Theoretical and Experimental Analyses of the Deprotonation of Thiirane *S*-Oxides: The Stereoselective Formation of *trans*-Alkyl- and *gem*-Silylethenesulfenate Anions

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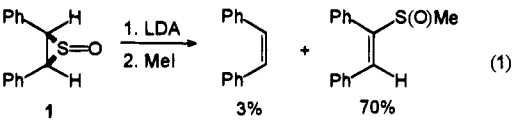
Received July 21, 1994[⊗]

Abstract: Experimental and theoretical studies of the regioselective deprotonation of thiirane *S*-oxides are reported. Experimentally under the reaction conditions of LiHMDS/THF/−78 °C with *anti*-alkylthiirane *S*-oxides or *anti*-silylthiirane *S*-oxides as starting materials, the products of ring-opening are (*E*)-2-alkylethenesulfenate and 1-silylethenesulfenate anions, respectively. Experiments involving deuterium labeling clearly indicate that a regioselective deprotonation reaction was followed by a stereoselective ring-opening. *Ab initio* methods at both the Hartree−Fock and Møller−Plesset perturbation theory levels with the 6-31+G(d) basis set were used to examine both lithiated methyl- and silylthiirane *S*-oxides. Of the possible *anti*-substituted species, the coordination of the lithium *anti* to the methyl and *gem* to the silyl is predicted to be the most stable. These stable intermediates with the lithium *syn* to the sulfoxide could ring-open to yield the experimentally observed products.

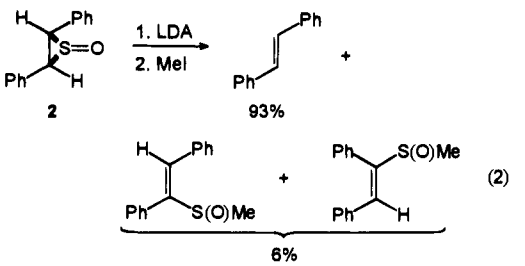
Introduction

The reactions of strong bases with sulfur containing three-membered rings usually afford alkenes via base attack at sulfur and eventual extrusion of that sulfur.[1,2] However, in a recent communication,[3] we demonstrated that thiirane *S*-oxide itself and some *anti*-substituted analogs underwent a deprotonation/ring-opening reaction in good yield when treated with amide bases. Moreover, the hexamethyldisilazide-mediated reaction gave a single geometrically pure sulfenate in most instances. This outcome was surprising since earlier experimental data[4] suggested that non-aryl-substituted systems could only undergo desulfurization. Independent of experiment, previous computational work[5] had indicated that both the *syn* and the *anti* anions, if generated, could produce sulfenates. Since a lone sulfenate was observed in most cases,[3] we undertook a theoretical study of the structure and relative energies of more realistic model compounds, methyl- and silyl-substituted lithiated thiirane *S*-oxides, in an effort to account for the experimental results of the communication.[3] This paper presents the outcomes of both our theoretical study and of further experimental work on the behavior of alkylated and silylated thiirane *S*-oxides and a deuterated thiirane *S*-oxide.

Previous studies[2] have shown that both desulfurization and deprotonation processes take place with phenyl-substituted thiiranes and thiirane *S*-oxides. For example, the reaction of *cis*-1,2-diphenylthiirane *S*-oxide (**1**) with lithium diisopropylamide (LDA) followed by methyl iodide (MeI) quenching affords (*E*)-1,2-diphenyl-1-(methylsulfinyl)ethene (70%) in addition to the desulfurization product *cis*-stilbene (3%) (reaction 1). In a related experiment, the LDA mediated reaction of *trans*-



diphenylthiirane *S*-oxide (**2**) yielded *trans*-stilbene (93%) and both (*E*)-1,2-diphenyl-1-(methylsulfinyl)ethene and (*Z*)-1,2-diphenyl-1-(methylsulfinyl)ethene (6% total) (reaction 2).



The explanation of Bonini *et al.*[2] for the formation and geometry of the sulfenates follows. In reaction 1, the base may attack at sulfur to eventually extrude that element in a process that requires 2 equiv of base. The base may also attack thiirane *S*-oxide **1** at hydrogen (deprotonation) to afford a lithiated anion (**3**) which is stabilized by an attractive electrostatic interaction of the lithium with the *syn* oxygen. Intermediate **3** then rearranges to sulfenate **4**, which is captured at sulfur by the MeI (Scheme 1). The situation with *trans*-1,2-diphenylthiirane *S*-oxide (**2**) is more complicated in that there are two different

⊗ Abstract published in *Advance ACS Abstracts*, December 1, 1994.

(1) (a) Marshall, J. A.; DuBay, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1450. (b) Vilsmaier, E.; Tropitzsch, R.; Vostrowsky, O. *Tetrahedron Lett.* **1974**, 3987. (c) Trost, B. M.; Ziman, S. D. *J. Org. Chem.* **1973**, *38*, 932. (d) Morton, M.; Kammereck, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 3217. (e) Matsumore, S.; Nagai, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2672. (f) Schuetz, R. D.; Jacobs, R. L. *J. Org. Chem.* **1961**, *26*, 3467. (g) Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1959**, *81*, 578.

(2) (a) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P. *Gazz. Chim. Ital.* **1990**, *120*, 115. (b) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Piccinelli, P. *Tetrahedron Lett.* **1979**, 3987.

(3) Schwan, A. L.; Pippert, M. F.; Pham, H. H.; Roche, M. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1312. For a recent example of deprotonation of thiirane *S,S*-dioxides, see: Muccioli, A. B.; Simpkins, N. S.; Mortlock, A. *J. Org. Chem.* **1994**, *59*, 5141.

(4) Maccagnani, G. in *Organic Sulfur Chemistry*; Freidlina, R. Kh., Skorova, A. E., Eds.; Pergamon Press: Oxford, 1981; pp 134−138.

(5) Maccagnani, G.; Schlegel, H. B.; Tonachini, G. *J. Org. Chem.* **1987**, *52*, 4961.

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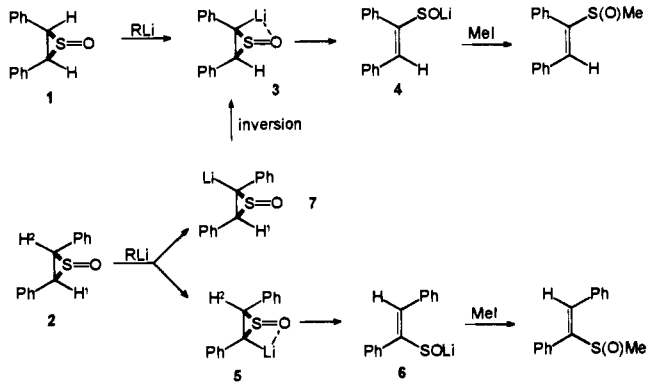
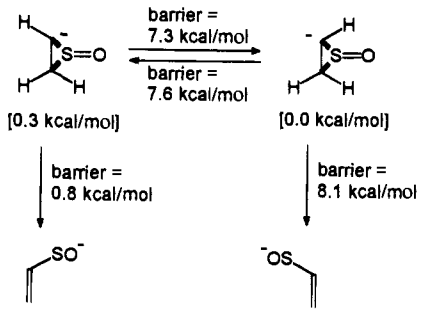
Scheme 1



Scheme 2



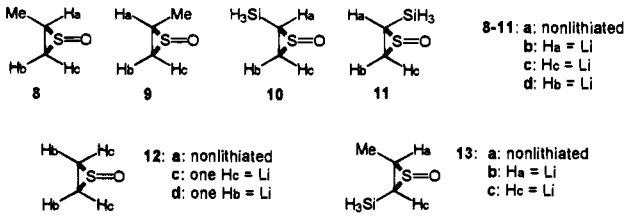
ring hydrogens available for removal and both are *cis* to a phenyl group. The phenyl groups offer steric protection which hinders the deprotonation and thus desulfurization is the major outcome. The deprotonation that does occur can be at H^1 to give the lithiated compound **5**, which then opens to afford sulfenate **6** and eventually the vinyl sulfoxide. Those authors suggested that removal of H^2 yielded the lithiated species **7**, which then inverts to **3** before ring-opening due to the driving force provided by the stabilization of the lithium interacting with the *syn*-oxygen.[2] Hence, the formation of both vinyl sulfoxide geometric isomers (reaction 2) can be accounted for by their mechanism.

