic anhydride (ArSO$_2$OSO$_2$Ar) was suggested as the other sulfur-containing species.[24] Barnard has identified arenesulfonic acids as products in the aqueous workup of thiolsulfinate decomposition.[25a] Attempts to prepare aryl thiolsulfinates containing electron-attracting groups have failed.[13c,25b,26]

To complicate matters further thiolsulfinates and thiolsulfonates react with nucleophiles, such as water, to form sulfinic acids and thiols (eq 6 and 7).[13,23b] Note that water is produced in the disproportionation of sulfenic acids (eq 4).

$$ArS(O)SAr + H_2O \rightarrow ArSO_2H + ArSH \qquad (6)$$

$$ArSO_2SAr + H_2O \rightarrow ArSO_2H + ArSOH \qquad (7)$$

Table VI. Thermolysis of **1** in Benzene for 36–100 h at 77 °C under Nitrogen

|	Sulfinimine $XC_6H_4S(O)N=CHR$		Product (% yield)				
Entry	X	R	RCN	RCHO	ArSSAr	ArSO$_2$SAr	ArSO$_2$H
1	H	Ph (**3d**)	83		56	44[a]	Trace
2	3-NO$_2$	Ph (**3g**)	88	3	46	24[b]	23
3	3-NO$_2$	Me (**6a**)	79	4	47	25[b]	17
4	4-NO$_2$	Me (**4h**)	76	9	36	25[c]	24

[a] S. Oae, R. Nomana, Y. Yoshikawa, and W. Tabaki, *Bull. Chem. Soc. Jpn.*, **42**, 2903 (1969). [b] G. Leandri and A. Tundo, *Ann. Chim. (Paris)*, **44**, 225 (1954); *Jpn., Chem. Abstr.*, **49**, 15782h (1955). [c] Reference 13c.

Table VII. Thermolysis of *N*-Benzylidene-3-nitrobenzenesulfinamide (**3g**) for 60 h at Reflux

		Product (% yield)				
Entry	Reaction conditions	PhCN	PhCHO	ArSSAr	ArSO$_2$SAr	ArSO$_2$H (**12**)
1	Benzene (air)	78	5	40	20	18
2	Benzene (N$_2$)	88	3	46	24	23
3	Benzene (N$_2$4A mol sieves)	98		50	23	26
4	THF (40 mol excess H$_2$O)	65	18	43	21	23
5	THF (145 mol excess H$_2$O)	15	74	11	6	76
6	Benzene (O$_2$)	88	4	59		37

Refluxing sulfinimines **1** in benzene for 36–120 h affords nitrile, aldehyde, disulfide, and thiosulfonate (Scheme I). Sulfinimines, **1**, containing electron-attracting 3- and 4-nitro groups gave the corresponding sulfinic acid. Products were isolated by chromatography on Florisil or GLC and were identified by comparison with authentic samples of reaction products (Table VI).

Scheme I

$$1 \rightarrow \begin{matrix} \text{RCN} & \text{ArSSAr} & \text{ArSO}_2\text{H} \\ \text{RCHO} & \text{ArSO}_2\text{SAr} \end{matrix}$$
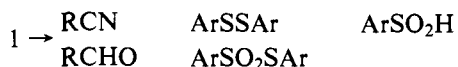
The 3- and 4-nitrobenzenesulfinic acids were not isolated as the free acid, but rather their sodium salts. Ethanol elution of the Florisil column gave water-soluble, yellow solids. The infrared spectra of these solids were similar to those of the corresponding sulfinic acids, but unlike the sulfinic acids these compounds had melting points approaching 300 °C. Elemental analysis and atomic absorption gave the formula ArSO$_2$Na·1.5–1.6H$_2$O. Additional evidence for the structure of these sulfinic acids was their conversion to the corresponding methyl sulfones (ArSO$_2$Me) on treatment with iodomethane.

The isolation of disulfide and thiosulfonate in the thermolysis of **1** (Scheme I) is readily explainable in terms of reactions that have been proposed for sulfenic acids. Thus, thermolysis of **1** affords the corresponding arenesulfenic acids and nitrile (eq 3). Disproportionation of the sulfenic acids yield an intermediate thiolsulfinate (eq 4) which disproportionates further to disulfide and thiolsulfonate (eq 5).

The results, summarized in Table VI, for the thermolysis of some representative sulfinimines reveal a disulfide to thiolsulfonate ratio greater than unity. Fava et al.[24] observed similar results, but in contrast to their findings we isolate sulfinic acids rather than sulfonic acid (sulfonic anhydride) as the other major sulfur-containing species in the thermolysis of **1**.

