σ_{CCl} and σ^*_{CCl} in a three molecular orbital four-electron interaction (Figure 4).

As we have described elsewhere,[13a] interactions of this type can be net stabilizing. The initial four-electron interaction gives rise to a bonding combination, ψ_1, which is lowered in energy. The accompanying antibonding component is increased in energy to a point where it begins to mix into itself the higher lying virtual orbital (σ^*_{CX}) in a two-electron interaction. In most of the cases that we have examined thus far, the magnitude of this two-electron stabilization increases to a point where it equals or exceeds the intrinsic four-electron destabilization of this three MO four-electron interaction. Thus the HOMO orbital ψ_2 is stabilized at the expense of an empty orbital ψ_3 such that $\Delta E_1 > \Delta E_2$ (Figure 4). For both of these above cases when a charged nucleohile is involved, there is a significant stabilizing contribution to the overall energetics of the reaction early along the reaction coordinate. For a neutral nucleophile such as an amine, we would expect a greater influence of the four-electron interaction early along the reaction coordinate. Only after the level of the relatively low lying amine lone pair has been sufficiently raised in energy, as a result of its closed shell repulsion with the filled σ_{CCl} orbital, should any significant two-electron stabilization resulting from the interation of the developing HOMO orbital with the σ^*_{CCl} be realized. As pointed out elsewhere,[13] such reactions typically exhibit a barrier in the gas phase and involve a relatively late transition state. This is partially responsible for the smaller degree of rate enhancement observed with neutral nucleophiles. One must also take into consideration that charged nucleophiles are typically more highly solvated which also contributes to the activation barrier.

In our comparison of the S_N2 attack by Cl^- at saturated carbon, we have concluded that the more polarizable carbonyl bond[7a] has a stronger activating influence than a carbon–carbon double bond. The difference in reaction rate is an obvious consequence of the ability of the carbonyl functionality to stablize a developing negative charge at the transition state. We propose a unifying mechanism where the increased rate of S_N2 displacement of allylic (benzylic) substrates relative to methyl chloride and especially *n*-propyl chloride[17] may also be attributed to the stabilizing influence of the delocalized allylic MO (ψ_{23}) in the transition state (Figure 3). Thus, no special explanation or multicenter bonding of the nucleophile to the electrophilic center and the adjacent carbonyl carbon need be involved in an explanation of the enhanced reactivity or "electrophilicity" of α-halo carbonyls. Increased reactivity toward nucleophiles in the S_N2 reaction should be anticipated whenever the repulsive or four-electron component of the reaction can be decreased by electron delocalization via a conjugated molecular orbital (ψ_{22}) as depicted in Figure 2.[18]

Acknowledgment. Support of this work by the donor of Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are grateful to Wayne State University Computing Center for generous amounts of computation time, and to Professor H. Bernhard Schlegel for his helpful assistance with the calculations.

Registry No. Allyl chloride, 107-05-1; α-chloroacetaldehyde, 107-20-0.

(17) Streitwieser, A. "Solvolytic Displacement Reactions"; McGraw-Hill Book Company: New York, 1962; p 13.

(18) For a particularly clever theoretical experiment that demonstrates the importance of the four-electron interaction in S_N2 reactions, see: Kost, D.; Aviram, K. *Tetrahedron Lett.* **1982**, *23*, 4157.

Chemistry of Sulfenic Acids. 7.[1,2] Reason for the High Reactivity of Sulfenic Acids. Stabilization by Intramolecular Hydrogen Bonding and Electronegativity Effects

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It is proposed that the reason sulfenic acids (RSOH) are so reactive and usually not isolated or even detected is that they form thiosulfinates (RS(O)SR) so readily. This is a consequence of the sulfenic acid hydrogen-bonded dimer, **1**, which lowers the energy of activation for thiosulfinate formation. The stability of the few sulfenic acids that have been isolated can be explained in terms of steric, electronic, and intramolecular hydrogen-bonding effects which prevent dimer formation. The importance of these effects on the stability of simple unstable sulfenic acids was demonstrated by flash vacuum pyrolysis (FVP) and the thiosulfinate/vinyl sulfoxide ratio. A novel, high yield, rearrangement of sulfenic acid **19f** to 1,3-benzothiazine **26** was observed.

Sulfenic acids (RSOH) have been of interest for more than three-quarters of a century. Their importance as transient intermediates in organic and bioorganic sulfur reactions is now well recognized.[3,4] The two most important reactions of a sulfhydryl group (RSH) in living systems, oxidation to higher sulfur oxides (RSO_xH) and to disulfides (RSSR), has recently been shown to involve sulfenic acid intermediates.[4a] Much of the chemistry of the penicillin sulfoxides is related to the relatively stable 2-oxazetidine-4-sulfenic acid.[5] Indeed, the spectrum of

(1) Part 6: Davis, F. A.; Billmers, R. L. *J. Org. Chem.* **1985**, *50*, 2593.

(2) These results were taken in part from the Ph.D. Theses of R. L. Billmers, Drexel Univeristy, 1984, and L. A. Jenkins, Drexel University, 1985.

(3) For reviews on the chemistry of sulfenic acids see: Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65; Hogg, D. R. *Compr. Org. Chem.* **1979**, *4*, 261.

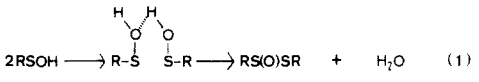
(4) For leading references on the biological reactions of sulfenic acids see: (a) Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 7016. (b) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293.

(5) Sammes, P. G. *Chem. Rev.* **1976**, *76*, 113; Stoodley, R. J. *Tetrahedron* **1975**, *31*, 2321.

0022-3263/86/1951-1033$01.50/0

reactivity displayed by these species is exhibited by few other functionalities.[3,4] Despite the importance and interest in the chemistry of sulfenic acids they are seldom isolated or even detected. To date, only a few very special examples are known, and the reasons for their high reactivity remain unclear.[3,4]

We, as well as others, have shown that the most common reaction of sulfenic acids is thiosulfinate formation, illustrating their ability to act as both electrophiles and as nuclephiles (eq 1).[6,7] Infrared evidence for the involvement of hydrogen-bonded sulfenic acids in this reaction has recently been described by us using flash vacuum pyrolysis (FVP) and low temperature matrix isolation techniques.[1] Many workers have suggested that a hydrogen-bonded dimer such as **1** is a prerequisite for thiosulfinate formation.[6,7] While reasonable, other hydrogen-bonded sulfenic acid species cannot be excluded. Because sulfenic acids are so reactive, few mechanistic details of reaction 1 are known.[8]

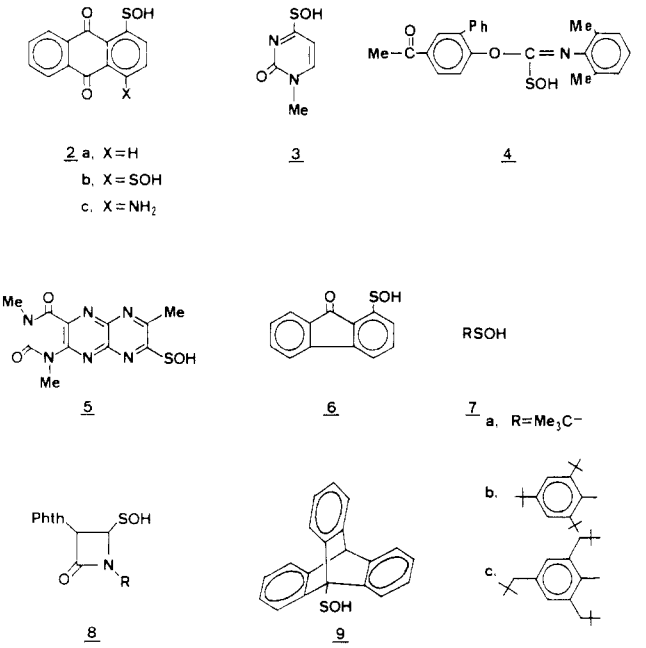


1

In this paper we propose that the high reactivity of sulfenic acids is due to the ease with which they form thiosulfinates (eq 1). This in turn is governed by the rate of intermolecular hydrogen bonding by the sulfenic acid, i.e., the dimer, **1**, or related species. Using this concept it is possible to explain the low reactivity of the few sulfenic acids that have been isolated.