As mentioned above, the earlier theoretical study[5] of the deprotonation/ring-opening sequence was performed using the parent thiirane *S*-oxide. The key features from the earlier theoretical work that pertain to our study are summarized in Scheme 2. Note that the nonlithiated *syn* and *anti* anions were essentially equal in energy with a barrier to inversion of *ca.* 7.5 kcal/mol between them. The barrier for ring-opening of the *syn* anion was predicted to be very small (0.8 kcal/mol) and since the comparable barrier for the *anti* anion was *ca.* 8 kcal/mol, the earlier theoretical study indicated that most, but not necessarily all, of the ethenesulfenates arose from the *syn* anion. Those authors also found a reasonable geometry for the transition state for ring-opening. Their work suggested that the stereospecific sense of the ring-opening is preferred as it offered increased overlap between the p orbitals on the carbon atoms.

Results and Discussion

The theoretical approach differs from the earlier study in several respects. Advances in *ab initio* methodology[6] and in computer workstation technology have allowed us to perform higher level calculations. In particular, a larger split valence basis set augmented by diffuse and polarization functions (6-31+G(d)) was used. The diffuse functions are included to better describe any anions. The effects of electron correlation, both on energies and geometries, were determined through second-order Møller–Plesset perturbation theory (MP2).[7] A preliminary study of general solvation effects was made through reaction field calculations.[8]

Chart 1



Since the anions that precede the sulfenates are better represented as lithiated species than as naked electron pairs, the lithium cation was explicitly included in our study. Somewhat larger and more realistic molecules, methyl thiirane *S*-oxides (**8**, **9**) and silyl thiirane *S*-oxide (**10**, **11**), were examined in addition to the unsubstituted thiirane *S*-oxide **12**. The additional substituent creates two isomers for each molecule (Chart 1) and renders the remaining three ring hydrogens nonequivalent. The substituent also allows for the experimental determination of the mode of ring-opening as it offers a handle to determine the point of attachment of the sulfinyl group.

Theoretical Results

Tables 1 and 2 summarize the key structural and energetic predictions from the theoretical portion of the present study. The reported geometries are all at the MP2/6-31+G(d) level of theory. Energetics with both the SCF and MP2 models and with corrections for changes in zero-point vibrational energies determined from HF/6-31+G(d) analytically evaluated vibrational frequencies are presented. In this section, the optimized geometries of the various minimum energy structures will be discussed first. Then the energetic results which may be tied most closely with the experimental work to be described in subsequent sections will be analyzed. Species are labeled according to the scheme in Chart 1, e.g. **10c** is *anti*-1-silyl-2-lithiothiirane *S*-oxide.

In Table 1, the most interesting structural features are those associated with the coordination of the lithium to the thiirane *S*-oxide at the carbanion site. The carbon to lithium distances range from 1.982 Å in **9b** to 2.130 Å in **13c**. For comparison,[9a] the C–Li distance in methyllithium is 2.001 or 2.003 Å at the HF or MP2/6-31+G(d) levels. The shorter C–Li bond lengths occur for compounds in which the Li is bonded only to the carbanion center while the slightly longer distances (*ca.* 2.1 Å) are found in species where the metal also interacts with the sulfoxide group's oxygen. Where these interactions occur, the lithium to oxygen distances (e.g. **9c**) are approximately 1.87 Å and reflect a favorable electrostatic interaction. Such a distance is consistent with the ionic radius of Li^+ of *ca.* 0.6 Å and the

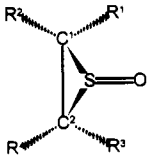
(6) (a) Gaussian 90, Revision F, Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990. (b) Gaussian 92, Revision B, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(7) Møller, C.; Plesset, M. S. *Physical Rev.* **1934**, *46*, 618.

(8) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; (a) p 403, (b) p 182, (c) p 358.

Table 1. *Ab Initio* Theoretical Predictions (MP2/6-31 + G(d)) for the Bond Lengths of the Lithiated Methyl- and Silyl-Substituted Thiirane *S*-Oxides



	R^1	R^2	R^3	R^4	C^1—C^2	C^1—S	C^2—S	S=O	R^1—O	C^1—R^1	C^1—R^2	C^2—R^3	C^2—R^4
8b	Li	C	H	H	1.490	1.825	1.831	1.587	1.865	2.105	1.517	1.090	1.098
8c	Li	H	H	C	1.490	1.816	1.840	1.588	1.865	2.094	1.095	1.093	1.512
8d	H	Li	H	C	1.496	1.854	1.830	1.530	*a*	1.098	1.993	1.093	1.509
9b	C	Li	H	H	1.487	1.891	1.834	1.531	*a*	1.522	1.982	1.096	1.090
9c	Li	H	C	H	1.489	1.814	1.848	1.587	1.867	2.100	1.094	1.509	1.096
9d	H	Li	C	H	1.498	1.851	1.853	1.532	*a*	1.100	1.995	1.509	1.092
10b	Li	Si	H	H	1.495	1.784	1.828	1.582	1.866	2.124	1.851	1.092	1.096
10c	Li	H	H	Si	1.511	1.803	1.834	1.581	1.875	2.093	1.095	1.094	1.885
10d	H	Li	H	Si	1.533	1.806	1.849	1.523	*a*	1.095	2.025	1.095	1.858
11b	Si	Li	H	H	1.494	1.827	1.831	1.524	*a*	1.855	1.984	1.094	1.091
11c	Li	H	Si	H	1.516	1.797	1.827	1.579	1.883	2.116	1.094	1.878	1.099
11d	H	Li	Si	H	1.522	1.826	1.827	1.531	*a*	1.099	2.007	1.888	1.094
12c	Li	H	H	H	1.495	1.810	1.826	1.586	1.870	2.095	1.093	1.089	1.093
12d	H	Li	H	H	1.503	1.841	1.824	1.529	*a*	1.097	1.996	1.091	1.089
13b	Li	C	H	Si	1.507	1.812	1.840	1.583	1.868	2.106	1.519	1.095	1.897
13c	Li	Si	H	C	1.489	1.784	1.844	1.585	1.860	2.130	1.850	1.095	1.513

a A nonbonded distance.