A probable source of aldehyde (Scheme I) is hydrolysis of the starting material (eq 8). The necessary water is available

$$1 + H_2O \longrightarrow \underset{\mathbf{11}}{\text{Ar}-\overset{\overset{\displaystyle O}{\|}}{S}-NH_2} + RCHO \qquad (8)$$
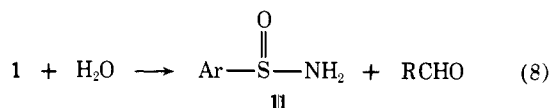
either from the solvent and/or the disproportionation of sulfenic acid (eq 4). Sulfinimines are known to be hydrolyzed to the corresponding carbonyl and sulfinamide **11**.

The formation of sulfinic acid is less readily explained and a number of sources are possible. One potential source of sulfinic acid is hydrolysis of **11** formed via hydrolysis of **1** (eq 9).

$$\underset{}{\text{Ar}-\overset{\overset{\displaystyle O}{\|}}{S}-NH_2} + H_2O \longrightarrow ArSO_2H + H_2O \qquad (9)$$
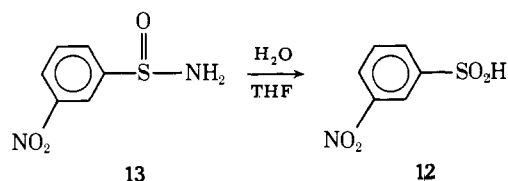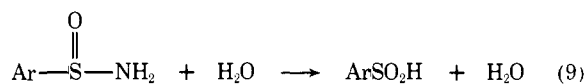
A 65–70% yield of 3-nitrobenzenesulfinic acid (**12**) was isolated on refluxing 3-nitrobenzenesulfinamide (**13**) in aqueous THF for 36 h. Sulfinic acid (Scheme I) may also be formed directly from the sulfenic acid by oxidation (eq 10)[7] and attack of water on the intermediate thiolsulfinate or thiolsulfonate (eq 6 and 7).

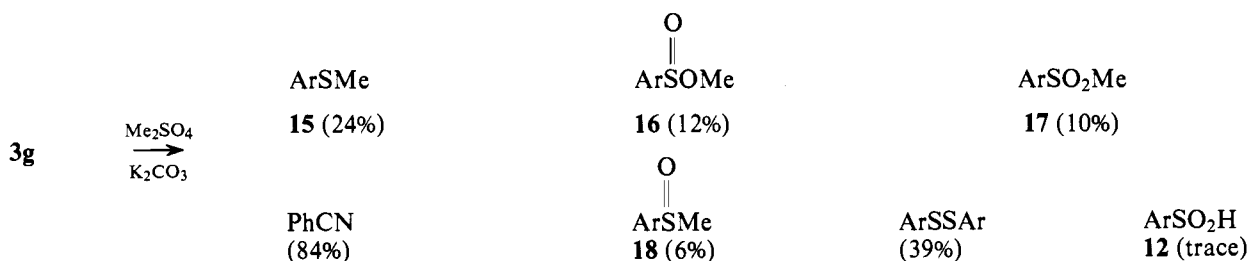$$2ArSOH + O_2 \rightarrow ArSO_2H \qquad (10)$$

To determine the relative importance of eq 6, 7, 9, and 10 as sources of sulfinic acid in the thermolysis of **1**, *N*-benzylidene-3-nitrobenzenesulfinamide (**3g**) was thermolyzed under a variety of conditions. These results are summarized in Table VII.

Hydrolysis of **3g** (eq 8 and 9) can contribute no more than 3–5% of **12** as indicated by the yield of benzaldehyde. When the thermolysis of **3g** was carried out in the presence of 4 Å molecular sieves, which presumably scavenge water formed in situ (Table VII, entry 3), benzaldehyde was not detected. Thus, hydrolysis of **3g** (eq 8 and 9) can be ruled out as a source of sulfinic acid formed under these conditions.

When the thermolysis of **3g** is carried out in THF with a 40 molar excess of water (Table VII, entry 4) hydrolysis increased from 5 to 18% as indicated by the yield of benzaldehyde. Little effect on the disulfide–thiolsulfonate yields was noted. A large excess of water (145 molar excess; Table VII, entry 5) results in nearly complete hydrolysis of **3g** with a corresponding increase in sulfinic acid.

These results eliminate the possibility that hydrolysis of **3g** (eq 8 and 9) is the origin of sulfinic acid. Furthermore, hydrolysis of the intermediate thiolsulfinate and thiolsulfonate (eq 6 and 7) cannot be an important source of sulfinic acid since addition of water to the reaction mixture failed to increase

Scheme II

$$
\begin{array}{cccc}
 & \text{ArSMe} & \overset{\displaystyle O}{\overset{\|}{\text{ArSOMe}}} & \text{ArSO}_2\text{Me} \\
 & \mathbf{15}\ (24\%) & \mathbf{16}\ (12\%) & \mathbf{17}\ (10\%)
\end{array}
$$

3g $\xrightarrow[\text{K}_2\text{CO}_3]{\text{Me}_2\text{SO}_4}$

$$
\begin{array}{cccc}
\text{PhCN} & \overset{\displaystyle O}{\overset{\|}{\text{ArSMe}}} & \text{ArSSAr} & \text{ArSO}_2\text{H} \\
(84\%) & \mathbf{18}\ (6\%) & (39\%) & \mathbf{12}\ (\text{trace})
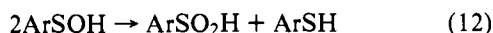\end{array}
$$

Ar = 3-nitrophenyl

significantly the yield of sulfinic acid or alter the disulfide-thiolsulfonate ratio (Table VII; compare entries 3 and 4).

