Experimental and Computational Evidence for the Formation of Iminopersulfinic Acids

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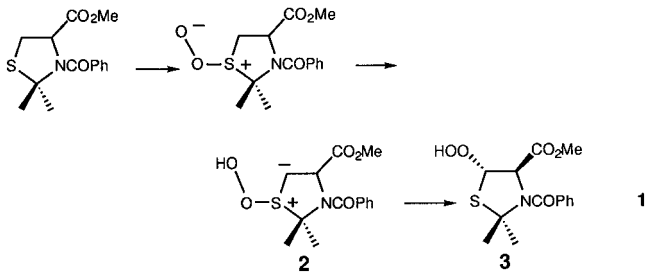
An experimental and computational study of the reactions of singlet oxygen with N-substituted sulfenamides is reported. Intermediates capable of epoxidizing norbornene were observed during the photooxidations of three sulfenamides. These results are used to argue for formation of iminopersulfinic acids. The structural integrity of two iminopersulfinic acids was supported by their successful location at the MP2/6-31G* level of theory. Furthermore, the inability to locate computationally significant persulfinimide precursors suggests that the iminopersulfinic acids form by enelike reactions involving near-simultaneous addition of singlet oxygen to sulfur and hydrogen abstraction.

The formation of *S*-hydroperoxysulfonium ylides, **1**, was first proposed by Corey and Ouannés in 1976[1] in order to rationalize the sulfur−carbon bond cleavage observed during the photooxidations of a series of benzylic sulfides. (Scheme 1) The transformation of **1** to the fragmentation products was later described as a Pummerer rearrangement,[2] and in support of that description an α-hydroperoxy sulfide was isolated.[3,4]

In 1991, Akasaka, Sakurai, and Ando[5] reported that epoxidation of norbornene occurred during photooxidation of a thiazolidine (eq 1). Control reactions demonstrated that the α-hydroperoxy sulfide **3** was not a competent oxygen donor under the reaction conditions (1.5 h at 0 °C) and led to the suggestion that the hydroperoxysulfonium ylide, **2**, was acting as the epoxidizing agent. Finally, in 1996, Ishiguro, Hayashi, and Sawaki[6] reported yet another facet of the chemistry of *S*-hydroperoxysulfonium ylides when they suggested that they were also capable of unimolecular rearrangements to sulfones.



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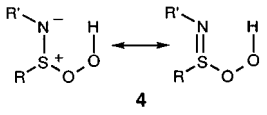
Despite the intense interest in the chemistry of *S*-hydroperoxysulfonium ylides and the debate surrounding their role in singlet oxygen reactions,[7] no attempt to produce a heteroatom-substituted analogue has been reported. In this regard, iminopersulfinic acids **4** are reasonable synthetic targets since they are isoelectronic to *S*-hydroperoxysulfonium ylides **1**. In addition, iminopersulfinic acids could potentially form to a greater extent in singlet oxygen reactions as a result of the lower pK_a of N−H in comparison to C−H bonds.[8] We now report the full details[9] of an experimental and computational study that provides the first compelling evidence for the formation of iminopersulfinic acids **4**.



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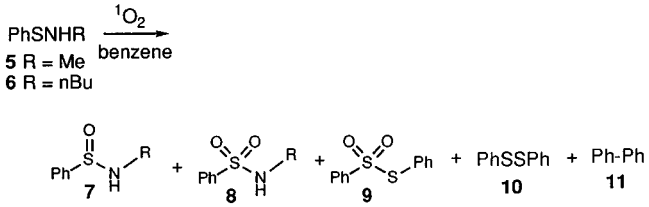
Results and Discussion

Photooxidations of sulfenamides **5** and **6** were conducted in oxygen-saturated benzene solutions by irradiation with a 500 W tungsten−halogen lamp through 1 cm of a 75 w/v % $NaNO_2$ filter solution. Each reaction mixture contained 2.3 mM of substrate, 5×10^{-5} M tetraphenylporphyrin (TPP), and an internal standard appropriate for capillary GC analysis. In addition to the anticipated formation of the sulfinamide **7** and sulfonamide **8**, thiosulfonate **9**, diphenyl disulfide **10**, biphenyl **11**, and several unidentified compounds were also detected by capillary gas chromatography in the reaction mixtures.



† University of Wyoming.
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(1) Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, 4263−4266.
(2) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154−156.
(3) Takata, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767−4770.
(4) Takata, T.; Tamura, Y.; Ando, W. *Tetrahedron* **1985**, *41*, 2133-2137.
(5) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696−2701.
(6) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265−7271.
(7) Jensen, F.; Greer, A.; Clennan, E. L. Submitted for publication.
(8) For example, pK_a Et_2NH 36 and pK_a $(CH_3)_2CH_2$ 51. Scudder, P. H. *Electron Flow in Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1992.
(9) A preliminary account of the computational studies has appeared: Greer, A.; Chen, M.-F.; Jensen, F.; Clennan, E. L. *J. Am. Chem. Soc.* **1997**, *119*, 4380−4387.