Table 2. Theoretical Predictions for the Total (in hartree) and Relative (in kcal/mol) Energies of Lithiated Methyl- and Silyl-Substituted Thiirane *S*-Oxides*a*

	HF		MP2		MP2:
	E	ΔE	*E*	ΔE	$\Delta E + \Delta$(ZPVE)
			Li, CH_3, H, H Substituents		
8b	−596.279 005	2.2	−597.005 917	3.3	3.1
8c	−596.283 522	−0.6	−597.010 697	0.3	0.3
8d	−596.235 808	29.4	−596.966 949	27.7	27.0
9b	−596.228 960	33.7	−596.960 781	31.6	30.9
9c	−596.282 590	0.0	−597.011 104	0.0	0.0
9d	−596.234 669	30.1	−596.966 393	28.1	27.6
			Li,SiH_3,H,H Substituents		
10b	−847.330 212	0.0	−848.006 388	0.0	0.0
10c	−847.322 699	4.7	−847.997 908	5.3	5.0
10d	−847.277 150	33.3	−847.957 415	30.7	29.6
11b	−847.282 233	30.1	−847.963 092	27.2	26.6
11c	−847.323 621	4.1	−847.999 565	4.3	4.0
11d	−847.277 739	32.9	−847.956 095	31.6	30.9
			Li, H, H, H Substituents		
12c	−557.244184	0.0	−557.836 650	0.0	0.0
12d	−557.196342	30.0	−557.792 271	27.8	27.3
			Li,CH_3,SiH_3,H Substituents		
13b	−886.354 544	8.6	−887.165 225	9.3	8.8
13c	−886.368 279	0.0	−887.180 010	0.0	0.0

a The 6-31+G(d) basis set was employed. Changes in zero-point vibrational energies were determined from HF/6-31+G(d) harmonic vibrational frequencies.

van der Waals radius of oxygen of approximately 1.4 Å.[10] The coordination of the oxygen to lithium leads to an increase in the SO bond length by about 4% from *ca.* 1.53 to *ca.* 1.59 Å. The prediction of 1.53 Å for the S-oxide bond length is approximately 0.05 Å greater than the experimental values in analogous compounds such as the parent thiirane *S*-oxide. Such a longer bond length may be due to the unusual lithium substituent. However, it may reflect the choice of the MP2 model and the 6-31+G(d) basis set. At the SCF level the sulfur−oxygen bond distances in sulfoxides are close to experimental values[9b] with the 3-21G (d) basis set. The inclusion of electron correlation effects via MP2 would be expected to lengthen this bond and a still larger basis set such as 6-311+G(2d) would be needed at the initial SCF stage in order to recover agreement with experiment.

The bond distances in the three-membered rings of the various thiirane *S*-oxides show significant changes with the different substituents. The C1−C2 distances (See the structure at the top of Table 1) all lengthen if a silyl group replaces a methyl. Comparing **9c** and **11c**, that distance changes from 1.489 to 1.516 Å. The combined effect of geminal substitution of lithium and silyl groups at C1 leads to a considerable distortion of the ring as the two carbon to sulfur distances differ by as much as 0.06 Å in **13c** and 0.04 Å in **10b**. Geminal interactions of SiH_3 and Li are predicted theoretically to be large and stabilizing.[9c] The effect has been rationalized as due to both groups acting as σ donors and π acceptors. These very strong interactions of the carbon with the substituents render it very different from the carbon in the methylene group in the ring. This difference then accounts for the rather large distortion of the ring bond lengths relative to those in unsubstituted **12c** and **12d**.

The trisubstituted thiirane *S*-oxides, **13b** and **13c**, represent the largest model compounds considered in the present theoretical study. However, for the common geometrical parameters such as the sulfoxide bond length and even the ring distances, **13b** and **10c** or **13c** and **10b** are very similar. Thus the effect of the methyl group is relatively innocuous as far as the structures go, particularly in comparison to the silyl group.

Table 2 collects the total energies and relative energies for the various molecules. All species were verified as minimum energy structures through harmonic vibrational frequency analyses at the HF/6-31+G(d) level. The results for **12c** and **12d** give the clearest indication of the energetic preference for *syn* coordination of the lithium cation by the anion. The best prediction places the *syn* species, favored by the electrostatic interaction of the positively charged lithium with the negatively charged oxygen, 27.3 kcal/mol lower in energy than the *anti* form. Such a large exothermicity could provide a driving force for the *anti* to *syn* geometry change by an "inversion-like" process at the carbanion center probably involving removal then reattachment of the lithium.

(10) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 260.

The methyl-substituted molecules **9c** and **8c** differ by just 0.3 kcal/mol and **8b** is only 3.1 kcal/mol higher in energy. These small energy differences indicate that the position of the methyl substituent in the *syn* species is energetically rather insignificant. These three intermediates all involve the favorable electrostatic interaction between the *syn* lithium and the oxygen. The other three species, **9b**, **9d**, and **8d**, with the lithium *anti* to the S−O group are 27.0−30.9 kcal/mol less stable. Although this large energy difference may be damped somewhat in solution, it appears that the *anti* species are not viable intermediates and probably convert to the *syn* forms.

A similar picture emerges for the silyl-substituted molecules with **10b**, **11c**, and **10c** within 5.0 kcal/mol of each other. All three involve the favorable lithium−oxygen interaction. If the lithium is *anti* to the sulfoxide as in **11b**, **10d**, and **11d**, the species lie 26.6−30.9 kcal/mol above **10b**. Comparing **13b** to **13c** produces a 8.8 kcal/mol preference for geminal substitution by lithium and silyl groups as compared to lithium and methyl.

Note that the same general pattern of energy differences emerges whether SCF or MP2 results are considered. Treating electron correlation more completely (MP4) for the prototypes **12c** and **12d** gives a predicted energy difference after correction for changes in the zero-point vibrational energies of 26.9 kcal/mol, within 0.5 kcal/mol of the MP2 result. Thus in this case, the MP2 energetic results are fairly representative of those from still more elaborate correlated methods.

Self-consistent reaction field (SCRF) methods also were applied to **12c** and **12d** to give a first indication of the possible effects of solvation on the relative energies of these species. The molecular volumes were determined using Gaussian92 and yielded radii of 3.63 and 3.64 Å for the spheres surrounding **12c** and **12d**. A dielectric constant of 7.58 was chosen with reference to tetrahydrofuran. **12c** is predicted to be 12.2 kcal/mol more stable than **12d** by the SCRF method and with the inclusion of zero-point vibrational energy changes. Conventional SCF predicted 27.3 kcal/mol for the comparable energy difference. For these lithiated intermediates, the energy difference is damped between the isolated molecule results and those from the SCRF model for the solvated species. The energy of the more polar **12d** decreases more with the inclusion of this crude treatment of solvation.

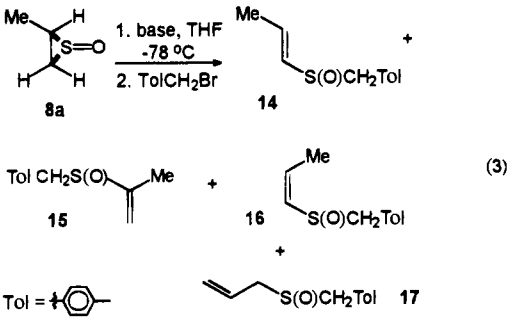
Reactions of Alkylated Thiirane *S*-Oxides

The theoretical data on the energetics indicate that the formation of *syn*-lithiothiirane *S*-oxide (**8c**) should be slightly favored over that of the geminal lithio species (**8b**) and significantly preferred over the *anti*-lithio compound (**8d**). It was anticipated that this trend revealed by the *ab initio* computations on isolated molecules would be matched at the experimental level in solution. Thus thiirane *S*-oxide **8a** was prepared as previously described.[11] Thiirane *S*-oxide **9a** is not accessible experimentally since it is known to undergo a sigmatropic ring-opening reaction at *ca.* −30 °C.[11] As indicated in the introduction, ethenesulfenate ions can be captured efficiently by certain reactive alkyl halides. In our experience,[3,12] methyl iodide and benzyl bromides are the preferred electrophiles and the result is a vinyl sulfoxide. The structure of the sulfenate can be inferred confidently from the structure of the isolable vinyl sulfoxides. Hence, in our experiments, all reaction mixtures were quenched with a reactive alkyl halide. When **8a** was exposed to LDA, LiTMP, or lithium dicyclohexylamide, two products were obtained, those from deprotonation at the geminal site and at the unsubstituted carbon.