We believe that the reason sulfenic acids form thiosulfinates so easily is that intermolecular hydrogen bonding is particularly effective in lowering the potential energy or enthalpy of reaction 1.[8] This may be related to the fact that the structure of hydrogen-bonded sulfenic acids and the geometry of the transition state for thiosulfinate formation (eq 1) are similar. Thiosulfinates are formed at appreciable rates even at temperatures as low as −50 °C.[1] If these arguments are correct then those features that inhibit intermolecular hydrogen bonding, as in **1**, will reduce the propensity of the sulfenic acid to form thiosulfinates, lowering its reactivity.

Intramolecular hydrogen bonding of the sulfenic acid with an adjacent functional group is one way of inhibiting the intermolecular hydrogen bonding in **1**. Indeed Kharasch et al. were the first to propose that the low reactivity of anthraquinone-1-sulfenic acid (**2a**) was due to such hydrogen bonding.[10] However, this suggestion was based only on the fact that anthraquinone-2-sulfenic acid could not be isolated.[11] The relative stability of other anthraquinonesulfenic acids,[12] such as **2b**,[13] pyrimidinesulfenic acid, **3**,[14] and aryloxyiminomethanesulfenic acid, **4**,[15] has also been attributed to intramolecular hydrogen bonding. Similar arguments can be made for the recently reported 1,3,6-trimethyllumazine-7-sulfenic acid (**5**).[16]



2 a, X=H; b, X=SOH; c, X=NH_2 **3** **4** **5** **6** **7** a, R=Me_3C- **8** **9**

A significant contributor to the overall properties of sulfenic acids is their α-effect nucleophilicity, i.e., the sulfenic acid sulfur is much more nucleophilic than sulfenyl sulfur.[17] Reducing the nucleophilicity of the sulfenic acid would also be expected to slow the rate of reaction 1. Based on the act that fluorenone-1-sulfenic acid (**6**)[18] and 4-aminoanthraquinone-1-sulfenic acid (**2c**)[19] could not be isolated, Barltrop and Morgan,[20] and later Bruice and Markiw,[13] suggested that in addition to intramolecular hydrogen bonding the SOH group needed to be attached to an electronegative carbon atom for stability.

The stability of 2-methyl-2-propanesulfenic acid (**7a**),[21] in solution, and the unusual thermal stability of 2-oxoazetidine-4-sulfenic acid (**8**)[22] have been attributed to steric inhibition of reaction 1. Although our attempts to prepare 2,4,6-tri-*tert*-butyl- and 2,4,6-trineopentylbenzenesulfenic acids (**7b–c**) were unsuccessful, the reason is probably related to the method used to generate them, i.e., flash vacuum pyrolysis (FVP) at 280–600 °C.[6,23] The recent isolation of 9-triptycenesulfenic acid (**9**), which can only be stabilized by steric inhibition of reaction 1, supports this contention.[24]

Shelton and Davis have shown that 2-methyl-2-propanesulfenic acid (**7a**) is relatively stable in polar and

(6) Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467.
(7) Block, E.; O'Conner, J. *J. Am. Chem. Soc.* **1974**, *96*, 3921, 3929.
(8) Formation of thiosulfinates from **1** requires a frontside nucleophilic displacement at sulfur. Both incoming and outgoing groups could, for example, occupy the axial and radial positions. The longer bond lengths in **1** may also be able to accommodate a more favorable displacement geometry. Intramolecular hydrogen bonding in the dimer, **1**, may result in a considerable gain in energy off setting any loss due to an unfavorable frontside displacement. Fronside nucleophilic attack at sulfur has been proposed.[9]
(9) Shreeve, J. *Acc. Chem. Res.* **1973**, *6*, 387. Tsukamoto, G.; Watanabe, T.; Utsumi, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2566. Day, J.; Cram, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 4398. Oae, S.; Yokoyama, M.; Kise, M.; Furukawa, N. *Tetrahedron Lett.* **1968**, 4131.
(10) Kharasch, N.; Potempa, S. J.; Wehrmister, H. L. *Chem. Rev.* **1946**, *39*, 269.
(11) Fries, K.; Schurmann, G., *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 2170, 2182.
(12) Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 326.
(13) Bruice, T. C.; Markiw, P. T. *J. Am. Chem. Soc.* **1957**, *79*, 3150.
(14) Pal, B. C.; Uziel, M.; Doherty, D. C.; Cohn, W. W. *J. Am. Chem. Soc.* **1969**, *91*, 3634.
(15) Kato, K. *Acta Crystallogr., Sect. B. Struct. Chrystallogr. Cryst. Chem.* **1972**, *28*, 55.
(16) Heckel, A.; Pfleiderer, W. *Tetrahedron Lett.* **1983**, 5047.
(17) For leading references on the "α-effect" nucleophilicity of sulfenic acids see: reference 4a.
(18) Kharasch, N.; Bruice, T. C. *J. Am. Chem. Soc.* **1951**, *73*, 3240.
(19) Bruice, T. C.; Sayigh, A. B. *J. Am. Chem. Soc.* **1959**, *81*, 3416.
(20) Barltrop, J. A.; Morgan, E. J. *J. Chem. Soc.* **1956**, *4245*.
(21) (a) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 197. (b) Shelton, J. R.; Davis, K. E. *Ibid.* **1973**, *8*, 205.
(22) Chou, T. S.; Burgtorf, J. R.; Ellis, A. L.; Lammert, S. R.; Kukolja, S. P. *Int. J. Sulfur Chem.* **1975**, *96*, 1609. Bachi, M. D.; Gross, A., *J. Org. Chem.* **1982**, *47*, 897.
(23) Davis, F. A.; Awad, S. B.; Jenkins, Jr., R. H.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* **1983**, *46*, 3071.
(24) Nakamura, N. *J. Am. Chem. Soc.* **1983**, *105*, 7172.

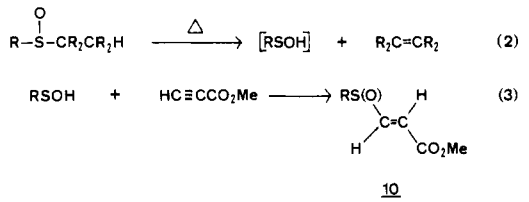
aromatic solvents.[21b] This was thought to be due to complexation of the sulfenic acid with the solvent. Such complexation would also inhibit production of 1.

In contrast to sulfenic acids, sulfenate ions (RSO^-), their conjugate base, are relatively stable in solution.[25,26] This can be attributed to the fact that, lacking hydrogen atoms, they are incapable of forming the intermolecular hydrogen bonds.

In this paper we extend these ideas to simple sulfenic acids. We demonstrated that the relative stability of such sulfenic acids can be improved by intramolecular hydrogen bonding and by reducing the electron density of the sulfenic acid sulfur atom.

Results and Discussion

Previous studies from these laboratories have shown that FVP of sulfoxides (eq 2) is a powerful technique for preparing most sulfenic acids in good concentration under conditions where they are stable.[6,23] The sulfenic acids



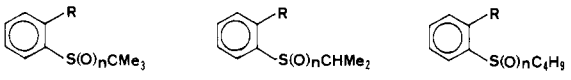
(2)

(3)

10

are generated in the gas phase and deposited on a cold-finger condenser cooled to liquid nitrogen temperatures (−196 °C). On warming of the cold-finger condenser the principal reaction of sulfenic acids prepared in this manner is thiosulfinate formation (eq 1). Under certain conditions sulfenic acids can be trapped as the *trans*-vinyl sulfoxides, **10**, when they are deposited on the cold-finger condenser containing methyl propiolate (eq 3). Short of actual isolation, one of the best methods for determining the presence of sulfenic acids is by trapping with an alkene or alkyne such as methyl propiolate (eq 3).[6]

Synthesis of Sulfides and Sulfoxides. The sulfides, **11–13**, used in these studies were prepared by three different methods depending on the alkyl group, *tert*-butyl, isopropyl, or *n*-butyl, desired. The choice of alkyl group determines the rate of at which the sulfenic acid is formed (eq 2).[27] These methods, all previously described, include (a) the reaction of a thiol with an alkyl halide, **13a–h**,[6] (b)