Oxidation of the sulfenic acid to the sulfinic acid by a molecular oxygen (eq 10) can also be ruled out. Thermolysis of **3g** under rigorously degassed conditions failed to decrease the yield of sulfinic acid (Table VII, entries 2 and 3). When oxygen was passed through the reaction mixture the yields of disulfide and sulfinic acid were increased. Thiolsulfonate (ArSO$_2$SAr) was not detected (Table VII, entry 6). Oxygen may be reacting with the sulfinyl radical produced in the disproportionation of the intermediate thiosulfinate (eq 5).

There are at least two other ways in which sulfinic acid may be formed in the thermolysis of **3g**. Sulfenic acids are reported to be excellent nucleophiles, and Kice has estimated that benzenesulfenic acid (PhSOH) is some 10^5 times more reactive toward nucleophilic attack at sulfenyl sulfur than water.[23d] Thus, sulfinic acid may be formed by attack of sulfenic acid on thiolsulfonate (eq 11). Under our conditions, however, the concentration of sulfenic acid must be very small at any given time, and it is unclear whether this reaction (eq 11) will be fast enough to be the primary source of sulfinic acid in the thermolysis of **3g**.

$$\text{ArSOH} + \text{ArSO}_2\text{SAr} \rightarrow \text{ArSO}_2\text{H} + \text{ArS(O)SAr} \quad (11)$$

An alternative source of sulfinic acid, which has not previously been considered, is the direct disproportionation of two sulfenic acid units to sulfinic acid and thiol (eq 12).[27] This reaction is particularly attractive from the standpoint that it may take place from the same hydrogen-bonded complex proposed necessary for sulfenic acid disproportion (eq 4).[3a–c] Furthermore, eq 12 can explain the increased yield of disulfide (Table VII) which may arise as shown in eq 13–15.[23c]

$$2\text{ArSOH} \rightarrow \text{ArSO}_2\text{H} + \text{ArSH} \quad (12)$$

$$\text{ArSH} + \text{ArSOH} \rightarrow \text{ArSSAr} + \text{H}_2\text{O} \quad (13)$$

$$\text{ArSH} + \text{ArS(O)SAr} \rightarrow \text{ArSSAr} + \text{ArSOH} \quad (14)$$

$$\text{ArSH} + \text{ArSO}_2\text{SAr} \rightarrow \text{ArSSAr} + \text{ArSO}_2\text{H} \quad (15)$$

The reason that sulfinic acids are isolated only when the sulfenic acid contains electron-attracting 3- and 4-nitro groups is unclear (Table VII). Perhaps the increased acidity of the sulfenic acid favors sulfenic acid to sulfinic acid–thiol disproportionation (eq 12) over sulfenic acid to thiosulfinate–water disproportionation (eq 4).

1-Anthraquinonesulfenic acid is reported to react with dimethyl sulfate to afford the corresponding sulfenate ester.[8] In an attempt to trap 3-nitrobenzenesulfenic acid as it was formed, **3g** was thermolyzed for 7 days in benzene with dimethyl sulfate–anhydrous potassium carbonate. As Scheme II illustrates a variety of methylated products were isolated, but the expected methyl 3-nitrobenzenesulfenate (**14**, 3-NO$_2$C$_6$H$_4$SOMe) was not detected. Products were separated by GLC and chromatography on Florisil and identified by comparison with authentic samples.

The high yield of benzonitrile (84%) indicates that these products (Scheme II) are formed primarily from the sulfenic acid and/or from products derived from the sulfenic acid. The isolation of **15, 16**, and **17** is supportive of eq 12 since methylation of thiol would yield **15** and methylation of sulfinic acid would afford **16** and **17**. In a separate experiment 3-nitrobenzenesulfinic acid (**12**), when treated with dimethyl sulfate–potassium carbonate, gave **16** (60%) and **17** (7%). As predicted by eq 12, the combined yields of **16** and **17** (Scheme II) closely correspond to the yield of **15**.