Table 3. Reactions of **8a** with Amide Bases MNR_2 (See Reaction 3)

M	NR_2	products (% yields)[a]	M	NR_2	products (% yields)[a]
Li	$N(iPr)_2$	**14** (58), **15** (12)	Li	$N(TMS)_2$	**14** (72)
Li	$N(cC_6H_{11})_2$	**14** (58), **15** (22)	Na	$N(TMS)_2$	**14** (69), **16** (2)
Li	TMP[b]	**14** (62), **15** (18)	K	$N(TMS)_2$	**14** (58), **16** (3), **17** (12)

[a] The products reported are isomeric propenyl 4-methylbenzyl sulfoxides as the sulfenates were captured with 4-methylbenzyl bromide. All yields are of chromatographed material. [b] TMP is 2,2,6,6-tetramethylpiperidide.



(3)

Greater selectivity was observed with the hexamethyldisilazide (HMDS) bases (Table 3). Indeed, no geminal deprotonation occurred in the latter reactions. LiHMDS gave exclusively *trans*-vinyl sulfoxide **14**, while NaHMDS and KHMDS gave mostly **14** with additional byproducts. With LiHMDS as the base, experiment mirrors theory, in that the *ab initio* predictions on the gas phase species and experiment both favor deprotonation at the unsubstituted ring carbon. Since an energy difference of ~3 kcal/mol (*syn* vs *gem*) has been predicted reliably for this system, it may reasonably be inferred that the *syn* vs *anti* prediction of an energy difference of ~28 kcal/mol should also be quite accurate. Thus, our model tentatively requires that the *trans*-sulfenate arises exclusively through removal of the *syn* hydrogen.

The observed increased selectivity with the disilazide bases can be traced to the pK_a's of the amide bases. In THF, LDA, LiTMP, and lithium dicyclohexylamide have pK_a's in the 35−36 range while LiHMDS has a pK_a of 25.8.[13] The pK_a of thiirane *S*-oxide should be approximately 32.[14] Thus, deprotonation by LDA and similar bases should be exothermic in THF and, in accord with the Hammond postulate, will have an earlier transition state. The experimental energy difference of the transition states in THF for the formation of **8b** and **8c** will be reduced and the LDA will show less discrimination. With LiHMDS, the reaction is endothermic and the transition state for the reaction would be expected to be later along the reaction coordinate. Consequently, this transition state energy difference should reflect clearly the predicted energy difference of 3 kcal/mol for the fully lithiated, minimum energy species **8b** and **8c**. These inferences apply only to the generation of **8c**. It is possible that, after initial coordination to the sulfinyl oxygen, the LDA's limited selectivity is determined by steric as well as

(11) Kondo, K.; Negishi, A. *Tetrahedron* **1971**, *27*, 4821.
(12) Schwan, A. L.; Roche, M. R.; Gallagher, J. F.; Ferguson, G. *Can. J. Chem.* **1994**, *72*, 312.
(13) (a) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442. (b) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.
(14) This analysis requires that the trends in kinetic acidity of the ring hydrogens follow the trends in their thermodynamic acidity (i.e., pK_a). The pK_a of DMSO in DMSO (35) was used as a model for the pK_a of DMSO in THF (Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456). The value of 35 was then lowered by a few units to account for ring effects (Battiste, M. A.; Coxon, J. A. in *The Chemistry of the Cyclopropyl Group Part I*; Rappoport, Z., Ed.; Wiley: New York, 1987; Chapter 6).

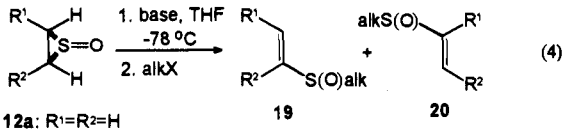
Table 4. Generation and Capture of *trans*-Substituted Ethenesulfenates (See Reaction 4)[a]

no.	R^1	R^2	base	products (% yields)[b]
12a	H	H	$NaN(TMS)_2$	**19a** (80)
18b	*n*Bu	H	$LiN(TMS)_2$	**19b** (75)
18b	*n*Bu	H	$LiN(iPr)_2$	**19b** (70), **20b** (11)
18c	$nC_{11}H_{23}$	H	$LiN(TMS)_2$	**19c** (79)[c]
18d	3-butenyl	H	$LiN(TMS)_2$	**19d** (75)
18e	cC_6H_{11}	H	$NaN(TMS)_2$	**19e** (68)
18f	$(iPr)_3SiCH_2$	H	$LiN(TMS)_2$	**19f** (60)
18g	Et	Et	$LiN(iPr)_2$	**19g** (66)
18h	$-(CH_2)_4-$		$LiN(iPr)_2$	**19h** (75)
18i	$PhOCH_2$	H	$NaN(TMS)_2$	**19i** (43), **20i** (24)[c]
18j	Ph	H	$LiN(iPr)_2$	**19j** (22), **20j** (13)[c-e]
18j	Ph	H	$LiN(TMS)_2$	**19j** (29), **20j** (15)[c,f]

[a] Sulfenates were captured with benzyl bromide unless otherwise indicated. [b] All yields are of chromatographed material. [c] The sulfenate was captured with MeI. [d] This line of data is from ref 2. [e] Styrene was detected but not quantitated. [f] No styrene was detected.

electronic properties, while LiHMDS shows discrimination based primarily on electronic properties (*vide infra*).

Having established the value of LiHMDS and to a lesser extent NaHMDS in performing the reactions selectively, we employed these two bases in a series of reactions with other thiirane *S*-oxides. The requisite starting materials were prepared by standard means from commercially available alkenes, oxiranes, or thiiranes. Each thiirane *S*-oxide (**18**) was reacted with



(4)

12a: R^1=R^2=H
18: R' s as indicated in Table 4

19 **20**

LiHMDS and NaHMDS and typical results are listed in Table 4. The reactions were quenched with a reactive alkyl halide after at least 5 min at −78 °C. The products were identified by their ^1H NMR vinyl coupling constants where possible. The systems $R^1 = R^2$ = alkyl (**19g**, **19h**) have only one vinyl hydrogen, and their structures were confirmed by lanthanide shift reagent experiments.[15]

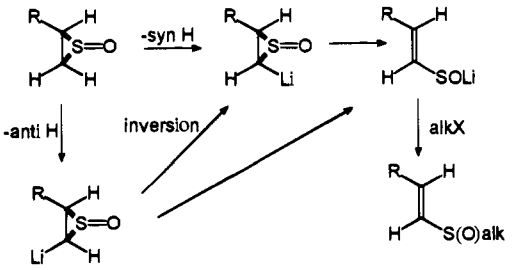
In all cases, a single geometric isomer was obtained, indicating that the ring-opening reaction afforded only one ethenesulfenate. LDA proved to be the preferred reagent for thiirane *S*-oxides **18g** and **18h**. Since those starting substrates possess equivalent ring hydrogens, there is no need for the regioselective deprotonation properties of the silazide bases. Selective deprotonation could not be achieved with thiirane *S*-oxides **18i** and **18j**. A probable explanation is that the attached phenyl and phenoxymethyl groups increase the acidity of the geminal hydrogen through induction. In these examples, the hexamethyldisilazide bases are no longer capable of selectivity and products **19** and **20** are both formed.