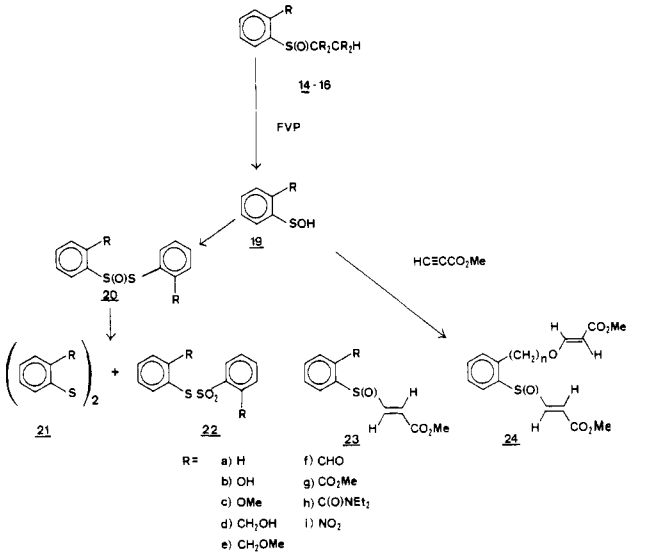


11 n=0 **12** n=0 **13** n=0
14 n=1 **15** n=1 **16** n=1

R= a) H f) CHO
b) OH g) CO_2Me
c) OMe h) $CONEt_2$
d) CH_2OH i) NO_2
e CH_2OMe

the reaction of a thiol with 2-hydroxy-2-methylpropane in

Scheme I

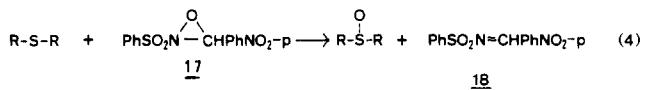


R= a) H f) CHO
b) OH g) CO_2Me
c) OMe h) $C(O)NEt_2$
d) CH_2OH i) NO_2
e) CH_2OMe

the presence of sulfuric acid, **11f**,[21] and (c) the heating of *o*-nitrobenzaldehyde with an alkyl mercaptan, **11f** and **13f**.[28] All sulfides prepared in these ways have spectral properties consistent with their structures.

Although these sulfides, **11–13**, can be oxidized to the corresponding sulfoxides, **14–16**, by *m*-chloroperbenzoic acid (MCPBA), it has been found that overoxidation to the sulfone (10–20%) is a troublesome side reaction. This necessitates separating the sulfide and sulfone from the desired sulfoxide by chromatography. Furthermore, attempts to oxidize the 2-formyl sulfides, **11f** and **13f**, to the corresponding sulfoxides failed. This is undoubtedly due to preferential oxidation of the aldehydic group by the peracid.

A superior oxidant for preparing **14–16**, in high isolated yield (>90%), without overoxidation, is 2-(phenylsulfonyl)-3-(*p*-nitrophenyl)oxziridine (**17**) (eq 4).[23,29,30] Oxidations with this reagent are carried out in chloroform by adding an equivalent amount of **17** to the sulfide. These oxidations are complete in minutes with the sulfonimine, **18**, precipitating from solution in 70–80% yield. In con-



(4)

17 18

trast to *m*-CPBA, oxidation of **11f** and **13f** with **17** proceeds uneventfully to the corresponding sulfoxides, **14f** and **16f**, respectively.

Because many of the sulfoxides are oils, some difficulty is experienced in obtaining satisfactory elemental analysis. However, these sulfoxides all have ^1H NMR and EI-MS consistent with their structures.

Thermolysis of Sulfoxides. Generation of sulfenic acids **19** (Scheme I) under thermolysis conditions involves heating sulfoxides, **14–16**, in toluene for up to 72 h (Table I). Under these conditions the concentration of the sulfenic acid, at any one time, is very small. This minimizes production of the thiosulfinate (eq 1) while maximizing trapping of the sulfenic acid by methyl propiolate (eq 3). Sulfenic aciids **19a,c,e–h** give *trans*-vinyl sulfoxides **23a,c,e,h**, while **19b,d** gives diadducts **24d,d**. The vinyl sulfoxide protons in sulfoxide **23** and the vinyl ether pro-

(25) Vinkler, E.; Kivernyi, F. *Int. J. Sulfur Chem.* **1973**, *8*, 111.
(26) Davis, F. A.; Friedman, A. J. *J. Org. Chem.* **1976**, *41*, 897.
(27) In thermolysis and FVP of sulfoxides the rate at which the sulfenic acids are formed is important. *tert*-Butyl sulfoxides are used in the thermolysis of sulfoxides because the rate of sulfenic acid formation is so much faster than the *n*-butyl sulfoxides. On the other hand the *n*-butyl sulfoxides are desirable for the FVP experiments. In the FVP experiments gas phase pyrolysis is desired over thermal decomposition in the inlet section of the FVP apparatus.
(28) Meth-Cohn, O.; Tranowski, B. *Synthesis* **1978**, 56.
(29) Davis, F. A.; Jenkins, Jr., R. H.; Yochlovich, S. G. *Tetrahedron Lett.* **1978**, 5171.
(30) Davis, F. A.; Stringer, O. D. *J. Org. Chem.* **1982**, *47*, 1744.

Table I. Thermolysis of Sulfoxides at 110 °C in Toluene

entry	sulfoxide (R =)	time, h	products, % yield[a] RSSR **21**	RSO_2SR **22**	$RS(O)CH{=}CHCO_2Me$[b] **23/24**	other
1	**15b** (OH)	72	40	38	–	
2			8	5	70	
3	**16c** (OMe)	76	35	–		**16c** (66)
4		72	83	–	10	
5	**16d** (CH_2OH)	96	45	38	–	
6		72	5	4	75	
7	**16e** (CH_2OMe)	24			20	**16e** (60)
8	**14f** (CHO)	48	42	39		
9		48	10	8	78	
10	**16g** (CO_2Me)	72	47	45	–	
11		72	7	4	80	
12	**16h** ($CONEt_2$)	72	15		45	**16h** (15)
13	**16i** (NO_2)	72	37			**13i** (60)

[a] Isolated yields. [b] In the presence of 5% methyl propiolate.

Table II. FVP Sulfenic Acid Trapping Experiments with Methyl Propiolate

entry	sulfoxide (R =)	FVP temp,[a] °C	products, % yield[b] **20**[c]	**21**[d]	**22**[e]	**23/24**[f]	other
1	**14a** (H)	350	58	8	8	–	
2	**15b** (OH)	500	–	38	40	–	
3	**16c** (OMe)	550	–	54	14	5	
4	**16d** (CH_2OH)	650	–	38	30	–	
5	**16e** (CH_2OMe)	550	–	11	14	22	
6	**14f** (CHO)	600	–	30	45	25	
7	**16g** (CO_2Me)	550	–	25	20	35	
8	**16i** ($CONEt_2$)	500	–				**26** (89)
9	**29** (*p*-NO_2)	400	–	45		12	

[a] See experimental for details. [b] Isolated yields. [c] RS(O)SR. [d] RSSR. [e] RSO_2SR. [f] $RS(O)CH{=}CHCO_2Me$.

tons in **24** appear as AB quartets at 6.8 and 5.2–5.8 ppm. The fact that the coupling constants for these vinyl protons are 14–15 Hz is consistent with the SOH and OH groups adding to the alkyne in a syn stereospecific manner. These results are summarized in Table I.

When the thermolysis of sulfoxides **14–16** are carried out in the absence of a trapping reagent, disulfides, **21**, (RSSR) and thiosulfonates, **22**, (RSO_2SR) are formed. These products result from disproportionation of the intermediate, thermally labile, thiosulfinate **20** according to reaction 5.[6] Preparative TLC (silica Gel G) was used to

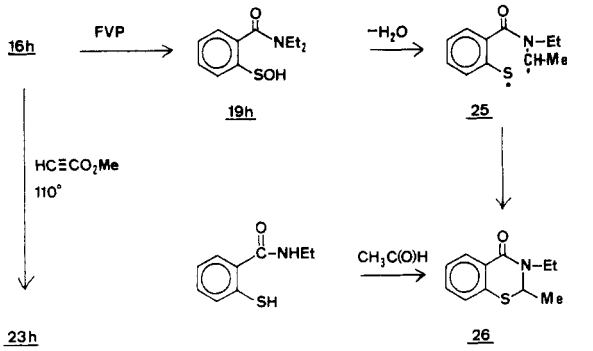
$$2\ RS(O)SR \longrightarrow RSSR + RSO_2SR \qquad (5)$$

separate these products (Table I). All new disulfides and thiosulfonates have spectral properties consistent with their structures.