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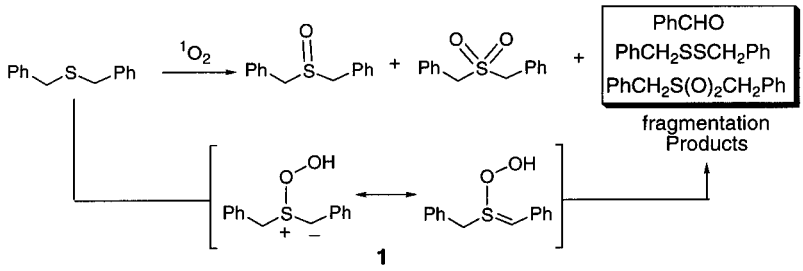
Scheme 1



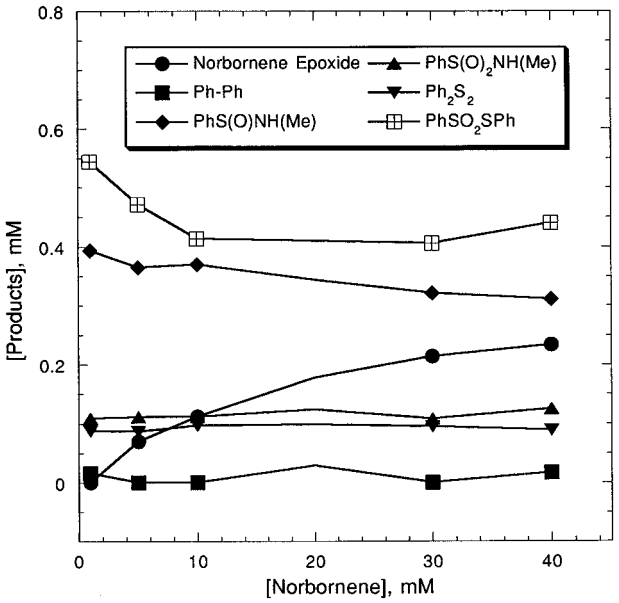


Figure 1. Product concentrations formed in the photooxidations of **5** as a function of norbornene concentration.

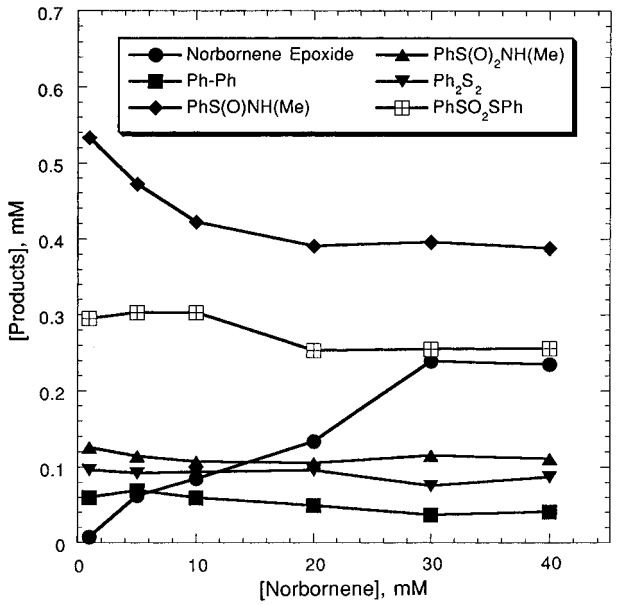
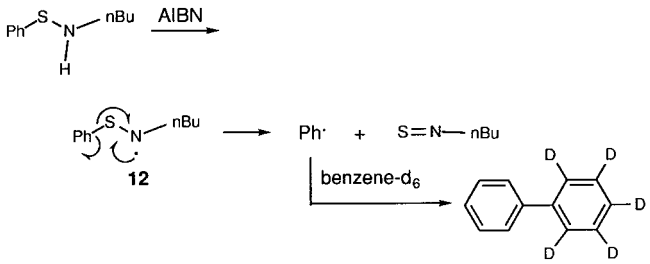


Figure 2. Product concentrations formed in the photooxidations of **6** as a function of norbornene concentration.