Deuterium Labeling Experiments

Even though geometrically pure ethenesulfenates can be generated, it is still unclear how the *trans*-sulfenates arise. One possibility is the removal of the *syn* H, followed by ring-opening, making the reaction a stereoselective process. On the other hand, that process could be accompanied by deprotonation from the *anti* position. The transient lithiated compound could then invert before or during the ring-opening to afford the *trans* sulfenate (Scheme 3). In order to determine which of the

(15) The LIS approach was based on established methods. See refs 2 and 12 and the supplementary material for details.

Scheme 3



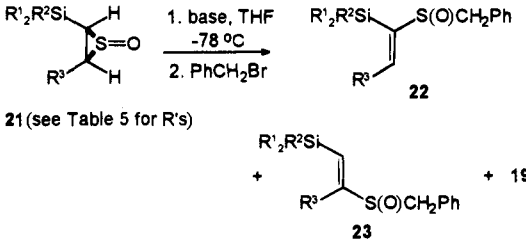
possible processes dominates, we synthesized a thiirane *S*-oxide bearing a deuterium label on one of the ring carbons.

trans-1-Deuteriohexene[16] was oxidized to the corresponding oxirane, which was then converted to the thiirane in the usual manner.[12,17] Similarly, the oxidation to thiirane *S*-oxide was uneventful. Exposure of the deuterated thiirane *S*-oxide (**18b**−**D**) to LiHMDS afforded only **19b** (77%), which contained no deuterium. Consequently, it can be concluded that deprotonation of **18b**−**D** occurs exclusively at the deuterium. Moreover, this experiment offers unequivocal proof that *the deprotonation/ring-opening sequence that provides trans-alkenesulfenates is a stereoselective process.*

The reaction of **18b**−**D** with LDA confirms that no inversion of the *gem*-lithio species occurred. The reaction of **18b** provided an expected pair of products, **19b** and **20b** (Table 4 and Scheme 4). The LDA-mediated reaction of **18b**−**D** gave **19b** as expected and also **20b**−**D**. The location of the deuterium in **20b**−**D** was confirmed by lanthanide shift experiments which included a noteworthy downfield movement of the deuterium.[15] The presence of the deuterium *cis* to the sulfinyl functionality in **20b**−**D** strongly supports a stereoselective ring-opening mechanism since the hydrogen was in the *gem* position in the starting thiirane *S*-oxide.

Reactions of Silylated Thiirane *S*-Oxides

The theoretical predictions on the silylthiirane *S*-oxides suggest that geminal lithiation is preferred over *trans* (or *cis*) lithiation (Table 2). In light of the strong similarity between the gas phase predictions and the experimental results for the alkyl-substituted thiirane *S*-oxides, similar experiments on silyl-substituted thiirane *S*-oxides were merited. *anti*-(Triethylsilyl)-thiirane *S*-oxide (**21a**) was chosen as the compound for detailed study. Its preparation was straightforward from vinyltriethylsilane.[17] Thiirane *S*-oxide **21a** was treated with several bases and the mixtures were quenched with benzyl bromide. The results are tabulated in Table 5 (reaction 5). The best results



21 (see Table 5 for R's)

22

(5)

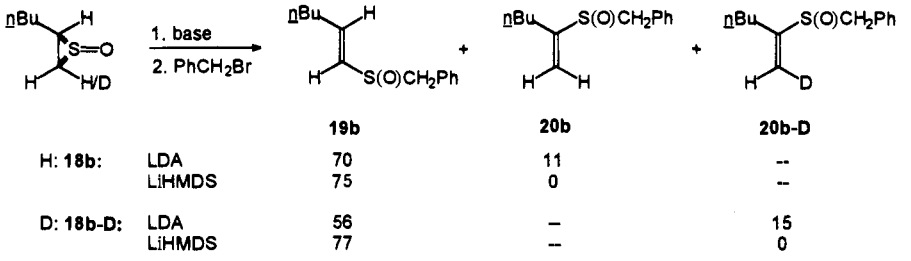
23

were obtained with LiHMDS, which gave exclusively geminal deprotonation. The increased acidity of hydrogens α to a silyl group is a well-recognized phenomenon. Reactions with LDA gave a mixture of products favoring *trans* deprotonation. The

(16) Kabalka, G. W.; Newton, R. J., Jr.; Jacobus, J. *J. Org. Chem.* **1978**, *43*, 1567.

(17) See the supplementary material for a detailed experimental for the synthesis of all thiiranes.

Scheme 4



		19b	20b	20b-D
H: 18b:	LDA	70	11	--
	LiHMDS	75	0	--
D: 18b-D:	LDA	56	--	15
	LiHMDS	77	--	0

Table 5. Generation and Capture of Silylated Sulfenates (See Reaction 5)[a]

no.	$R^1{}_2R^{2b}$	R^3	base	products (% yields)[c]
21a	Et_3	H	$LiN(iPr)_2$	**22a** (18), **23a** (49)
21a	Et_3	H	$LiN(TMS)_2$	**22a** (58)
21a	Et_3	H	$NaN(TMS)_2$	**22a** (59), **19a** (3)
21a	Et_3	H	$KN(TMS)_2$	**22a** (36), **19a** (15)
21b	Me_3	H	$LiN(TMS)_2$	**22b** (35)
21c	Ph_3	H	$LiN(TMS)_2$	**22c** (36)
21d	Me_3	*n*Bu	$LiN(iPr)_2$	**22d** (58), **23d** (12)[d]
21d	Me_3	*n*Bu	$LiN(TMS)_2$	**22d** (57)
21e	Me_2tBu	*n*Bu	$LiN(iPr)_2$	**22e** (26), **23e** (29)[d]
21e	Me_2tBu	*n*Bu	$LiN(TMS)_2$	**22e** (54)

[a] Sulfenates were captured with benzyl bromide. [b] This designation corresponds to the groups on the silicon. [c] All yields are of chromatographed, pure material unless otherwise indicated. [d] This material could not be separated from its corresponding isomer **22**. Relative yields were obtained by ^1H NMR analysis of the chromatographed mixtures.

sodium and potassium hexamethyldisilazide mixtures were contaminated with benzyl vinyl sulfoxide (**19a**). Control experiments indicated that this product may have resulted from the protodesilylation of benzyl 1-(triethylsilyl)ethenyl sulfoxide (**22a**) in solution after addition of benzyl bromide.[18] This product was sometimes observed in LiHMDS mixtures, but it could be suppressed by following the mixtures carefully by TLC and working them up as soon as the sulfenate had fully reacted. The chemistry was extended to two other silyl systems. Yields were low, but the reaction mixtures were exceptionally clean. Passing the crude material through silica gel afforded pure compounds.

Alkyl- and silyl-substituted thiirane *S*-oxides also reacted with LiHMDS as theory predicts for the parent system **13**. Thus, the reaction of **21d** and **21e** with LiHMDS and quenching with benzyl bromide afforded a single product in each case. The isolation of vinyl sulfoxides **22d** and **22e**, respectively, is consistent with the prediction that deprotonation should be exclusively from the silicon-bearing carbon. As indicated in Table 5, LDA again fails to demonstrate useful selectivity.