Sulfoxide **18** is undoubtedly formed directly from the sulfenic acid and dimethyl sulfate. The sulfenate ester **14**, if it were formed, might not have been stable under the reaction conditions. Alkyl arenesulfenates are thermally unstable, decomposing to give, among other products, disulfides.[28] Compound **14** may also react according to eq 16. Similar reactions have been proposed for alkyl alkanesulfenates.[29]

$$\text{ArSOMe} + \text{ArS(O)SAr} \xrightarrow{\displaystyle O} \overset{\displaystyle O}{\overset{\|}{\text{ArSOMe}}} + \text{ArSSAr} \quad (16)$$
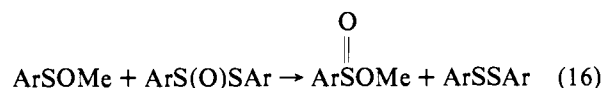
Thermolysis of **3g** in aqueous methanol for 7 days affords **12, 13, 16**, and bis(3-nitrophenyl) disulfide (Table VIII). It is probable that the sulfinate ester, **16**, is formed by direct attack of the solvent on the intermediate thiolsulfinate (eq 17). A similar mechanism has been proposed for the formation of ethyl 2-nitrobenzenesulfinate in the ethanolysis of 2-nitrobenzenesulfenic acid.[9]

$$\text{ArS(O)SAr} + \text{MeOH} \xrightarrow{\displaystyle O} \overset{\displaystyle O}{\overset{\|}{\text{ArSOMe}}} + \text{ArSH} \quad (17)$$
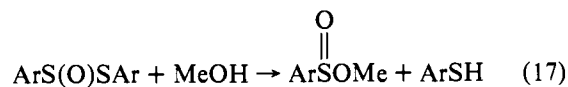
Methyl 3-nitrobenzenesulfinate (**16**) is apparently not formed by methanolysis of **13** (eq 9, H$_2$O = MeOH) since thermolysis of **3g** in aqueous methanol for 14 days resulted in an increase of sulfinic acid **12** at the expense of **13** (Table VIII). Thus hydrolysis rather than methanolysis of **13**, even in the presence of a large excess of methanol, appears to be the dominant reaction for **13**. No detectable amounts of **16** were observed on refluxing **13** with anhydrous methanol for 7 days.

Table VIII. Thermolysis of N-Benzylidene-3-nitrobenzenesulfinamide (**3g**) in Methanol under Nitrogen at Reflux

Products Ar = 3-nitrophenyl	% yield— 7 days methanol– H$_2$O^a	% yield— 7 days anhydrous methanol	% yield— 14 days methanol– H$_2$O^a
ArSSAr	45	40	41
ArS(O)OMe (**15**)	30	34	31
ArSO$_2$H (**12**)	11	10	28
ArS(O)NH$_2$ (**13**)	14	16	0
PhCHO	25	Trace	26
PhC≡N	74	75	74

^{a} 0.01–0.03% water.

In anhydrous methanol, where hydrolysis of **3g** to benzaldehyde cannot take place, **13** was still isolated (Table VIII). Methanol is known to add to the C–N double bond of **1** (R = alkyl)[14] and over a long period of time methanol may add to the C–N bond of **3g** to form **13** and presumably benzaldehyde dimethyl acetal.

The difficulty in studying the reactions and properties of sulfenic acids results not only from the high reactivity of this species, but also from the high reactivity of the reaction products. The lack of mild nonaqueous synthetic routes to these compounds has contributed to these difficulties. Although arenesulfenic acids can be prepared from **1** using conditions milder than the solution pyrolysis of sulfoxides, the rate at which this reaction (eq 3) occurs reveals that the concentration of the sulfenic acid at any one time is relatively small. Furthermore, the sulfenic acid and thiolsulfinate are unstable at temperatures where the thermolysis of **1** occurs at a convenient rate. The desirability of developing even milder, lower temperature methods for the synthesis of sulfenic acid is evident. Such a synthetic method would appear to be the flash vacuum pyrolysis (FVP) of aryl and alkyl *tert*-butyl sulfoxides. We have reported that this technique affords the corresponding arene- and alkanesulfenic acids in high concentrations under stable conditions.[30]

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were measured on a Varian A-60A spectrometer and IR spectra on a Perkin-Elmer 457 spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6 mass spectrometer at 70 eV. Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph using a 6 ft × ⅛ in. FFAP column. The analyses were determined by comparison of peak areas with standard solutions of the reaction products. Elemental analyses were obtained form Chemalytics. Inc., Tempe, Ariz. Sodium analyses were measured on a Perkin-Elmer Model 303 atomic absorption spectrometer with DCR1 read-out. Solvents were purified by standard procedures unless otherwise noted.

Preparation of *N*-Alkylidenearenesulfenamides (2). Sulfenimines **2** were prepared from the corresponding disulfide, aldehyde, ammonia, and silver nitrate using the metal-assisted procedure previously described (Table I).[15] **2**, $XC_6H_4SN=CHR$, X, R (% yield, mp (bp), °C): 2-Me, Ph (83, unstable liquid); 4-Br, Me (85, 139–140 (0.75)); 4-Cl, Me (61, 96–97 (0.02)); 4-NO_2, Me (74, 83–84); 3-NO_2, Et (91, unstable liquid), 3-NO_2, *t*-Bu (70, 126–127 (0.015)); 3-NO_2, 4-methoxyphenyl (64, 113–114); 3-NO_2, *p*-tolyl (68, 99–100); 3-NO_2, 4-chlorophenyl (58, 126–127); 3-NO_2, 3-nitrophenyl (80, 151–153); 3-NO_2, 4-nitrophenyl (70, 186–187).