Biphenyl, **11**, was always a minor component of these reactions as shown in Figures 1 and 2. In addition, it was not found by capillary GC in photooxidations conducted in chloroform, acetone, or methanol, suggesting that the benzene solvent was incorporated into the biphenyl product. Exclusive formation of biphenyl-d_5 when the photooxidation was conducted in benzene-d_6 provides compelling evidence for this suggestion. The origin of the small amount of biphenyl, **11**, was further explored by irradiation of **6** in benzene using our standard reaction protocol (vide supra) followed by low-temperature removal of the solvent, addition of benzene-d_6, and subsequent analysis by GC−MS. This analysis revealed nearly exclusive formation of biphenyl-d_5 rather than biphenyl-d_0. Clearly, the small amount of biphenyl observed in all of the reactions is formed by thermolysis of a yet unidentified reaction component on the GC column. Indeed, in separate experiments, we have shown that thermal decomposition of AIBN in a benzene solution of **6** results in formation of biphenyl. Thioaminyl radicals **12** have previously been generated for ESR examinations by a variety of methods, including hydrogen abstraction from the parent sulfenamide with either PbO_2 or *tert*-butoxy radical.[10] The products of their thermolysis, however, have not been investigated. Examination of the photooxidation of **6** by reversed-phase HPLC verified the absence of biphenyl in the reaction mixture prior to GC analysis and also confirmed the presence of the other four products in addition to several unidentified components.



We have previously demonstrated that N,N-disubstituted sulfenamides react with singlet oxygen quantitatively to give predominately the sulfinamide and a trace of sulfonamide.[11] In contrast, the N-monosubstituted sulfenamides studied here undergo far more complex reactions with singlet oxygen and give poor mass balances. In the photooxidation of **5**, the identified products account for only 67% of the SPh groups and 22% of the NMe groups that were present in the starting material. The recovery of the NR group improves to 33% in **6**, reflecting an increase in the yield of the sulfonamide, $PhS(O)_2NH(n\text{-Bu})$, and perhaps increased stability of the iminopersulfinic acid intermediate (vide infra).

Two main lines of evidence support the involvement of singlet oxygen in these reactions: (1) The product

(10) Bassindale, A. R.; Iley, J. In *The Chemistry of Sulphenic Acids and their Derivatives*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1990; pp 101−186.

(11) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218−4227.

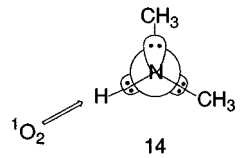
Table 1. Product Ratios in the Chemical and Photochemical Oxidations of Sulfenamide 6 (R = *n*-Bu)

singlet oxygen source	7	8	9	10	11
TPP[a,b]	45.6	10.0	32.3	7.3	4.8
C_{60}[a,c]	29.4	10.0	49.5	6.2	4.5
endoperoxide[d]	28.2	12.7	45.9	8.3	4.9

[a] Reactions 3.04 mM in PhSNH(*n*-Bu) and 4.67×10^{-4} M in the internal standard 4-*tert*-butylcyclohexanone. [b] [Tetraphenylporphyrin] = [TPP] = 5×10^{-5} M. [c] [C_{60}] = 6.4×10^{-5} M. [d] 100-fold molar excess of 1,4-dimethylnaphthalene endoperoxide.

ratios in the reaction of **6** as determined by capillary GC were independent of the source of singlet oxygen. A comparison of the product ratios when using photochemical (TPP or C_{60}[12] sensitization) or chemical (1,4-dimethylnaphthalene endoperoxide) generation of singlet oxygen is shown in Table 1. (2) Both **5** and **6** quench the emission of singlet oxygen at 1270 nm.[13,14]

The k_T values measured by examining the abilities of sulfenamides **5**, **6**, and *N*-*tert*-butylphenylsulfenamide **13** (PhSNH-*t*-Bu) to quench singlet oxygen emission are a composite of all chemical, k_r, and physical, k_q, channels of singlet oxygen deactivation induced by these substrates. The observed values of $(3.4 \pm 0.5) \times 10^8$ M^{-1} s^{-1} for **5**, $(1.88 \pm 0.06) \times 10^8$ M^{-1} s^{-1} for **6**, and $(1.0 \pm 0.2) \times 10^8$ M^{-1} s^{-1} for **13** are 2 orders of magnitude larger than the k_T (3.33×10^6 M^{-1} s^{-1}) reported for $PhCH_2SN(CH_2)_5$.[11] We believe that the rate acceleration for the N-monosubstituted sulfenamides reflect a decrease in steric interaction upon approach of singlet oxygen to sulfur. This difference in steric interaction can best be seen by examination of Newman projections of the ab initio-generated geometries of CH_3SNHCH_3, **14**, and $CH_3SN(CH_3)_2$, **15**.[9] Both compounds adopt geometries that minimize electronic interactions between the lone pair on nitrogen and the lone pairs on sulfur.[15,16] In these conformations, destabilizing steric interactions between the methyl group on sulfur and the methyl(s) on nitrogen are also minimized. Consequently, only in its approach to the N-monosubstituted sulfenamide, **14**, can singlet oxygen avoid a destabilizing steric interaction with an NMe group. In contrast, within the N-monosubstituted sulfenamide series, the decrease in k_T by a factor of 3.4 as the substituent is changed from *t*-Bu− to *n*-Bu− to Me− is best described as an electronic effect. This suggestion is supported by the observation that a plot of $\log(k_T(X)/k_T(Me))$ vs the Taft polar parameter, σ^*, gives an excellent straight line, $r = 0.9964$, with a slope of $\rho^* = -1.76$.[17]