The theoretical predictions suggest that, in the gas phase, lithiated species **13c** should be *ca.* 8 kcal/mol more stable than its corresponding regioisomer **13b**. This is the largest energy difference that we can probe experimentally. Nevertheless, it is not large enough to direct LDA to only one reaction site. Similarly the predicted increased acidity of the geminal proton of silylated thiirane *S*-oxide **21a** has little effect on the regioselectivity exhibited by LDA. The reactivity of LDA is better explained by a combination of steric and electronic arguments.

Summary

Ab initio predictions on isolated molecules indicate that there should be regioselective deprotonation of thiirane *S*-oxides. The immediate products of the deprotonation, lithiated thiirane *S*-oxides, are predicted to be stable to an inversion-like process at the ring carbon, provided the lithium is *syn* to the sulfinyl oxygen. Experiments parallel the gas phase predictions rather well when the reaction conditions are LiHMDS/THF/−78 °C. The products of ring-opening are (*E*)-2-alkylethenesulfenate anions and 1-silylethenesulfenate anions when *anti*-alkylthiirane *S*-oxides and *anti*-silylthiirane *S*-oxides, respectively, are employed as starting materials. Deuterium labeling experiments offer clear evidence for a regioselective deprotonation reaction followed by a stereoselective ring-opening.

Sulfenic acids and their derivatives are of interest to both synthetic and mechanistic organic chemists.[19] The sulfenates described herein hold excellent synthetic potential, as they are expected to be reactive toward a large collection of electrophiles at both sulfur and oxygen.[20]

Experimental Section

General. Melting points were obtained on a Gallencamp capillary melting point apparatus and are uncorrected. All ^1H NMR spectra were run in $CDCl_3$ solution on a Varian Gemini 200 MHz NMR instrument or a Varian Unity 400 MHz NMR spectrometer using TMS or residual protium in $CDCl_3$ as internal standard. ^{13}C NMR spectra were obtained on the same instruments and were calibrated to the 77.00 ppm peak of $CDCl_3$. Infrared spectra were recorded as neat samples on a Bomem MB 100 IR spectrometer. Mass spectra were obtained using a Kratos MS890 double focusing mass spectrometer. Elemental analyses were performed by Guelph Chemical Laboratories and M-H-W Labs, Phoenix, AZ. Unless otherwise indicated, chromatographic separations were done either by flash chromatography on Merck silica gel or by centrifugal chromatography on a Chromatotron T instrument equipped with a 4 mm Merck Kieselgel 60 P_{254} silica gel plate. Analytical TLC was performed using 0.25 mm Merck Kieselgel 60 P_{254} precoated, glass-backed silica gel plates. Visualization was accomplished with UV light and/or an anisaldehyde/sulfuric acid solution. Solvents were distilled prior to use on the Chromatotron. THF was freshly distilled from benzophenone ketyl before use. The MCPBA was made by Janssen Chimica and was purchased through Spectrum Chemical.

The syntheses of the thiiranes or references for their synthesis can be found in the supplementary material. The preparation of thiirane *S*-oxides **8a**, **12a**, **18h**, and **18j** has been reported.[11]

General Procedure for Oxidation of Thiiranes. MCPBA (73% active, 1 equiv) in CH_2Cl_2 (10−25 mL) was added dropwise to a solution of the thiirane (2−6 mmol) in CH_2Cl_2 (10−25 mL) at −78 °C. The mixture was stirred until TLC indicated completion, usually 1−2 h. Dry NH_3 was impinged on the cold solution and the precipitate was removed by suction filtration through Celite. This process was repeated until no more precipitate formed. The mixture was then allowed to stand at 3 °C for 12 h.[21] After filtration, the mixture was

(18) Exposure of silylated vinyl sulfoxide **22a** to LiBr in THF at room temperature resulted in the slow formation of vinyl benzyl sulfoxide over a few hours.

(19) (a) Block E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135. (b) *The Chemistry of Sulphenic Acids and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1990. (c) Mazzanti, G.; Ruinaard, R.; Van Vliet, L. A.; Zani, P.; Bonini, B. F.; Zwanenburg, B. *Tetrahedron Lett.* **1992**, *33*, 6383.

(20) Hogg, D. R.; Robertson, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1125.

(21) This is an important step of the purification as it allows the labile *syn* isomer to decompose to a thiosulfinate which can be readily separated from the desired *anti* isomer by chromatography.

flash chromatographed on silica gel in a water-jacketed column using ether as the eluent.

***anti-n*-Butylthiirane *S*-oxide (18b):** 56% yield; ^{1}H NMR (200 MHz), δ 2.92 (m, 1H), 2.66 (dd, J = 6.6, 10.2 Hz, 1H), 2.01 (dd, J = 6.6, 9.5 Hz, 1H), 1.56−1.21 (m, 6H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50.3 MHz), δ 50.10, 41.37, 29.50, 28.92, 21.86, 13.55; IR (neat) cm^{-1} 2959, 2926, 2864, 1460, 1403, 1379, 1065 (s).

***anti-n*-Undecylthiirane *S*-oxide (18c):** 55% yield; ^{1}H NMR (200 MHz), δ 2.94 (m, 1H), 2.64 (dd, J = 6.6, 10.2 Hz, 1H), 2.08 (dd, J = 6.6, 9.5 Hz, 1H), 1.45 (m, 2H), 1.24 (s, 18H), 0.86 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 50.38, 41.63, 31.89, 29.57 (2 C's), 29.53, 29.50, 29.33 (2 C's), 29.02, 27.66, 22.67, 14.10; IR (neat) cm^{-1} 2923, 2853, 1460, 1066.

***anti*-3-Butenylthiirane *S*-oxide (18d):** 42% yield; ^{1}H NMR (200 MHz), δ 5.83 (m, 1H), 5.12 (m, 2H), 2.97 (m, 1H), 2.71 (dd, J = 6.7, 10.3 Hz, 1H), 2.31 (q, J = 7.0 Hz, 2H), 2.04 (dd, J = 6.7, 10.3 Hz, 1H), 1.57−1.31 (m, 2H); ^{13}C NMR (50.3 MHz), δ 136.18, 116.37, 49.59, 41.49, 31.72, 28.76; IR (neat) cm^{-1} 3074, 2978, 2920, 2847, 1640, 1443, 1065 (vs), 999.

***anti*-Cyclohexylthiirane *S*-oxide (18e):** 45% yield; ^{1}H NMR (200 MHz), δ 2.82 (m, 1H), 2.64 (dd, J = 10.3, 6.5 Hz, 1H), 2.07 (dd, J = 6.5, 9.5 Hz, 1H), 2.03−1.94 (m, 1H), 1.76−1.58 (m, 4H), 1.30−1.13 (m, 5H), 0.84−0.73 (m, 1H); ^{13}C NMR (50.3 MHz), δ 56.17, 40.44, 38.10, 32.01, 30.57, 25.95, 25.62, 25.54; IR (neat) cm^{-1} 2925, 2953, 1448, 1058 (s), 1011.