FVP of Sulfoxides. FVP of sulfoxides **14–16** was carrier out as previously described, with condensation of the sulfenic acids, **19**, on a cold-finger condenser cooled to −196 °C (Scheme I, Table II).[6] In contrast to previous studies where thiosulfinates, **20**, were the principal FVP products, only disulfide **21** and thiosulfonate **22** were isolated on thawing of the cold-finger condenser. The possibility that sulfenic acids are not formed under these conditions or decomposed in the gas phase can be excluded for several reasons. First, a similar product distribution is observed for both thermolysis and FVP (Table I and III). Secondly, under thermolysis conditions the sulfenic acids are trapped (eq 3), demonstrating their formation. Finally, in certain cases the sulfenic acids, generated under FVP conditions can be trapped on the cold-finger condenser (vide infra).

The mechanism for the thermal disproportionation of thiosulfinates, reaction 5, is thought to involve thiyl (RS·) and sulfinyl (RSO·) radicals which recombine to give disulfide and thiosulfonate, **21** and **22**.[3,31] The most likely

Scheme II



reason that we were unable to detect **20b–g** in these FVP experiments is the increased stability of the thiyl and sulfinyl radicals caused by the aromatic ring substituents. In this context it is interesting to note that thiosulfinates of the nitro aromatic disulfides have never been detected.[3a]

2-(*N*,*N*-diethylcarboxamide)benzenesulfenic acid (**19h**) is the only sulfenic acid that fails to survive the gas phase pyrolysis conditions. FVP of sulfoxide **16h** at 500 °C affords *N*-ethyl-2-methyl-1,3-benzothiazin-4-one (**26**) in 89% isolated yield. The structure of **26** is supported by satisfactory elemental analysis, NMR, IR, and MS and by independent synthesis (Scheme II).

The two diastereotopic methylene protons, of the *N*-ethyl group appear as hextets (J = 7.2 Hz) centered at 4.2 and 5.0 ppm (J = 7.2 Hz) in the ^1H NMR of **26**. The methyl group, attached to the chiral center is a doublet at 2.6 ppm (J = 7 Hz). In the EI-MS the base ion of **26** (m/e 136) results from a retro Diels–Alder rearrangement eliminating the elements of *n*-ethylaldimine (EtN=

(31) (a) Koch, P.; Ciuffarin, E.; Fava, A. *J. Am. Chem. Soc.* **1970**, *92*, 5971. (b) Kice, J. L.; Large, G. B. *Tetrahedron Lett.* **1965**, 3573.

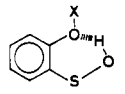
CHMe). 1,3-Benzothiazine, **26**, was prepared independently in 63% yield by base-catalyzed condensation of acetaldehyde with *N*-ethyl-2-mercaptobenzamide (Scheme II).

The fact that sulfenic acid **19h** could be trapped with methyl propiolate to give **23h** in 48% yield is evidence that this sulfenic acid is generated under the FVP conditions. The most likely source of **26** is diradical **25**, formed in the gas phase from **19h** by homolytic cleavage of the S–OH bond (Scheme II). Abstraction of a hydrogen atom from the adjacent ethylamide group would afford **25**. A mechanism involving concerted loss of water cannot, howver, be excluded. A similar diradical mechanism has been offered to explain the formation of a benzo[*b*]thiapyran derivative in the FVP of trineopentylbenzenesulfenic acid (**7c**).[23] Gas phase, homolytic cleavage of the S–OH bond has been noted in other studies of sulfenic acids.[6]

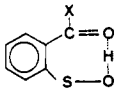
The FVP studies with sulfenic acid **19h** illustrate one of the limitations of this technique for preparing sulfenic acids. Some sulfenic acids are unstable under the high temperature FVP conditions. Although **19h** is stable when generated at low temperatures (Table I, entry 13) it was unstable in the gas phase at 500 °C under FVP conditions (Table II, entry 8).

Intramolecular Hydrogen Bonding. The influence of structural changes on the reactivity or stability of sulfenic acids can be estimated using the vinyl sulfoxide/thiosulfinate ratio (**23**/**20**) (Scheme I).[6] For sulfenic acids, **19**, this is the vinyl sulfoxide/disulfide–thiosulfinate ratio (**23**/**21**–**22**) since the intermediate thiosulfinates could not be detected. As previously discussed, this method is based on the premise that changes in the steric, electronic, and hydrogen bonding character of the sulfenic acid influences the rate of reaction 1 much more so than the rate of reaction 3.[32] Thus the less prone the sulfenic acid is to thiosulfinate formation the higher the yield of the vinyl sulfoxide. Experimentally this has been verified.[6]

Table II summarizes the results of FVP-sulfenic acid trapping experiments with methyl propiolate. Benzenesulfenic acid (**19a**), which cannot be stabilized by intramolecular hydrogen bonding, gives none of the vinyl sulfoxide **23a**, the major product being the thiosulfinate, **20a** (Table II, entry 1). Sulfenic acids **19b** and **19d** also failed to give any detectable amounts of the vinyl sulfoxides, **23b** and **23d**, respectively. Intramolecular six- and seven-member hydrogen-bonded species, **27** and **28**, respectively,



27

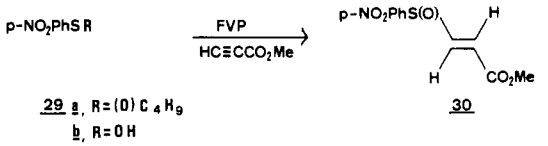


28

in principal could have prevented dimer 1 production. When these sulfenic acids were transformed to their corresponding methyl esters, **19c,e**, vinyl sulfoxides **23c** and **23e** were obtained in 5 and 22% yield (Table II, entries 3 and 5). A possible explanation for the failure to trap the hydroxy sulfenic acids, **19b,d** vs. their methyl ethers, **19c,e** is that the free hydroxyl groups may promote, rather than inhibit, intermolecular hydrogen bonding. Caution is necessary in interpreting the results for **19c** because of the low, but reproducible, yields.

2-Formyl- and 2-carboxymethylbenzenesulfenic acids, **19f** and **19g**, appear to be the most stable sulfenic acids as indicated by the trapping experiments. These sulfenic acids were trapped, as the vinyl sulfoxides **23f** and **23g** in 25 and 35% yield, respectively (Table II, entries 6 and 7). Dimer production of these sulfenic acids is most likely inhibited by formation of seven-membered, intramolecular hydrogen bonds, **28**. Another factor that may be responsible for the lower reactivity of these sulfenic acids is substituent electronegativity effects. Both groups in **19f,g** are moderately strong electron-attracting groups. Indeed the higher yield of **23g** vs. **23f** may reflect the greater substituent electronegativity of a carbomethoxy vs. *o*-formyl group.[33]

Comparison of FVP-trapping experiments with benzenesulfenic acid (**19a**) and *p*-nitrobenzenesulfenic acids (**29b**) provide incontrovertible evidence of the stabilizing effect of having the SOH group attached to an electronegative carbon atom. Whereas FVP-trapping experiments with **19a** gave none of the vinyl sulfoxide, **29a** gave a 12% yield of **30** (Table II, compare entries 1 and 9).



29 a, R=(O)C$_4$H$_9$; b, R=OH **30**

o-Nitrobenzenesulfenic acid (**19i**), was anticipated to be more stable than **29b**, because it is stabilized by both intramolecular hydrogen bonding and electronegativity effects. Unfortunately, the *n*-butyl sulfoxide, **16i**, proved to be so thermally liable that it decomposed in the inlet portion of the FVP apparatus prior to gas phase pyrolysis. Unexpectedly, sulfoxide **16i** decomposed on heating in the solid state, at 65 °C, to give a 60% isolated yield of sulfide, **13i**, in addition to decomposition products.

Finally, it is of interest to consider the importance of the hydrogen-bonding ring size on the reactivity of sulfenic acids. Sulfenic acids **19c** and **19e–g**, can form six and seven-membered hydrogen-bond rings, **27** and **28**, respectively. Sulfenic acids **19e–g** are less reactive than **19c**, i.e., 22–35% vs. 5% of **23** (Table II, compare entries 5–7 with 3). This suggests that a seven-membered ring, **28**, is more effective than a six-membered ring, **27**, at reducing the reactivity of sulfenic acids. However, this difference could also be due to substituent electronegativity effects. The methoxy group in **19c** is electron-donating while the substituents in **19e–g** range from weakly to strongly electron-withdrawing. At this time a definitive answer as to the importance of **27** vs. **28** on sulfenic acid reactivity is not possible since reactivity increases as the electron density on the sulfenic acid sulfur decreases. It is interesting to note, however, that anthraquinonesulfenic acids (**2a–b**) form seven-membered intramolecular hydrogen bonds. Furthermore, Kingsbury et al. have shown that intramolecular hydrogen bonding involving seven-membered rings is actually favored over six-membered rings in certain sulfoxide alcohols.[34]

Summary and Conclusions. FVP trapping experiments demonstrated that the relative reactivity of simple sulfenic acids is improved by intramolecular hydrogen bonding and by reducing the electron density of the sulfenic acid sulfur atom. Both of these effects inhibit intermolecular hydrogen bonding of the sulfenic acid.