Preparation of *N*-Alkylidenearenesulfinamides (1). In a 250-ml three-necked flask equipped with mechanical stirrer and dropping funnel were placed 10.0 mmol of the appropriate sulfenimine (**2**) in 60 mL of chloroform and 1.4 g of $NaHCO_3$ in 20 mL of water. The reaction mixture was cooled to 0 °C and rapidly stirred and 2.23 g (11.0 mmol) of *m*-CPBA (Aldrich) in 65 mL of chloroform added dropwise over 0.5 h. After the addition was complete, stirring was continued for 1 h and the chloroform phase dried over anhydrous K_2CO_3. Solvent was removed under vacuum (rotary evaporator at 25 °C) to give the crude sulfinimine, **1**. Solid **1** was crystallized from ether and liquid **1** was chromatographed on Florisil (Table II).

Preparation of Methyl *trans*-Arenesulfinylacrylate (9) and Ethyl Arenesulfinylpropionate (10). In a 50-mL round-bottom flask equipped with condenser and nitrogen inlet were placed 0.5 mmol of the appropriate **1** and 10.0 mmol of methyl propiolate (Chemical Samples Co.) or ethyl acrylate. The reaction mixture was heated at 110 °C in an oil bath for 24 h, at which time excess solvent was removed under vacuum. The residue was chromatographed on Florisil to yield **9** or **10** (Table III).

Methyl *trans*-3-nitrophenylsulfinylacrylate (9b): mp 91–92 °C; NMR (CDCl₃) δ 3.80 (s, 3, Me), 6.65–7.72 (q, *J* = 15 Hz, 2 H), 7.65–8.5 (m, 4 H). Anal. Calcd for C₁₀H₉NO₅S: C, 47.06; H, 3.55. Found: C, 46.75; H, 3.60.

Methyl *trans*-4-nitrophenylsulfinylacrylate (9d): mp 96–98 °C; NMR (CDCl₃) δ 3.88 (s, 3 H, Me), 7.20 (d, *J* = 15 Hz, 1 H), 7.5–7.9 (m, 5 H). Anal. Calcd for C₁₀H₉NO₅S: C, 47.06; H, 3.55. Found: C, 47.38; H, 3.82.

Ethyl Phenylsulfinylpropionate (10a). Chromatography on Florisil gave a yellow oil for which a satisfactory elemental analysis could not be obtained: IR (film) 1725 (s, C=O), 1080 cm⁻¹ (s, S=O); NMR (CDCl₃) δ 1.2 (t, *J* = 7 Hz, 3 H, Me), 2.4–3.3 (m, 4 H), 4.1 (q, *J* = 7 Hz, 2 H, CH₂), 7.5 (d, 5 H) (see below).

Ethyl 3-Nitrophenylsulfinylpropionate (10b). Chromatography on Florisil gave a yellow oil for which a satisfactory elemental analysis could not be obtained: IR (thin film) 1720 (s, C=O), 1080 cm⁻¹ (s, S=O); NMR (CDCl₃) δ 1.23 (t, *J* = 7 Hz, 3 H, Me), 2.9 (m, 4 H), 4.1 (q, *J* = 7 Hz, 2 H, CH₂), 7.63–8.50 (m, 4 H); M⁺ *m/e* 271.

Ethyl 4-Chlorophenylsulfinylpropionate (10e): mp 78–79 °C (hexane); IR (KBr) 1722 cm⁻¹ (s, C=O); NMR (CDCl₃) δ 1.23 (t, *J* = 7 Hz, 3 H, Me), 2.92 (m, 4 H), 4.0 (q, *J* = 7 Hz, 2 H, CH₂), 7.50 (m, 4 H). Anal. Calcd for C₁₁H₁₃ClO₃S: C, 50.67; H, 5.03. Found: C, 50.41; H, 5.24.

Ethyl Phenylmercaptopropionate. This compound was prepared from 22 g (0.2 mol) of benzenethiol, 0.2 g of sodium methoxide, and 35 g of ethyl acrylate according to the procedure of Hurd and Gershbein.[31] The residue remaining after removal of solvent was distilled to yield 26 g (63%) of ethyl phenylmercaptopropionate: bp 116–117 °C (3.0 mm); IR (thin film) 1725 cm⁻¹ (s, C=O); NMR (CDCl₃) δ 1.22 (t, *J* = 7 Hz, 3 H, Me), 2.6 (t-d, *J* = 8 Hz, 2 H, CH₂), 3.55 (t-d, *J* = 8 Hz, 2 H, CH₂), and 7.3 (m, 5 H).