***anti*-Tris(1-methylethyl)silylmethylthiirane *S*-oxide (18f):** 56% yield; ^{1}H NMR (200 MHz), δ 2.98 (dq (br), J = 4.4, ca. 10.4, 1H), 2.66 (dd, J = 6.7, 9.9 Hz, 1H), 2.03 (dd, J = 6.7, 9.5 Hz, 1H), 1.30 (dd, J = 4.4, 14.7 Hz, 1H), 1.07 (s, 21H), 0.31 (dd, J = 10.9, 14.7 Hz, 1H); ^{13}C NMR, δ 48.73, 45.26, 18.56, 11.40, 10.93; IR (neat) cm^{-1} 2943, 2866, 1464, 1070, 883.

***anti,cis*-1,2-Diethylthiirane *S*-oxide (18g):** 59% yield; ^{1}H NMR (400 MHz), δ 3.00 (m, 1H), 1.55 (m, 1H) 1.31 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 44.05, 29.19, 13.83; IR (neat) cm^{-1} 2967, 2933, 2875, 1458, 1093, 1048 (vs), 955.

***anti*-(Phenoxymethyl)thiirane *S*-oxide (18l):** 54% yield; mp 95.5−96 °C; ^{1}H NMR (200 MHz), δ 7.32−6.79 (m, 5H), 4.24 (dd, J = 4.7, 11.0 Hz, 1H), 3.97 (dd, J = 5.5, 11.0 Hz, 1H), 3.30 (m, 1H), 2.83 (dd, J = 7.1, 10.6 Hz, 1H), 2.38 (dd, J = 7.1, 9.9 Hz, 1H); ^{13}C NMR (50.3 MHz), δ 157.52, 129.56, 121.73, 114.44, 64.06, 47.36, 38.19; IR (neat) cm^{-1} 3005, 2867, 1597, 1585, 1494, 1393, 1242, 1049 (s), 1017, 750; MS, *m/z* (%) 182 (1.2), 134 (76), 133 (49), 119 (21), 105 (22), 94 (66), 91 (22), 88 (21), 77 (51), 65 (34), 51 (17).

Base Reactions of Methylthiirane *S*-Oxide (8a). A dry round-bottom flask was charged with THF (10 mL) and the amide base (1.1 equiv) and was cooled to −78 °C. A solution of thiirane *S*-oxide **8a** (*ca.* 150 mg, 1.65 mmol) in *cold*, dry THF (6 mL) was added dropwise via syringe. The mixture was stirred for 10 min at −78 °C and was quenched by the addition of 4-methylbenzyl bromide (305 mg, 1.65 mmol) in THF (5 mL). The cold bath was removed and stirring continued for 12 h. Aqueous NH_4Cl was added, and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 10 mL) and the organic phases were combined, washed with brine, and dried over $MgSO_4$. Filtration and concentration gave a crude mixture the components of which were separated by centrifugal chromatography (EtOAc/hexanes) to give the amounts shown in Table 3. The elution order was **15**, **14** then **16**. Sulfoxide **17** coeluted with **14**.

Spectral Data for 15: mp 109−109.5 °C; ^{1}H NMR (200 MHz), δ 7.14 (s, 4H), 5.52 (s, 1H), 5.50 (s, 1H), 3.90 (AB q, J = 12.7 Hz, 2H), 2.34 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (50.3 MHz), δ 147.39, 138.00, 129.89, 129.27, 126.71, 118.70, 57.86, 21.13, 14.23; IR (neat) cm^{-1} 3024, 2965, 2918, 1524, 1443, 1418, 1261, 1104, 1044 (vs), 921, 814; MS, *m/z* (%) 194 (0.1), 106 (21), 105 (100), 103 (14), 79 (18), 77 (23). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.27; H, 6.93. Spectral data for **14**: mp 53−54 °C; ^{1}H NMR (200 MHz), δ 7.16 (s, 4H), 6.32 (dq, J = 6.3, 15.1 Hz, 1H), 6.19 (d, J = 15.1 Hz, 1H), 3.96 (AB q, J = 12.5 Hz, 2H), 2.35 (s, 3H), 1.87 (d, J = 6.3 Hz, 3H); ^{13}C NMR (50.3 MHz), δ 138.08, 137.29, 132.59, 130.12, 129.39, 126.40, 60.21, 21.14, 17.77; IR (neat) cm^{-1} 3008, 2964, 1633, 1513, 1443, 1415, 1035 (s); MS, *m/z* (%) 194 (0.3), 106 (16), 105 (100), 79 (15), 77 (20). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.09; H, 7.29. Spectral data for **16**: ^{1}H NMR (400 MHz), δ 7.15 (s, 4H), 6.21 (dq, J = 7.0, 9.8 Hz, 1H), 6.09 (d, J = 9.8 Hz, 1H), 4.13 (d, J = 12.4 Hz, 1H), 3.89 (d, J = 12.4 Hz, 1H), 2.34 (s, 3H), 1.60, (d, J = 7.0 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 138.33, 138.05, 134.75, 130.21, 129.37, 126.17, 59.75, 21.14, 15.03; IR (neat) cm^{-1} 3019, 2924, 1633, 1514, 1437, 1026; MS, *m/z* (%) 194 (0.5), 138 (15), 106 (39), 105 (100), 103 (14), 88 (21), 86 (86), 83 (93), 79 (21), 77 (21).

Reactions of Other Alkylthiirane *S*-Oxides. The various thiirane *S*-oxides were treated with amide bases as described for the reactions of **8a**. After 10 min of stirring at −78 °C, the mixtures were quenched with either MeI (excess) or benzyl bromide (1 equiv) in THF. Workup and separation were performed as described above.

Reaction of 12a with NaHMDS. After addition of benzyl bromide, workup and chromatography afforded benzyl vinyl sulfoxide (**19a**) (80%).[12]

Reaction of 18b with LiHMDS. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-1-hex-1-enyl sulfoxide (**19b**) (75%). Spectral data for **19b**: ^{1}H NMR (400 MHz), δ 7.37−7.24 (m, 5H), 6.30 (dt, J = 15.2, 6.9 Hz, 1H), 6.13 (dt, J = 15.2, 1.1 Hz, 1H), 3.98 (AB q, J = 12.7 Hz, 2H), 2.17 (dq, J = 6.9, 1.1 Hz, 2H), 1.38−1.24 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 141.96, 131.22, 130.17, 129.56, 128.59, 128.11, 60.49, 31.63, 30.06, 21.93, 13.67; IR (neat) cm^{-1} 3030, 2962, 2937, 2862, 1638, 1508, 1458, 1054 (s), 973; MS, *m/z* (%) 222 (2.1), 92 (69), 91 (100), 65 (26). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.06; H, 7.99.

Reaction of 18b with LDA. After addition of benzyl bromide, workup and chromatography afforded benzyl 2-hex-1-enyl sulfoxide (**20b**) (11%) followed by **19b** (70%). Spectral data for **20b**: ^{1}H NMR (400 MHz), δ 7.37−7.22 (m, 5H), 5.57 (s, 1H), 5.52 (s, 1H), 3.92 (AB q, J = 12.9 Hz, 2H), 2.30 (dt, J = 15.5, 8.0 Hz, 1H), 2.09 (dt, J = 15.5, 7.6 Hz, 1H), 1.57 (pentet, J = ca. 7.8 Hz, 2H), 1.39 (sextet, J = ca. 7.4 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 152.20, 130.12, 129.97, 128.53, 128.16, 116.73, 58.82, 29.99, 27.91, 22.23, 13.76; IR (neat) cm^{-1} 3062, 3030, 2959, 2930, 2867, 1629, 1602, 1495, 1457, 1265, 1072, 1047 (s), 920, 751, 698; MS, *m/z* (%) 222 (2), 173 (38), 92 (55), 91 (100), 65 (50), 55 (18). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.04; H, 7.97.