The reason that sulfenic acids are so reactive and generally can not be isolated is that the formation of thiosulfinates is such a facile reaction (eq 1). This is related

(32) The reverse of vinyl sulfoxide formation, sulfoxide pyrolysis (eq 2) has been shown to be insensitive to structural changes in the sulfoxide. For a detailed discussion see ref 6.

(33) March, J., "Advanced Organic Chemistry," 3rd ed.; Wiley: New York, 1985; pp 242.

(34) Kingsbury, C. A.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1980**, *45*, 5255.

to the ability of the sulfenic acid to form intermolecular hydrogen bonds which lowers the energy of activation for thiosulfinate production. Those factors that prevent hydrogen bonding, steric, electronic, and intramolecular hydrogen bonding effects lead to a less reactive or more stable sulfenic acid. The few sulfenic acids that have been isolated can be explained in terms of these concepts.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were measured on JEOL FX 90Q (90 MHz) and Bruker WM-250 (250 MHz) NMR spectrometers. GC/MS data were obtained on a Finnigan 4000 GC/MS using a 6 ft × $^1/_4$ in., 3% OV-17 on 90/100 mesh Sulpelcoport, glass column. Gas chromatography was performed on a Varian 3700 gas chromatograph equipped with an FID and Varian CDS-111 electronic integrator. Solvents were purified by standard methods. 2-*tert*-Butyl- and 2-*n*-butylthiobenzaldehyde (**11f** and **13f**) were prepared as previously described.[28] Thiols were purchased from Aldrich Chemical co. and Fairfield Chemical Co. 2-Nitrobenzenethiol was prepared by the method of Reid.[35]

2-Mercapto-*N*,*N*-diethylbenzamide. In a 200-mL single-necked round-bottom flask equipped with an addition funnel and a magnetic stirring bar was placed 2.0 g (5.84 mmol) of 2,2′-dithiobis(benzoyl chloride)[36] in 20 mL of dry benzene. Added dropwise with stirring was 1.1 g (14.6 mmoles) of diethylamine in 20 mL of benzene. After the addition was complete the reaction mixture was stirred for 0.5 h at which time 100 mL of ether was added and the precipitated diethylamine hydrochloride removed by filtration. Removal of the solvent under vacuum gave a yellow oil which was further purified by chromatography on silica gel eluting with diether ether. **2,2′-Dithiobis(*N*,*N*-diethylbenzamide)** had the following properties: 1.48 g (61%) mp 63–5 °C (Lit.[37] mp 65–67 °C); NMR ($CDCl_3$) δ 1.22 (sextet, 12 H, J = 7.0 Hz), 3.12 (q, 4 H, J = 7.7 Hz), 3.54 (q, 4 H, J = 7.0 Hz) and 7.12–8.44 (m, 8 H); IR (KBr) 1740, 1720 cm^{-1} (C=O).

In a 250-mL three-necked flask equipped with a magnetic stirrer, a reflux condenser, an addition funnel, and a nitrogen inlet was placed 6.5 g (15.7 mmoles) of **2,2′-dithiobis(*N*,*N*-diethylbenzamide)** in 50 mL of absolute ethanol. The solution was warmed to 65–70 °C, and 1.2 g (31.4 mmol) of sodium borohydride in 50 mL of absolute ethanol was added dropwise. When the addition was complete, the reaction mixture was allowed to stir for 1 h, 50 mL of cold water was added, and the acidity of the mixture was adjusted to pH 3 with dilute HCl. After cooling the reaction mixture was extracted with ether (3 × 25 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave a white solid, 4.2 g (65%), of **2-mercapto-*N*,*N*-diethylbenzamide** which was crystallized from *n*-hexane: mp 56–58 °C (Lit.[37] mp 58–60 °C); NMR ($CDCl_3$) δ 1.2 (sextet, 6 H, Me, J = 7.2 Hz), 3.16 (q, 2 H, J = 7.2 Hz), 3.56 (q, 2 H, J = 7.2 Hz), 3.76 (s, 1 H, SH) and 7.12–8.44 (m, 8 H); IR (KBr) 2550 (SH) and 1650 (C=O) cm^{-1}.

Preparation of Alkyl Aryl Sulfides (12b, 16c–i). In a 100-mL 3-necked flask equipped with a magnetic stirrer, a reflux condenser, an additional funnel, and a nitrogen inlet was placed the appropriate aryl thiol (10 mmol) in 25 mL of absolute ethanol. Potassium hydroxide, 1.1 g (20 mmol), was added to the reaction mixture with heating. The solution was cooled to room temperature and isopropyl bromide or *n*-butyl bromide (20 mmol) added dropwise to the reaction mixture in 5 mL of absolute ethanol. After refluxing for 1 h the reaction mixture was cooled to room temperature, and 30 mL of water added and the solution extracted with ether (3 × 25 mL). After the solution had been dried over anhydrous $MgSO_4$, the solvent was removed under vacuum to give the crude sulfides which were purified by column chromatography (silica gel) eluting with 1:1 ether/*n*-pentane.

Isopropyl 2-hydroxyphenyl sulfide (12b): bp 47–49 °C (0.35 torr); 2.78 g (83%); NMR ($CDCl_3$) δ 1.2 (d, 6 H, Me, J = 7 Hz), 3.05 (quintet, 1 H, CH, J = 7 Hz), 7.0–7.3 (m, 4 H); IR (film) 3425 cm^{-1}.

Anal. Calcd for $C_9H_{12}OS$: C, 64.30; H, 7.14. Found: 64.55; H, 7.10.

***n*-Butyl 2-methoxyphenyl sulfide (13b)**: oil; 1.5 g (77%); NMR ($CDCl_3$) δ 0.9 (t, 3 H, Me, J = 5 Hz), 1.70 (m, 4 H), 2.8 (t, 2 H, J = 7 Hz), 3.5 (s, 3 H, OMe), 6.7–7.7 (m, 4 H).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.34; H, 8.16. Found: C, 67.32; H, 8.33.

***n*-Butyl 2-(hydroxymethyl)phenyl sulfide (13d)**: bp 85–88 °C; 2.8 g (83%); NMR ($CDCl_3$) δ 0.9 (t, 3 H, Me, J = 7 Hz), 1.55 (m, 4 H), 2.14 (s, 1 H, OH), 2.9 (t, 2 H, CH_2, J = 7 Hz) 4.8 (d, 2 H, J = 5 Hz) 7.0–7.6 (m, 4 H).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.32; H, 8.22. Found: C, 67.08; H, 8.20.

***n*-Butyl 2-(Methoxymethyl)phenyl Sulfide (13e).** In a 100-mL 3-necked flask equipped with a magnetic stir bar, a reflux condenser, an addition funnel and a nitrogen inlet was placed 1.0 g (5.1 mmol) of sulfide **13d** and 0.5 mL (7.7 mmol) of iodomethane in 50 mL of dry THF. Added portionwise to the reaction mixture over a 1 h period was 0.24 g (5.6 mmol) of 57% sodium hydride after which time the solution was heated at reflux for 1 h and cooled to room temperature and 50 mL of saturated brine solution was cautiously added. The reaction mixture was extracted with methylene chloride (3 × 25 mL) followed by drying the organic phase over anhydrous Na_2SO_4. Removal of solvent afforded 0.61 g (57%) of a light yellow oil which was purified by chromatography on silica gel eluting with 3:1 *n*-pentane/ether. Sulfide **13e** had the following properties: oil, 0.6 g (57%); NMR ($CDCl_3$) δ 0.95 (t, 3 H, Me, J = 7 Hz)8 1.5 (m, 4 H), 2.9 (t, 2 H, J = 7 Hz)8 3.55 (s, 3 H, OMe), 4.6 (s, 2 H, CH_2O), 7.1–7.6 (m, 4 H); IR (film) 1100 cm^{-1}; EI-MS, m/z (relative abundance) 210 (30, M), 153 (82), 121 (39), 91 (43), 77 (33), 45 (100).