Oxidation of Ethyl Phenylmercaptopropionate. In a 250-mL three-necked flask equipped with mechanical stirrer and dropping funnel were placed 4.4 g (0.021 mol) of ethyl phenylmercaptopropionate in 50 mL of chloroform and 2.6 g of $NaHCO_3$ in 25 mL of water. The reaction mixture was cooled in an ice bath and rapidly stirred and 4.6 g (0.023 mol) of *m*-CPBA in 30 mL of chloroform added dropwise over 30 min. The ice bath was removed and the reaction mixture allowed to stir for 3 h. The chloroform solution was dried over anhydrous K_2CO_3 and the solvent removed under vacuum to give an oil, 4.5 g (87%), whose spectral properties were identical with those of ethyl phenylsulfinylpropionate (**10a**) prepared above.

3-Nitrobenzenesulfinamide (13). In a 250-mL three-necked flask equipped with mechanical stirrer and dropping funnel were placed 1.0 g (0.0058 mol) of 3-nitrobenzenesulfenamide[15a] in 50 mL of chloroform and 0.6 g of $NaHCO_3$ in 30 mL of water. The reaction mixture was cooled in an ice bath and rapidly stirred and 1.2 g (0.006 mol) of *m*-CPBA in 40 mL of chloroform added dropwise over 30 min. After stirring for 2 h at room temperature the chloroform phase was dried over anhydrous K_2CO_3. Removal of solvent gave 1.0 g (93%) of white needles: mp 110–111 °C; IR (KBr) 3200 (bd, NH₂) and 1030 cm⁻¹ (s, S=O); NMR (CD₃CN) δ 5.0 (bs, 2 H, NH₂) and 7.3–8.4 (m, 4 H). Anal. Calcd for C₆H₆SO₃S: C, 38.71; H, 3.25. Found: C, 38.56; H, 3.29.

Thermolysis of *N*-Alkylidenearenesulfinamides (1). Rate Studies. In a 1-mL volumetric flask, 1.0 mmol of the appropriate *N*-alkylidenearenesulfinamide (**1**) was mixed with 0.488 g (0.33 mmol) of 4-*tert*-butyltoluene and the mixture dissolved in about 0.5 mL of benzene-d_6. Additional benzene-d_6 was added to dilute the solution to the 1-mL mark at which point the solution was divided into two 0.5-mL portions and transferred to two separate NMR tubes. After the initial NMR spectra were run with five separate integrations of the peak areas of the imidoyl proton (U_0) and methyl protons (S_0) of 4-*tert*-butyltoluene the NMR samples were heated in a thermostatically controlled oil bath at 77.0 ± 0.1 °C for periods ranging from 5.0 to 1500 min. The time interval chosen was dependent from the rate of decrease in the peak area of the imidoyl proton. Following heating for the specified time period the samples were plunged into an ice bath and allowed to come to ambient temperature and the NMR sample integrations of the imidoyl proton (U_x) and methyl protons (S_x) of 4-*tert*-butyltoluene were measured. The entire process was repeated until at least eight separate determinations were made. The concentration of **1** at each time interval (x) was obtained using the equation

$$\text{mol of sulfinimine at time } x = (\text{initial concn of sulfinimine}) \frac{U_x S_0}{U_0 S_x}$$

where U_0 = integrated area of imidoyl proton at $t = 0$, U_x = integrated area of imidoyl proton $t = x$, S_0 = integrated area of methyl proton of standard at $t = 0$, and S_x = integrated area of methyl proton of standard at $t = x$.

The rate constants (K_r) were determined from the slope of the least-squares plot of the natural logarithm of the concentrations with respect to time, x (Table V).

Thermolysis of N-Alkylidenearenesulfinamides (1). Product Studies. The appropriate sulfinimine (2.0 mmol) in 50 mL of dry benzene was placed in a 100-mL round-bottom flask equipped with gas inlet, magnetic stir bar, condenser, and Dean-Stark column. The reaction mixture was refluxed in a nitrogen atmosphere for the specified time period and the solvent removed under vacuum. 1-Chlorodecane (1.0 mmol) was added to the residue in 50 mL of chloroform. Benzaldehyde and benzonitrile yields were determined by GLC.

The residue remaining after removal of the solvent was chromatographed on Florisil to obtain disulfide (pentane-benzene), thiosulfonate (CH₂Cl₂-ether), and sulfinic acid (ethanol). Analyses were performed at least twice and the results averaged. See Table II.

Sodium 3-Nitrobenzenesulfinate: mp 246–248 °C; IR (KBr) 1025 cm⁻¹ (s, S=O). Anal. Calcd for NO₂C₆H₄SO₂Na·1.7H₂O: C, 30.13; H, 3.09; N, 5.86; S, 13.41; Na, 9.61. Found: C, 30.13; H, 2.81; N, 5.98; S, 13.27; Na, 9.50.