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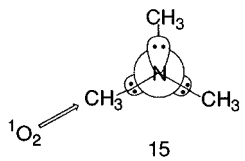

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Photooxidations of sulfenamides **5**, **6**, and **13** in the presence of norbornene resulted in formation of norbornene oxide. The concentrations of all the products including the epoxide were followed as a function of norbornene concentration. The data for **5** and **6** are presented in Figures 1 and 2 and compared to the results obtained with sulfenamide **13** in Figure 3. The concentration profiles in these figures demonstrate that epoxide was observed with as little as 5 mM norbornene, and its yield increased with increasing norbornene concentration. At 40 mM norbornene, the yield of norbornene oxide was between 10 and 15% based on the concentrations of the sulfenamide substrates. Formation of norbornene oxide did not occur if norbornene was added to the reaction mixtures after the photolysis was complete except in the case of *N*-*tert*-butylphenylsulfenamide, **13**. The *tert*-butyl group appears to sterically enhance the kinetic stability of the oxygen-donating species, and epoxide yields were always slightly higher using this sulfenamide.

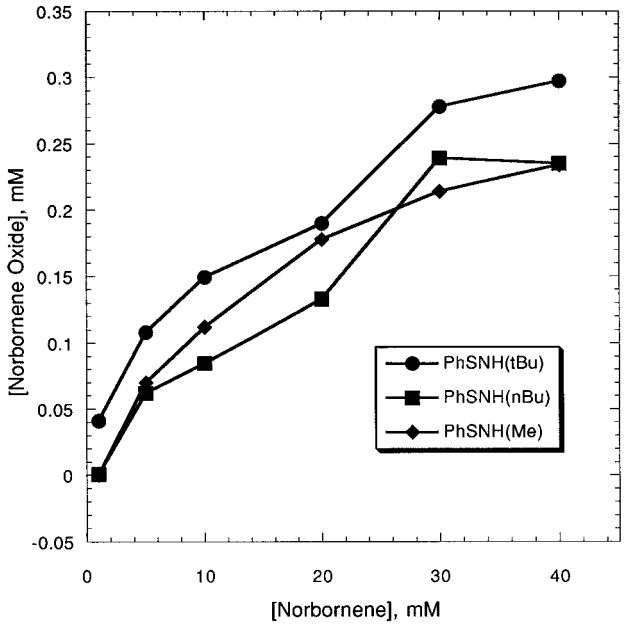
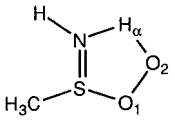


Figure 3. Concentrations of norbornene oxide formed in the photooxidations of **5**, **6**, and **13** as a function of norbornene concentration.

The formation of an epoxide is reminiscent of the behavior of hydroperoxy sulfonium ylides[5] and implies that an iminopersulfinic acid, **4**, is formed in the reactions of **5**, **6**, and **13** with singlet oxygen. To provide further evidence for the formation of these new peracids, we have conducted detailed ab initio searches for the iminopersulfinic acids derived from the additions of singlet oxygen to methylsulfenamide, **16** (CH_3SNH_2), and *N*-methylmethylsulfenamide, **17** (CH_3SNHCH_3).[9] In both cases, location of the iminopersulfinic acid was successful, and a careful search of conformational space resulted in the location of eight different conformers. Selected structural features and the relative MP2/6-31G* energies of these conformers for **16** and **17** are given in Tables 2 and 3, respectively. Each conformer is related to three other conformers by rotations around O−O, S−O, and S−N bonds. These relationships are best depicted using a conformational interconversion diagram, Scheme 2, with the O−O, S−O, and S−N rotations depicted as diagonal, horizontal, and vertical equilibria, respectively.

(12) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11−12.
(13) Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581−3584.
(14) Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080−5085.
(15) Craine, L.; Raban, M. *Chem. Rev.* **1989**, *89*, 689−712.
(16) Raban, M.; Kost, D. *Tetrahedron* **1984**, *40*, 3345−3381.
(17) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987.