Anal. Calcd for $C_{12}H_{18}OS$: C, 68.57; H, 8.57. Found: C, 69.12; H, 8.75.

***n*-Butyl 2-(carbomethoxy)phenyl sulfide (13g)**: bp 89–90 °C (0.1 torr); 1.9 g (87%); NMR ($CDCl_3$) δ 0.93 (t, 3 H, Me, J = 5.5 Hz), 1.6 (m, 4 H), 2.88 (t, 2 H, SCH_2 J = 7 Hz), 3.9 (s, 3 H, OMe), 7.5 (m, 4 H); IR (film) 1720 (CHO) cm^{-1}.

Anal. Calcd for $C_{11}H_{16}OS$: C, 64.28; H, 7.14. Found: C, 64.08; H, 7.28.

***n*-Butyl 2-((*N*,*N*-diethylcarbamoyl)oxy)phenyl sulfide (13h)**: oil; 2.4 g (91%); NMR ($CDCl_3$) δ 0.93 (t, 3 H, Me, J = 5.5 Hz), 1.6 (m, 4 H), 2.88 (t, 2 H, SCH_2 J = 7 Hz), 3.9 (s, 3 H, OMe), 7.5 (m, 4 H); IR (film) 1720 cm^{-1}.

Anal. Calcd for $C_{15}H_{23}NOS$: C, 67.92; H, 8.68. Found: C, 68.03; H, 8.34.

***n*-Butyl 2-nitrophenyl sulfide (13i)**: oil; 1.1 g (50%); NMR ($CDCl_3$) δ 0.95 (t, 3 H, Me, J = 5.2 Hz), 1.55 (m, 4 H), 2.95 (t, 2 H, SCH_2 J = 5.2 Hz), 7.1–8.2 (m, 4 H) ppm; IR (KBr) 1500 and 1340 (NO_2) cm^{-1}.

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.87; H, 6.16. Found: C, 57.09; H, 6.27.

Oxidation of Sulfides to Sulfoxides Using 2-(Phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine (17).[30] In a 25-mL single-necked round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet, and a 10-mL dropping funnel was placed the appropriate sulfide (3.6 mmol) in 4 mL of methylene chloride. After cooling to 0 °C in an ice bath, 1.0 g (3.4 mmol) of oxaziridine **17** in 5 mL of methylene chloride was added dropwise with stirring to the sulfide. After 30 min the precipitated sulfonimine, **18**, was removed by filtration in 70–80% yield. Removal of the solvent under vacuum gave an oil which was extracted with *n*-pentane (3 × 10 mL) to afford the nearly pure sulfoxide. While these sulfoxides proved to be analytically pure by TLC and NMR, their hydroscopic nature and thermal instability precluded satisfactory elemental analysis.

Isopropyl 2-hydroxyphenyl sulfoxide (15b): mp 91–93 °C dec (*n*-pentane); 0.52 g (85%); NMR ($CDCl_3$) δ 1.25 (d, 3 H, Me, J = 5 Hz), 1.4 (d, 3 H, Me, J = 5 Hz), 3.4 (quintet, 1 H, J = 8 Hz), 7.4 (m, 4 H); IR (KBr) 1000 cm^{-1} (SO); EI-MS, m/z (relative intensity) 184 (3, M), 124 (20), 96 (100), 70 (12), 65 (24), 63 (10), 53 (12).

***tert*-Butyl 2-formylphenyl sulfoxide (14f)**: mp 121–123 °C dec (*n*-pentane); 0.6 g (81%); NMR ($CDCl_3$) δ 1.2 (s, 9 H, Me_3C) 7.9 (m, 4 H), 10.3 (s, 1 H, CHO); IR (KBr) 1700 (CO) and 1060

(35) Reid, E. E. *J. Am. Chem. Soc.* **1924**, *46*, 1937.
(36) Collman, J. P.; Groh, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 1391.
(37) Wolf, M. ; Sellstedt, J. H.; Fenichel, R. L. Ger. Offen. 2310572, 1973; *Chem. Abstr.* **1973**, *79*, P136848w.

(SO) cm^{-1}; EI-MS, m/z (relative intensity) 210 (2, M), 57 (100).

n-Butyl 2-formylphenyl sulfoxide (16f): mp 115–117 °C dec (*n*-pentane); 0.65 (87%); NMR ($CDCl_3$) δ 0.85 (m, 4 H), 1.0 (t, 3 H, Me, J = 5 Hz), 2.9 (m, 2 H, CH_2SO), 8.0 (m, 4 H), 10.4 (s, 1 H, CHO); IR (KBr) 1608 (CO) and 1070 (SO) cm^{-1}; EI-MS, m/z (relative intensity) 210 (1, M), 57 (100).

Oxidation of Sulfides to Sulfoxides Using *m*-CPBA. In a 100-mL 3-necked flask equipped with a magnetic stirrer, an addition funnel, and a nitrogen inlet was placed the appropriate sulfide (typically 4.5 mmol) dissolved in 25 mL of dry CH_2Cl_2. The reaction mixture was cooled to 0 °C in an ice bath and *m*-chloroperbenzoic acid (Aldrich), 0.7 g (85%, 4.5 mmol) in 20 mL of CH_2Cl_2 was added dropwise with stirring. After the addition was complete (30 min) the reaction mixture was stirred for an additional hour at 0 °C, at which time the solution was washed sequentially with water (2 × 50 mL), saturated Na_2SO_4 (2 × 50 mL), $NaHCO_3$, water (2 × 50 mL), and brine (2 × 50 mL). After drying over anhydrous $MgSO_4$, the solvent was removed to give the sulfoxides which were further purified by preparative or flash chromatography on silica gel eluting with (1:1) *n*-pentane/ether.

n-Butyl 2-methoxyphenyl sulfoxide (16c): oil, 0.95 g (99%); NMR ($CDCl_3$) δ 0.9 (?, 3 H, Me, J = 5 Hz), 1.75 (m, 4 H), 2.85 (m, 2 H, $S(O)CH_2$), 3.86 (s, 3 H, OMe), 6.9–79 (m, 4 H); IR (film) 1020 (SO) cm^{-1}; EI-MS, m/z (relative intensity) 212 (51, M), 195 (28), 156 (100), 141 (77), 108 (99), 77 (63).

n-Butyl 2-(hydroxymethyl)phenyl sulfoxide (16d): mp 35–6 °C (*n*-pentane), 0.76 g (80%); NMR ($CDCl_3$) δ 0.9 (t, 3 H, Me, J = 7 Hz) 1.6 (m, 4 H), 2.9 (m, 2 H, $S(O)CH_2$), 4.3 (bs, 1 H, OH), 4.5 (d, 2 H, CH_2O, J = 2 Hz) 7.6 (m, 4 H); IR (film) 3320 (OH), 1060 (SO) cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.25; H, 7.60. Found: C, 62.10; H, 7.55.

n-Butyl 2-(methoxymethyl)phenyl sulfoxide (16e): oil, 0.82 g (81%); NMR ($CDCl_3$) δ 1.0 (m, 3 H, Me) 1.6 (m, 4 H), 2.8 (m, 2 H, $S(O)CH_2$), 3.5 (s, 3 H, OMe), 4.5 (q, 2 H, CH_2O, J = 12 Hz) 7.2–8.1 (m, 4 H); IR (film) 1040 (SO) cm^{-1}; EI-MS, m/z (relative intensity) 226 (2.4, M), 169 (9.6), 139 (10), 138 (53), 137 (95), 109 (37), 77 (28), 41 (100).

n-Butyl 2-(carbomethoxy)phenyl sulfoxide (16g): oil, 0.7 g (90%); NMR ($CDCl_3$) δ 0.95 (t, 3 H, Me, J = 5 Hz) 1.6 (m, 4 H), 2.95 (t, 2 H, $S(O)CH_2$, J = 7 Hz), 3.9 (s, 3 H, OMe), 7.4 (m, 4 H); IR (film) 1715 (CO), 1012 (SO) cm^{-1}; EI-MS, m/z intensity) 240 (4.0, M), 184 (6.4), 168 (11), 136 (54), 107 (62), 105 (45), 91 (100), 77 (84).

n-Butyl 2-((*N*,*N*-diethylcarbamoyl)oxy)phenyl sulfoxide (16h): oil, 0.54 g (43%); NMR ($CDCl_3$) δ 1.2 (m, 13 H, Me) 1.6 (m, 4 H), 2.8 (m, 2 H, $S(O)CH_2$), 3.5 (s, 3 H, OMe), 4.5 (q, 2 H, CH_2O, J = 12 Hz), 7.2–8.1 (m, 4 H); IR (film) 1620 (CO) 1040 (SO) cm^{-1}; EI-MS, m/z (relative intensity) 281 (3, M), 209 (11), 153 (13), 72 (47), 58 (100).

n-Butyl 2-nitrophenyl sulfoxide (16i): mp 50–52 °C, 0.82 g (53%); NMR ($CDCl_3$) δ 0.95 (t, 3 H, Me, J = 6 Hz) 1.75 (m, 4 H), 3.0 (m, 2 H, $S(O)CH_2$), 7.3–8.9 (m, 4 H); IR (film) 1030 (SO) cm^{-1}.

Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.86; H, 5.73. Found: C, 52.72; H, 5.68.

Thermolysis of Sulfoxides. Typically 0.5 mmol of the sulfoxide (Table I) is placed in 15 mL of toluene in a 25-mL single-necked flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet. After the mixture had been refluxed under nitrogen for the appropriate time (Table I), the solvent was removed under vacuum and the reaction mixture purified by preparative TLC on silica gel eluting with 1:1 ether/*n*-pentane.

Trapping of Sulfenic Acids. Trapping of Sulfenic Acids under thermolysis conditions was carried out as described above except that 0.2 mL (2.5 mmol) of methyl propiolate was added to the toluene solution.

Sulfoxide **15b** gave disulfide **21b**[38] and thiosulfonate **22b**. **2-Hydroxyphenyl 2-hydroxybenzenethiosulfonate (22b)** had the following properties: mp 112–114 °C, NMR ($CDCl_3$) δ 3.5 (bs, 2 H, OH, D_2O exchange), δ 7.5 (m, 8 H); IR (KBr) 3425 (OH), 1040 and 1290 (SO_2) cm^{-1}; EI-MS, m/z (relative intensity) 282 (26, M), 218 (12), 157 (44), 141 (73), 126 (19), 125 (68), 109 (20), 97 (100), 65 (90), 64 (31).

Methyl *trans*-3-[2-[(*trans*-2-(methoxycarbonyl)vinyl)-sulfinyl]phenoxy]acrylate (24b) had the following properties: mp 92–3 °C; NMR ($CDCl_3$) δ 3.8 (s, 6 H, Me), 5.8 (d, 2 H, J = 14.4 Hz), 6.75 (d, 2 H, J = 14 Hz) 7.6 (m, 6 H); IR (film) 1730, 1720 (CO) and 1050 (SO) cm^{-1}.

Anal. Calcd for $C_{14}H_{14}O_6S$: C, 54.19; H, 4.52. Found: C, 55.10; H, 4.61.

Sulfoxide **16c** gave disulfide **21c**: mp 117–118 °C (lit.[39] mp 119 °C); NMR ($CDCl_3$) δ 3.8 (s, 6 H, OMe) and 7.8–7.5 (m, 8 H) ppm; IR (KBr) 1220 (OMe) cm^{-1}.

Methyl *trans*-[(2-methoxyphenyl)sulfinyl]acrylate (23c) had the following properties: mp 97–99 °C; NMR ($CDCl_3$) 3.75 (s, 3 H, Me), 3.8 (s, 3 H, Me), 7.75 (d, 1 H, J = 15 Hz), 8.2 (d, 1 H, J = 15 Hz) 6.9–8.2 (m, 4 H); IR (KBr) 1720, (CO) and 1040 (SO) cm^{-1}.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 55.0; H, 5.00. Found: C, 54.76; H, 5.00.

Sulfoxide **16d** gave disulfide **21d** and thiosulfonate **22d**.

2,2′-Dithiobis(benzenemethanol) (21d) had the folllowing properties: mp 140–1 °C (lit.[40] mp 142 °C); NMR ($CDCl_3$) δ 2.1 (bs, 2 H, OH, D_2O exchange), 4.8 (s, 4 H) and 7.2 (m, 8 H); IR (KBr) 3350 (OH) cm^{-1}.

2-(Hydroxymethyl)phenyl 2-(hydroxymethyl)benzenethiosulfonate (22d) had the following properties: mp 156–158 °C, NMR δ 3.0 (bs, 2 H, OH) 4.55 (s, 2 H, CH_2), 5.1 (s, 2 H, CH_2), 7.3–8 (m, 8 H) ppm; IR (KBr) 3350 (OH), 1040 and 1230 (SO_2) cm^{-1}; EI-MS, m/z (relative intensity) 310 (1, M), 207 (11), 152 (24), 92 (58), 91 (100), 89 (11), 78 (13), 77 (45), 73 (10), 65 (32), 63 (24), 52 (11), 51 (65).

Methyl *trans*-3-[[2-(*trans*-2-((methoxycarbonyl)vinyl)-sulfinyl)phenyl]methoxy]acrylate (24d) had the following properties: mp 101 °C (*n*-pentane); NMR ($CDCl_3$) δ 3.7 (d, 6 Hz, Me), 5.1 (AB quartet, 2 H, J = 11 Hz), 5.2 (d, 2 H, J = 14 Hz), 6.8 (d, 2 H, J = 14 Hz), 7.6 (m, 6 H); IR (KBr) 1710, 1690 (CO) and 1040 (SO) cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O_6S$: C, 55.55; H, 4.93. Found: C, 55.54; H, 4.83.

Sulfoxide **16e** was recovered unchanged in 85% yield on refluxing in toluene for 24 h.

Methyl *trans*-3-[(2-(methoxymethyl)phenyl)sulfinyl]-acrylate (23e) had the following properties: mp 60–2 °C; NMR ($CDCl_3$) δ 3.4 (s, 3 H, Me), 3.8 (s, 3 H, Me), 4.65 (q, 2 H, J = 11 Hz), 7.7 (d, 1 H, J = 15 Hz) 8.25 (d, 1 H, J = 15 Hz), 7.6–8.2 (m, 4 H); IR (KBr) 1690 (CO) and 1100 (SO) cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.69; H, 5.51. Found: C, 56.29; H, 5.77.

Sulfoxide **14f** gave disulfide **21f** and thiosulfonate **22f**. **2,2′-Dithiobis(benzaldehyde) (21f)** had the following properties: mp 140–2 °C (lit.[41] mp 142 °C); NMR ($CDCl_3$) δ 7.75 (m, 8 H) and 10.3 (s, 2 H, CHO); IR (KBr) 1690 (CO) cm^{-1}. **2-Formylphenyl 2-formylbenzenethiosulfonate (22f)** had the following properties: mp 139–141 °C; NMR ($CDCl_3$) δ 7.8 (m, 8 H) and 10.4 (d, 2 H, CHO) ppm; IR (KBr) 1690 (CO), 1210, and 1080 (SO_2) cm^{-1}; EI-MS, m/z (relative intensity) 306 (1.0 M), 138 (19), 137 (100), 109 (50), 108 (13), 106 (11), 105 (19), 104 (13), 77 (41), 76 (24), 69 (29), 65 (66).

Methyl *trans*-3-[(2-formylphenyl)sulfinyl]acrylate (23f) had the following properties: mp 101 °C (*n*-pentane); NMR ($CDCl_3$) δ 3.8 (s, 3 H, Me), 6.8 (d, 1 H, J = 14 Hz), 7.6 (d, 1 H, J = 14 Hz) 7.8 (m, 4 H) and 10.35 (s, 1 H, CHO); IR (film) 1710, 1720 (CO), 1690 (CO), and 1040 (SO) cm^{-1}.

Anal. Calcd for $C_{11}H_{10}O_4S$: C, 55.46; H, 4.20. Found: C, 55.17; H, 4.51.

Sulfoxide **16g** gave disulfide **21g** and thiosulfonate **22b**. **2,2′-Dithiobis(methyl benzoate) (21g)** had the following properties: mp 124–5 °C (lit.[42] mp 125–7 °C); NMR ($CDCl_3$) δ

(38) Greenwood, D.; Stevenson, H. A. *J. Chem. Soc.* **1953**, 1514.

(39) Pinnick, H. W.; Reynolds, M. A.; McDonald, R. T., Jr.; Brewster, W. D. *J. Org. Chem.* **1980**, *45*, 930.

(40) Grice, R.; Owen, L. N. *J. Chem. Soc.* **1963**, 1947.

(41) Brown, K. J.; Meth-Cohn, O. *Tetrahedron Lett.* **1974**, 4069.