Sodium 4-Nitrobenzenesulfinate: mp 330 °C dec; IR (KBr) 1028 cm⁻¹ (s, S=O). Anal. Calcd for NO₂C₆H₄SO₂Na·1.5H₂O: C, 30.51; H, 2.99; Na, 9.73. Found: C, 30.72; H, 2.73; Na, 9.55.

Thermolysis of N-Benzylidene-3-nitrobenzenesulfinamide (3g) with Removal of Water. Sulfinimine 3g (0.55 g, 2.0 mmol) was heated in benzene with 1.0 g of Davidson 4 Å molecular sieves. The reaction mixture was analyzed as described above (Table VII).

Thermolysis of 3g in Aqueous THF. Sulfinimine 3g (0.55 g, 2.0 mmol) in 50 mL of THF and specified amount of water (see Table VII) was refluxed in a nitrogen atmosphere for 60 h. The reaction mixture was analyzed as described above.

Thermolysis of 3g in an Oxygen Atmosphere. Sulfinimine 3g (0.55 g, 2.0 mmol) was thermolyzed as described above. Dry oxygen (passed through sulfuric acid, potassium hydroxide, and calcium chloride successively) was passed continuously through the reaction mixture by means of a fritted glass tube. The reaction mixture was analyzed as described above.

Thermolysis of 3g in the Presence of Dimethyl Sulfate. In a 50-mL round-bottomed flask equipped with magnetic stir bar, condenser, and nitrogen inlet was placed 0.274 g (0.001 mol) of 3g in 25 mL of dry benzene containing 0.154 g (0.0012 mol) of dimethyl sulfate and 0.15 g of anhydrous potassium carbonate. After refluxing under a nitrogen atmosphere for 7 days, the reaction mixture was cooled and filtered and the solvent removed under vacuum. Benzonitrile was determined by GLC as described above. The residue was chromatographed on Florisil to give (pentane-benzene) 0.04 g (24%) of methyl 3-nitrophenyl sulfide (15),³² NMR (CDCl₃) δ 2.5, S-Me; (benzene) 0.032 g (21%) of bis(3-nitrophenyl) disulfide, (chloroform) 0.084 g of a mixture of products identified by TLC and NMR using a toluene standard as (6%) methyl-3-nitrophenyl sulfoxide (18),³³ NMR (CDCl₃) δ 2.9, S(O)Me; (10%) methyl-3-nitrophenylsulfone (17),³⁴ NMR (CDCl₃) δ 3.1, SO₂Me; and (12%) methyl-3-nitrobenzenesulfinate (16), NMR (CDCl₃) δ 3.6, S(O)OMe.

Methyl 3-Nitrobenzenesulfinate (16). In a 100-mL round-bottom flask equipped with magnetic stir bar, condenser, and nitrogen inlet were placed 0.3 g (0.0016 mol) of 3-nitrobenzenesulfinic acid³⁵ in 50 mL of dry benzene containing 0.18 g (0.0014 mol) of dimethyl sulfate and 0.18 g of anhydrous potassium carbonate. After refluxing for 7 days under nitrogen the solvent was removed in vacuo and the oily residue chromatographed on Florisil. Elution with pentane-benzene gave 0.19 g (60%) of an oil identified as 16: IR (film) 1122 cm⁻¹ (s, S=O); NMR (CDCl₃) δ 3.62 (s, 3 H, MeO), and 7.33–8.68 (m, 4 H). Anal. Calcd for C₇H₇NO₄S: C, 41.74; H, 3.51. Found: C, 41.53; H, 3.48.

Further elution of the column with benzene gave 0.023 g (7%) of a white solid, mp 146 °C (lit.³⁴ mp 146–147 °C) identified as 17.

Thermolysis of 3g in Methanol. In a 50-mL round-bottom flask equipped with magnetic stir bar, condenser, and drying tube was placed 0.51 g (0.0019 mol) of 3g in 10 mL of methanol (methanol containing 0.01–0.03% water or anhydrous methanol prepared by distillation from magnesium methoxide). After refluxing for the appropriate time period (Table VIII) the solvent was removed in vacuo to give an oily solid. The yields of benzonitrile and benzaldehyde were determined by GLC as described above. The residue was chromatographed on Florisil to give (n-pentane) bis(3-nitrophenyl) disulfide; (n-pentane-benzene) methyl 3-nitrobenzenesulfinate (16); (ben-

zene-pentane) 3-nitrobenzenesulfinamide (13); and (ethanol) 3-nitrobenzenesulfinic acid (12). Yields are recorded in Table VIII.

Supplementary Material Available: Table I, properties of N-alkylidenearenesulfenamides (1 page). Ordering information is given on any current masthead page.