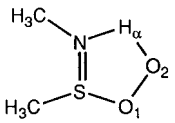
Table 2. Selected Structural Parameters for Iminopersulfinic Acid Conformers, 16[a]



	S−N	S−O_1	H_α−N	N−S−C	SO_1O_2	$SO_1O_2H_\alpha$	CSNH	CSO_1O_2	ΔE^b
I[c]	1.573	1.769	2.264	101.3	106.4	52.2	162.2	63.6	0
II	1.566	1.787	3.994	100.0	109.7	−120.7	166.1	55.1	3.59
III	1.550	1.781	4.024	109.4	108.3	−125.0	−34.2	60.0	4.44
IV	1.554	1.790	3.052	109.3	106.6	97.2	−30.3	66.4	1.72
V	1.565	1.800	4.085	100.4	102.9	−106.2	−166.9	178.5	1.41
VI	1.568	1.793	3.160	101.3	102.7	99.0	−163.4	−175.1	2.61
VII	1.554	1.781	3.159	109.9	104.1	91.3	31.0	170.5	2.54
VIII	1.550	1.790	4.030	109.7	104.5	−103.5	32.6	174.5	3.89

[a] Distance in Å; angles in deg; the dihederal angles, WXYZ, are positive for a clockwise movement from W to Z as you look from X to Y down bond XY. [b] Relative MP2/6-31G* energies in kcal/mol. [c] Conformers similar to those shown in Scheme 2 for **17** with NMe replaced with NH.

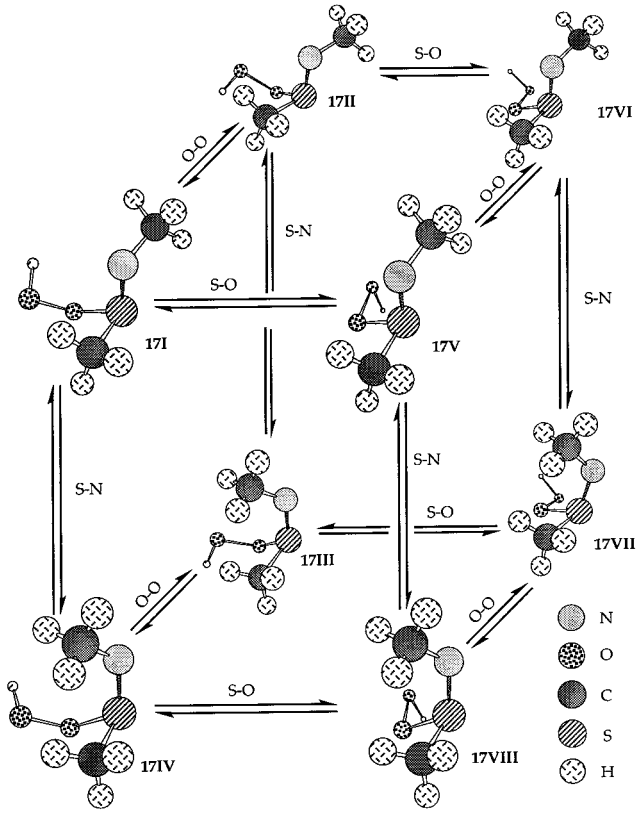
Table 3. Selected Structural Parameters for Iminopersulfinic Acid Conformers, 17[a]



	S−N	S−O_1	H_α−N	N−S−C	SO_1O_2	$SO_1O_2H_\alpha$	CSNH	CSO_1O_2	ΔE^b
I[c]	1.566	1.808	2.876	100.9	108.2	79.7	166.3	55.6	0
II	1.563	1.816	4.029	100.0	109.5	−120.0	169.6	55.0	2.46
III	1.546	1.804	4.126	111.3	109.5	−127.1	−34.5	57.6	2.68
IV	1.550	1.805	3.337	111.4	108.2	106.9	−31.0	61.6	0.94
V	1.563	1.827	4.073	100.5	102.2	−105.5	−170.0	−178.6	1.41
VI	1.565	1.819	3.338	100.9	102.1	106.0	−167.2	−177.1	0.72
VII	1.552	1.803	3.254	111.2	104.2	95.0	33.0	166.7	0.72
VIII	1.548	1.812	4.023	111.3	104.6	−102.7	34.8	173.7	1.58

[a] Distance in Å; angles in deg; the dihederal angles, WXYZ, are positive for a clockwise movement from W to Z as you look from X to Y down bond XY. [b] Relative MP2/6-31G* energies in kcal/mol. [c] Refer to Scheme 2 for structure of conformer.