(42) Urbanski, T.; Falecki, J.; Halski, L. *Rocz. Chem.* **1956**, *30*, 969; *Chem. Abstr.* **1957**, *51*, 14595i.

3.9 (s, 6 H, Me) and 7.75 (m, 8 H); IR (KBr) 1720, (C=O) cm^{-1}. **2-(Methoxycarbonyl)phenyl 2-(methoxycarbonyl)benzenethiosulfonate (22g)** had the following properties: mp 100–1 °C (lit.[43] mp 101–2 °C); NMR ($CDCl_3$) δ 3.7 (s, 3 H, Me), 3.97 (s, 3 H, Me), and 7.75 (m, 8 H); IR (KBr) 1720, 1700 (C=O), 1250 and 1045 (SO_2) cm^{-1}.

Methyl *trans*-3-[(2-(methoxycarbonyl)phenyl)sulfinyl]acrylate (23g) had the following properties: mp 121–122 °C; NMR ($CDCl_3$) δ 3.7 (s, 3 H, Me), 4.0 (s, 3 H, Me), 6.55 (d, 1 H, J = 14 Hz), 7.4 (d, 1 H, J = 14 Hz) 7.75 (m, 4 H); IR (KBr) 1720, 1680 (CO), and 1050 (SO) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.52. Found: C, 53.53; H, 4.59.

Sulfoxide **16h** gave disulfide **21h**. **2,2′-Dithiobis(*N*,*N*-diethylbenzamide) (21h)** had the following properties, mp 63–4 °C (lit.[37] mp 65–7°); NMR ($CDCl_3$) δ 1.1 (m, 12 H, Me), 3.3 (m, 8 H), 7.1–8.5 (m, 8 H); IR (KBr) 1620 (CO) cm^{-1}. **Methyl *trans*-3-[2-[2-((diethylamino)carbonyl)phenyl]sulfinyl]acrylate (23h)** had the following properties: oil; NMR ($CDCl_3$) δ 1.45 (m, 6 H, Me), 3.72 (m, 4 H, CH_2), 6.68 (d, 1 H, J = 14.3), 8.04 (d, 1 H, J = 14.3 Hz), and 7.2–8.1 (m, 4 H); IR (film) 1720, 1620 (C=O), 1070 (S=O) cm^{-1}; EI-MS, m/z (relative abundance) 309 (3.0 M), 225 (8), 153 (21), 137 (5) 72 (79), 58 (100).

Flash Vacuum Pyrolysis (FVP) of Sulfoxides. The appropriate sulfoxide, typically 150 mg, is placed in the inlet sample chamber of the FVP apparatus. The sample chamber is heated with a heating tape or hot-air bath at 25–75 °C depending on the thermal stability of the sulfoxide. The preheat section of the pyrolysis chamber is maintained at a temperature approximately 25 °C above the melting point of the sulfoxide. The pyrolysis chamber is set at the minimum temperature where most of the sulfoxide reacts and is determined by trial and error. FVP trapping experiments were carried out by placing 5 mL of a 20% solution of methyl propiolate in toluene on the cold-finger condenser cooled to −196 °C and under vacuum, using a long syringe needle. Sulfenic acids generated in the FVP experiments were deposited on this matrix.

FVP experiments were carried out at least twice and the results averaged. The lower product balance (Table II vs. Table I) results from a charing during the pyrolysis and sulfoxide decomposition in the inlet portion of the FVP apparatus.

Isolation of Products from the FVP Experiments. After completion of the FVP experiment the vacuum is disengaged and the system vented with dry nitrogen. The liquid N_2 is removed from the cold-finger Dewar, and the products, which have collected on the cold-finger condenser, washed into a receiver with chloroform (3 × 15 mL portions). The products are analyzed by preparative TLC (silica gel), GLC, and GLC/MS in the same manner as the thermolysis experiments. See Table II for a summary of these experiments.

FVP of *n*-Butyl 2-((*N*,*N*′-Diethylcarbamoyl)oxy)phenyl Sulfoxide (16h). FVP of **16** h (0.84 g, 3.0 mmol) at 500 °C gave 0.6 g (89%) of an oil identified as ***N*-ethyl-2-methyl-1,3-benzothiazin-4-one (26).** Compound **26** had the following properties: oil, NMR ($CDCl_3$) δ 2.25 (t, 3 H, J = 6.8 Hz), 2.6 (d, 3 H, J = 6.6), 4.25 (sextet, 1 H, J = 7.2 Hz), 5.0 (sextet, 1 H, J = 6.6), 5.65 (q, 1 H, J= 5.7 Hz), and 7.9–9.2 (m, 4 H); IR (KBr) 1620 (C=O); EI-MS, m/z (relative abundance) 207 (20, M), 136 (100), 108 (35).

Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.77; H, 6.28. Found: 63.46; H, 6.22.

Synthesis of *N*-Ethyl-2-methyl-1,3-benzothiazin-4-one (26). In a 100-mL three-necked flask equipped with a magnetic stirring bar, a jacketed addition funnel, and a nitrogen inlet was placed 0.9 g (5.0 mmol) of *N*-ethyl-2-mercaptobenzamide[37] in 50 mL of dry THF. Potassium hydroxide, 0.56 g (10.0 mmol), was dissolved in the solution followed by the dropwise addition of 0.088 g (2.0 mmol) of acetaldehyde cooled in the jacketed addition funnel. After the addition was complete the reaction mixture was stirred for an addition 0.5 h at which time the solvent was removed under vacuum. The resulting oil was purified using radial chromatography eluting with 1:1 *n*-pentane–ether to give 0.65 g (63%) of *N*-ethyl-2-methyl-1,3-benzothiazin-4-one (**26**) identical in all respects with the compound isolated in the FVP of sulfoxide 16h.

Attempted FVP of *n*-Butyl 2-Nitrophenyl Sulfoxide (16i). Sulfoxide **16i**, 0.4 g (1.7 mmol), decomposed in the inlet sample section of the FVP apparatus at 65 °C to give a dark oil which was purified by preparative TLC (silica gel) eluting with 1:2 *n*-pentane–ether to give 0.22 g (61%) of sulfide **13i**.

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Registry No. **11f**, 65924-65-4; **12b**, 29549-62-0; **12b** (thiol), 1121-24-0; **13c**, 100789-96-6; **13c** (thiol), 7217-59-6; **13d**, 37527-70-1; **13d** (thiol), 4521-31-7; **13e**, 100789-97-7; **13f**, 91827-97-3; **13g**, 100789-98-8; **13g** (thiol), 4892-02-8; **13h**, 100789-99-9; **13i**, 76697-39-7; **13i** (thiol), 4875-10-9; **14a**, 13153-10-1; **14f**, 100790-00-9; **15b**, 29634-42-2; **16c**, 100790-02-1; **16d**, 100790-03-2; **16e**, 100790-04-3; **16f**, 100790-01-0; **16g**, 31419-26-8; **16h**, 100790-05-4; **16i**, 100790-06-5; **17**, 86428-23-1; **20a**, 1208-20-4; **21a**, 882-33-7; **21b**, 6300-58-9; **21c**, 13920-94-0; **21d**, 35190-71-7; **21f**, 55164-16-4; **21g**, 5459-63-2; **21h**, 49755-52-4; **21i**, 1155-00-6; **22a**, 1212-08-4; **22b**, 100790-07-6; **22c**, 100790-18-9; **22d**, 100790-10-1; **22f**, 100790-13-4; **22g**, 4016-59-5; **23c**, 100790-09-8; **23e**, 100790-12-3; **23f**, 100790-14-5; **23g**, 100790-15-6; **23h**, 100790-16-7; **23i**, 58534-22-8; **24b**, 100790-08-7; **24d**, 100790-11-2; **26**, 100790-17-8; 2,2′-$ClCOC_6H_4S_2C_6H_4COCl$, 19602-82-5; 2,2′-$Et_2NCOC_6H_4S_2C_6H_4NEt_2$, 49755-52-4; 2-$Et_2NCOC_6H_4SH$, 49755-51-3; $BrCHMe_2$, 75-26-3; BrC_4H_9, 109-65-9; 2,2′-$O_2NC_6H_4S_2C_6H_4NO_2$, 22100-66-9; $HC{\equiv}CCO_2Me$, 922-67-8; 2-$HSC_6H_4CONHEt$, 65382-84-5; MeCHO, 75-07-0.

(43) Crenshaw, R. R.; Field, L. *J. Org. Chem.* **1965**, *30*, 175.