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Homolytic Displacement at Sulfur by the Hydrogen Atom. Formation of Hydrogen Sulfide in the Liquid-Phase Photolysis of Thiols

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Abstract: The photochemistry of several thiols in the liquid phase has been investigated, and the products are reported. In all cases, products are obtained that can be rationalized as arising from the primary photoscission of the carbon–sulfur bond. Possible mechanisms for the formation of these products are discussed, and evidence is presented for a mechanism involving a free-radical displacement reaction on the sulfur atom by hydrogen atoms, eq 8. This reaction appears to have an activation energy only some 3.8 kcal/mol higher than the activation energy for abstraction of the sulfhydryl hydrogen, eq 2. It is also suggested that in the presence of certain solvents (e.g., tetrahydrofuran), interactions between excited thiol and the solvent may alter the course of the photochemical decomposition of the thiol. This may be involved in the discrepancies in the literature on the photo- and radiation chemistry of alcohols when thiols are used as the H-atom source.

Introduction

Thiols and thiyl radicals have long been recognized as species which play important roles in many biochemical systems.[1] The discovery that certain thiols protect living cells from radiation damage has led to considerable interest in the radiochemistry and radiation biology of thiols and other sulfur-containing molecules of biological importance.[2]

Surprisingly, however, very little is known about the fundamental photochemistry of thiols in solution. We have made extensive use of thiol photolysis as a source of hydrogen atoms in solution,[3] and thiol photolysis has been studied by numerous workers in the gas phase[4] and in solid matrices at low temperatures.[5] However, there is only one report of a detailed study of the photochemistry of thiols in solution.[6]

In the single reported study of the photolysis of neat liquid ethanethiol, Carlson and Knight reported that the only observable products are hydrogen and diethyl disulfide. To account for these products, they proposed a simple three-reaction sequence involving thiyl radicals and hydrogen atoms as the only radical intermediates.

$$RSH \xrightarrow{h\nu} RS\cdot + H\cdot$$

$$H\cdot + RSH \rightarrow RS\cdot + H_2$$

$$2 RS\cdot \rightarrow RSSR$$
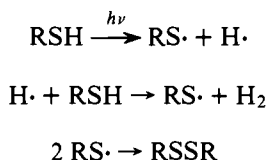
Their conclusions, if general for the photolysis of thiols, are quite surprising in view of the reported reaction of hydrogen atoms with thiols to form hydrogen sulfide when the hydrogen atoms are generated by radiochemical means[7,8] or by electrical discharge.[9,10]

$$H\cdot + RSH \rightarrow R\cdot + H_2S$$
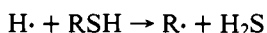
Since the photochemistry of thiols, thiyl radical chemistry, and the use of thiol photolysis as a source of hydrogen atoms are of interest to us, we undertook a detailed study of the solution photochemistry of thiols.

Experimental Section

Hydrogen Analysis. The irradiation cell containing the sample to be analyzed was attached to a Toepler pump, and the sample was frozen in a liquid nitrogen bath. Hydrogen was transferred from the irradiation cell to a manifold of known volume where its pressure was determined, and the number of moles present was calculated assuming ideal gas behavior. Several freeze–thaw cycles were employed to ensure the complete removal of hydrogen from the sample. The manifold was calibrated with known amounts of hydrogen gas.

Hydrogen Sulfide Analysis. A modification of the methylene blue procedure of Jacobs, Braverman, and Hochheiser[11] was followed. The following solutions were prepared.

Trapping Reagent. To a rapidly stirred solution of 4.30 g of cadmium sulfate ($3CdSO_4\cdot8H_2O$, Merck reagent) in 800 mL of H_2O in a 1-L volumetric flask was added a solution of 0.32 g of NaOH in 100 mL of H_2O (precipitate forms). The suspension was diluted to 1 L total volume, and was stirred rapidly as aliquots were withdrawn for use.

Diamine Stock Solution. In a mixture of 50 mL of concentrated H_2SO_4 and 30 mL of water was dissolved 16.32 g of N,N-dimethyl-p-phenylenediamine sulfate (Eastman, recrystallized from water–acetone). The stock solution was placed in a dark bottle and stored in the refrigerator.

Diamine Working Solution. To a 250-mL volumetric flask was added 12.5 mL of diamine stock solution, and the flask was filled to volume with 50% (v/v) H_2SO_4 solution and stored in the refrigerator.

Ferric Chloride Solution. A solution of 100 g of $FeCl_3$ in 50 mL of H_2O was diluted to 100.0 mL for use.

Hydrogen Sulfide Trapping Methods. The following three methods were used to separate H_2S from the reaction mixture and trap it as CdS.

Method A. The irradiation cell was attached to an evacuated double-trap manifold; the cell was opened, and the reaction mixture was allowed to distill into the first trap, precooled to −131 °C in a pentane slush bath. Hydrogen sulfide passed into the second trap, where it was condensed at liquid nitrogen temperature. The second trap was then