Scheme 2



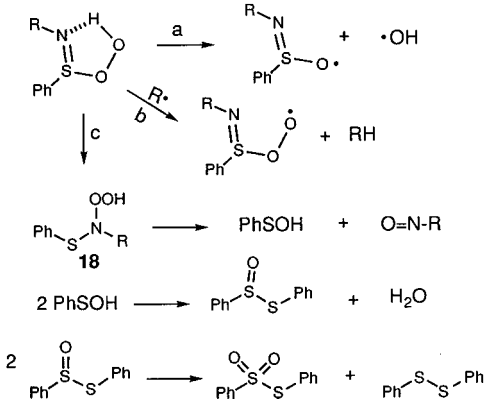
In the conformers related by rotations about the S−O bond, the structure with the peroxy hydrogen on the same face of the S−O−O plane as the nitrogen, **I**, **IV**, **VI**, and **VII**, are the most stable, with **I** representing the global minimum. The nitrogen−peroxy hydrogen distance in these four conformers is significantly shorter than in their rotomeric partners, implying the existence of a hydrogen bond. These hydrogen bonds in iminopersulfinic acids, **16I** and **17I**, are similar to those observed in peracids. Consequently, a lone pair on nitrogen is optimally situated to accept the hydroperoxy proton concomitantly with oxygen donation to an olefin via a Bartlett "butterfly-like" mechanism.[18]

The epoxidation yields with the iminopersulfinic acids derived from photooxidations of sulfenamides **5**, **6**, and **13**, however, are considerably smaller than those observed with peracids. The reduced epoxide yields reflect the fact that the iminopersulfinic acids are formed in the presence of sulfenamide substrates, which compete with norbornene for the active oxygen. An induction period for epoxide formation observed during photooxidation of sulfenamide **6** is consistent with this suggestion (i.e., norbornene oxide was never observed during the photooxidation of **6** until nearly 50% of the sulfenamide had reacted).

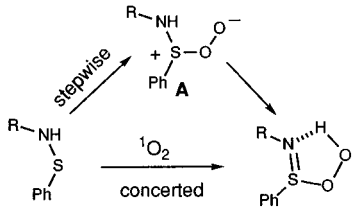
It is tempting to suggest that the complex reaction mixtures that are produced in these reactions are a result of a variety of decomposition and rearrangement pathways open to the iminopersulfinic acid/*S*-hydroperoxysulfonium ylides (Scheme 3). Thermal decompositions (path a, Scheme 3) and induced decompositions (path b, Scheme 3) are well-established routes for reactions of peracids.[19] Pummerer rearrangement of a hydroperoxy

(18) March, J. *Advanced Organic Chemistry. Reactions Mechanisms and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.

Scheme 3



Scheme 4



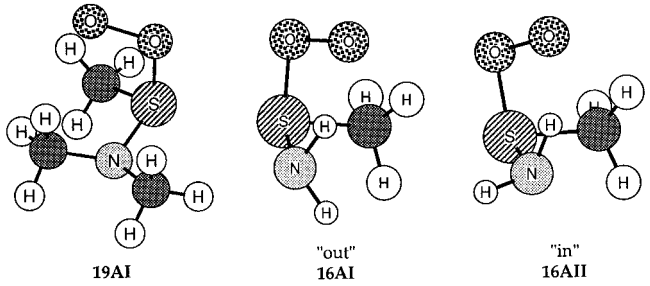
group from sulfur to an adjacent atom (path c, Scheme 3) is also well established.[2] Decomposition of the N-hydroperoxysulfenamide **18** followed by condensation of phenylsulfenic acid and disproportionation of the thiosulfinate would give the observed thiosulfonate and disulfide.[20] Unfortunately, our inability to isolate and identify all the products of these complex reactions prevented the generation of quantitative evidence in support of the mechanism depicted in Scheme 3.

An important mechanistic question that we have not yet addressed is related to the mechanism of iminopersulfinic acid formation. Two mechanistic extremes can be identified; a stepwise path via a persulfinamide intermediate, **A**, and a concerted pathway (Scheme 4). To explore the stepwise pathway, we have attempted to locate the persulfoxides **A** on the ab initio potential energy surfaces for reactions of singlet oxygen with sulfenamides **16**, **17**, and CH_3SNMe_2, **19**.

A single persulfoxide conformer was located for addition of singlet oxygen to sulfenamide **19**. In contrast, both "out" and "in" conformers (Scheme 5) were identified for the persulfoxides formed by addition of singlet oxygen to **16** and **17**. The nitrogen lone pair is syn to the S−C bond in the "in" conformer but anti to the S−C bond in the "out" rotomer. All of the persulfoxides, **16AI**, **16AII**, **17AI**, **17AII**, and **19AI** (Chart 1), optimized to structures in which the O−O bond nearly bisects the N−S−C bond angle. Selected structural parameters for these persulfoxides are given in Table 4.

The barriers for collapse of these persulfoxides to the iminopersulfinic acids at the MP2/6-31G* level are extremely small. The "out" rotomer, **16AI**, for example, has little chemical significance because its barrier to collapse to iminopersulfinic acid, **16I**, is only 0.0015 kcal/mol.

Chart 1



19AI "out" **16AI** "in" **16AII**

Conclusion

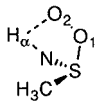
Intermediates formed in the photooxidations of sulfenamides **5**, **6**, and **13** have been shown to be competent as epoxidizing agents for norbornene. The suggestion that these intermediates are iminopersulfinic acids was supported by computational studies that successfully located these structures at the MP2/6-31G* level of theory. In addition, a "concerted ene"-type mechanism is implicated by the inability to computationally locate a chemically significant persulfinamide. The intriguing possibility that steric protection could provide a kinetically stabilized iminopersulfinic acid was provided by the observation that the epoxidizing agent formed in the photooxidation of *N-tert*-butylmethylsulfenamide persisted even after the photooxidation was complete. The syntheses of sulfenamides with even larger groups on nitrogen are currently being pursued to investigate this possibility.

Experimental Section

General Aspects. Gas chromatographic data were collected on a Hewlett-Packard GC/MS instrument consisting of a 5890 series II GC and a 5971 series mass selective detector or on a Perkin-Elmer Autosystem. An HP-5 (30 m × 0.25 mm × 0.25 μm (length × inside diameter × film thickness)) capillary column was used on the GC/MS and a 5% diphenyl−95% dimethyl polysiloxane (30 m × 0.32 mm × 1.0 μm (length × inside diameter × film thickness)) fused silica column was used on the Perkin-Elmer Autosystem. The HPLC analyses were done on a HP 1090 liquid chromatograph with diode array detection. A Hewlett-Packard 100 × 2.1 mm ODS Hypersil C_{18} column was used with H_2O−CH_3CN (35:65) as eluant at 0.2 mL/min. AIBN (2,2′-azobisisobutyronitrile) was obtained from Aldrich and used without further purification. Baker spectrophotometric-grade benzene was refluxed over phosphorus pentoxide for 5 h under a nitrogen atmosphere and distilled prior to use. *N*-Methyl-, *N-n*-butyl-, and *N-tert*-butylphenylsulfenamides (PhSNHMe, PhSNHnBu, and PhSNHtBu) were synthesized, isolated, and purified as described in the literature.[21] Sulfinimides **5SO**[22] and **6SO**[23] and sulfonamides **5SO$_2$**[24] and **6SO$_2$**[25] are all known compounds, and their spectral data including their mass spectra are consistent with their assigned structures.[26] Norbornene oxide was synthesized as reported in the literature[27] and purified by slow sublimation at 70 °C to give needlelike crystals. Tetraphenylporphyrin (TPP), 4-*tert*-butylcyclohexanone, and norbornene were obtained from Aldrich, dodecane was obtained from J. T. Baker, and 85% *m*-CPBA was obtained from ACROS, and all were all used without further purification.

(19) Sawaki, Y. In *Organic Peroxides*; Ando, W., Ed.; John Wiley & Sons: New York, 1992; p 425−477.
(20) Koch, P.; Ciuffarin, E.; Fava, A. *J. Am. Chem. Soc.* **1970**, *92*, 5971−5977.
(21) Armitage, D. A.; Clark, M. J.; Kinsey, A. C. *J. Chem. Soc. C* **1971**, 3867−3869.
(22) Schroeck, C. W.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5305−5306.
(23) Maricich, T. J.; Angeletakis, C. N. *J. Org. Chem.* **1984**, *49*, 1931−1934.
(24) Challis, B. C.; Iley, J. N. *J. Chem. Soc., Perkin Trans. 2* **1985**, 699−703.

Table 4. Selected Persulfoxide Structural Parameters[a]



	S−N	S−O_1	S−O_2	O_1−O_2	H_α−O_2	N−S−C	S−O_1−O_2	O_2−O_1−S−N
16AI	1.665	1.651	2.490	1.442	1.649	104.3	107.0	42.5
16AII	1.655	1.646	2.465	1.454	1.710	97.9	105.2	36.9
17AI	1.665	1.621	2.474	1.463	1.800	106.3	106.6	48.5
17AII	1.666	1.599	2.495	1.470	1.821	100.8	108.6	58.2
19AI	1.666	1.599	2.495	1.470		100.8	108.6	58.2

[a] Distance in Å. [b] Refer to Scheme 5 for conformer identification; CH_3SNH_2, **16**, CH_3SNHCH_3, **17**, $CH_3SN(CH_3)_2$, **19**.

Computational Methods. Ab initio calculations were performed using the Gaussian-94 program package[28] incorporating standard notations and procedures.[29] All geometry optimizations were done at the MP2/6-31G* level of theory. The nature of stationary points was verified by harmonic vibrational frequency calculations. A previous theoretical study has demonstrated that electron correlation is necessary to adequately describe the sulfide-$^1O_2$ potential energy surface (PES).[30,31]

Photooxidations. Tubes containing 1 mL of an oxygen-saturated benzene solution of 2.3 mM sulfenamides (PhSNHR; R = Me, *n*-Bu, and *t*-Bu), 5×10^{-5} M TPP, 1−50 mM norbornene, and an internal standard (4-*tert*-butylcyclohexanone or dodecane) were irradiated for 20−25 min with a 500-W tungsten halogen lamp through a 1 cm 75 w/v % $NaNO_2$ filter solution. The reaction mixtures were analyzed immediately by gas chromatography, and the concentrations of the reaction components were measured by reference to calibration curves constructed with authentic samples of the products.

AIBN Reaction. An excess of AIBN (2,2′-azobisisobutyronitrile) was added to a 2 mL benzene solution, which was 2.2 mM in **6**. This mixture was then refluxed for 4 h and analyzed by GC/MS.

k_T Measurements. The k_T values were obtained in benzene using the apparatus and procedure previously described.[13,14] Sulfenamide concentrations were chosen in order to observe decreases in lifetime of singlet oxygen over a range of approximately 25−15 μs. The k_T values were obtained from the experimental lifetimes by plotting k_{obsd} vs the concentration of sulfenamide used for the particular experiment. Each k_T value was determined at least twice with a precision of ±15%.

Chemical Oxidation. 1,4-Dimethylnaphthalene 1,4-endoperoxide[32] (ca. 40 mg) was added to a 1 mL volumetric flask containing a benzene solution 2.3 mM in **6** and 2.01×10^{-4} M in 4-*tert*-butylcyclohexanone. The resulting solution was then allowed to sit in the dark for 20 h and then analyzed by gas chromatography to give the results shown in Table 1.

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(25) Burchill, P.; Herod, A. A.; Marsh, K. M.; Pirt, C. A.; Pritchard, E. *Water. Res.* **1983**, *17*, 1891−1903.

(26) *N*-Methylphenylsulfenamide, **5**: EI/MS (*m*/*z*) 139 (M^+, 100), 124 ($PhSNH^+$, 22.9), 109 (PhS^+, 94.5), 97 (34.7), 80 (22.1), 69 (29.9), 65 (45.1). *N*-*n*-Butylphenylsulfenamide, **6**: EI/MS (*m*/*z*) 183 (M + 2, 28.1), 181 (M^+, 55.1), 138 ($PhSNHCH_2^+$, 91.0), 109 (PhS^+, 100), 94 (15.3), 77 ($C_6H_5^+$, 69), 65 (21.0). *N*-*tert*-Butylphenylsulfenamide, **13**: EI/MS (*m*/*z*) 181 (M^+, 44.2), 166 ($M^+ - CH_3$, 26.7), 125 ($PhSNH_2^+$, 100), 109 (PhS^+, 60.9), 93 (42.7), 65 (27.8). *N*-Methylphenylsulfinamide, **5SO**: EI/MS (*m*/*z*) 155 (M^+, 7.4), 125 ($PhSO^+$, 46.6), 107 (100), 97 (48.6), 77 (31.4), 51 (22.2). *N*-*n*-Butylphenylsulfinamide, **6SO**: EI/MS (*m*/*z*) 197 (M^+, 0.5), 180 (28.5), 154 (6.6), 149 (13.9), 125 ($PhSO^+$, 100), 106 (19.8), 97 (21.9), 77 ($C_6H_5^+$, 25.1). *N*-Methylphenylsulfonamide, **5SO$_2$**: EI/MS (*m*/*z*) 171 (M^+, 29.7), 141 ($PhSO_2^+$, 17.5), 107 (33.7), 77 ($C_6H_5^+$, 100), 51 (35.9). *N*-*n*-Butylphenylsulfonamide, **6SO$_2$**: EI/MS (*m*/*z*) 213 (M^+, 6.8), 171 (8.2), 170 ($PhSO_2NHCH_2^+$, 88.8), 158 (11.2), 141 ($PhSO_2^+$, 92.7), 77 ($C_6H_5^+$, 100), 51 (28.8).

(27) Budnik, R. A.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 1384−1389.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1994.

(29) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(30) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478−6487.

(31) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, pp 1−48.

(32) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972**, 253−254.