Reaction of 18c with LiHMDS. After addition of methyl iodide, workup and chromatography afforded methyl tridec-1-enyl sulfoxide (**19c**) (79%).[12]

Reaction of 18d with LiHMDS. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-1-hexa-1,5-dienyl sulfoxide (**19d**) (75%). Spectral data for **19d**: ^{1}H NMR (200 MHz), δ 7.38−7.22 (m, 5H), 6.29 (dt, J = 6.1, 15.0 Hz, 1H), 6.16 (d, J = 15.0 Hz, 1H), 5.71 (m, 1H), 5.00 (d, J = 16.0 Hz, 1H), 4.99 (d, J = 11.1 Hz, 1H), 3.97 (AB q, J = 12.6 Hz, 2H), 2.32−2.06 (m, 4H); ^{13}C NMR (50.3 MHz), δ 140.34, 136.59, 131.60, 130.02, 129.33, 128.41, 127.96, 115.44, 60.24, 31.79, 30.87; IR (neat) cm^{-1} 3066, 3030, 3002, 2919, 2846, 1639, 1495, 1453, 1072, 1043 (s), 915; MS, *m/z* (%) 220 (M^+, 0.2), 171 (2), 92 (9), 91 (100), 65 (10). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.70; H, 7.15.

Reaction of 18e with NaHMDS. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-2-cyclohexylethenyl sulfoxide (**19e**) (68%), mp 80.5−81.5 °C. Spectral data for **19e**: ^{1}H NMR (200 MHz), δ 7.40−7.21 (m, 5H), 6.21 (dd, J = 6.3, 15.4 Hz, 1H), 6.06 (d, J = 16.4 Hz, 1H), 3.97 (AB q, J = 12.6 Hz, 2H), 2.11 (m, 1H), 1.68 (s (br), 5H), 1.36−1.00 (m, 5H); ^{13}C NMR (100.6 MHz), δ 146.47, 130.16, 129.49, 129.24, 128.46, 128.01, 60.45, 40.14, 31.57, 25.68, 25.47; IR (neat) cm^{-1} 3029, 2963, 2924, 2851, 1627, 11450, 1259, 1073, 1038 (vs), 962, 759; MS, *m/z* (%) 248 (2.8), 92 (49), 91 (100), 81 (13), 79 (13), 67 (18), 65 (44), 55 (19). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12. Found: C, 72.42; H, 8.35.

Reaction of 18f with LiHMDS. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-2-[(triisopropylsilyl)-methyl]ethenyl sulfoxide (**19f**) (60%). Spectral data for **19f**: ^{1}H NMR (400 MHz), δ 7.37−7.25 (m, 5H), 6.48 (dt, J = 8.8, 15.0 Hz, 1H), 6.03 (d, J = 15.0 Hz, 1H), 3.98 (AB q, J = 12.6 Hz, 2H), 1.79 (d, J = 8.8 Hz, 2H), 1.01 (s (br), 21H); ^{13}C NMR (100.6 MHz), δ 142.21, 130.06, 129.97, 128.86, 128.67, 128.05, 60.62, 18.54, 17.17, 10.84; IR (neat) cm^{-1} 3062, 3030, 2940, 2865, 1612, 1495, 1461, 1142, 1041 (br), 883; MS (EI, ammonia), *m/z* (%) 337 ((M+H)$^+$, 14), 245 (52),

157 (51), 115 (62), 91 (100), 87 (47), 75 (20), 73 (61), 59 (72). Anal. Calcd for $C_{19}H_{32}OSSi$: C, 67.80; H, 9.58. Found: C, 67.90; H, 9.39.

Reaction of 18g with LDA. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-3-hex-3-enyl sulfoxide (**19g**) (66%), mp 49−49.5 °C. Spectral data for **19g**: ^{1}H NMR (400 MHz), δ 7.34−7.17 (m, 5H), 5.76 (t, J = 7.6 Hz, 1H), 3.89 (AB q, J = 12.7 Hz, 2H), 2.43 (m, 1H), 2.13 (m, 3H), 1.15 (t, J = 7.6 Hz, 3H), 0.90 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 141.94, 136.22, 130.19 (2 C's), 128.39, 127.95, 58.59, 21.21, 18.51, 14.48, 13.26; IR (neat) cm^{-1} 3061, 3020, 2967, 2931, 2873, 1646, 1602, 1495, 1456, 1050 (br), 765; MS, *m/z* (%) 222 (5), 173 (17), 92 (57), 91 (100), 67 (15), 65 (61), 55 (55), 53 (21); HRMS (*m/z*) calcd for $C_{13}H_{18}OS$ 222.1078, found 222.1073.

Reaction of 18h with LDA. After addition of benzyl bromide, workup and chromatography afforded benzyl (*E*)-cyclohex-1-enyl sulfoxide (**19h**) (75%), mp 44−45 °C. Spectral data for **19h**: ^{1}H NMR (400 MHz), δ 7.36 (m, 5H), 6.09 (br s, 1H), 3.95 (s, 2H), 2.34−2.28 (m, 1H), 2.17−2.05 (m, 3H), 1.80−1.56 (m, 4H); ^{13}C NMR (100.6 MHz), δ 139.93, 133.48, 130.31, 130.05, 128.52, 128.07, 58.00, 25.50, 22.13, 21.94, 20.63; IR (neat) cm^{-1} 3029, 2913, 1602, 1495, 1443, 1338, 1137, 1041 (br), 922, 766; MS, *m/z* (%) 220 (5), 171 (30), 92 (58), 91 (100), 81 (20), 79 (42), 77 (25), 65 (67), 53 (29), 51 (16). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.88; H, 7.38. Found: C, 70.44; H, 7.52.

Reaction of 18i with NaHMDS. After addition of methyl iodide, workup and chromatography afforded methyl 1-(phenoxymethyl)ethenyl sulfoxide (**20i**) (24%) followed by methyl (*E*)-2-(phenoxymethyl)-ethenyl sulfoxide (**19i**) (43%). Spectral data for **19i**: ^{1}H NMR (400 MHz), δ 7.29 (m, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 6.70 (m, 2H), 4.73 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100.6 MHz), δ 157.83, 134.94, 132.97, 129.56, 121.42, 114.63, 66.34, 40.58; IR (neat) cm^{-1} 3037, 2924, 1599, 1494, 1236, 1048, 954, 757; MS, *m/z* (%) 196 (21), 179 (19), 133 (77), 132 (21), 131 (22), 105 (35), 103 (88), 94 (36), 87 (41), 77 (64), 65 (47), 63 (25), 57 (25), 55 (100), 51 (26). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 60.89; H, 5.99. Spectral data for **20i**: mp 42.5−44 °C; ^{1}H NMR (200 MHz), δ 7.35−6.90 (m, 5H), 6.12 (s, 1H), 5.98 (s, 1H), 4.82 (AB q, J = 12.6 MHz, 2H), 2.75 (s, 3H); ^{13}C NMR (100.6 MHz), δ 157.67, 150.40, 129.65, 121.79, 120.04, 114.68, 64.88, 40.61; IR (neat) cm^{-1} 1595, 1494, 1231, 1048, 757; MS, *m/z* (%) 196 (33), 133 (69), 132 (36), 131 (41), 105 (38), 104 (99), 103 (100), 94 (75), 92 (36), 91 (50), 77 (75), 65 (81), 63 (66), 51 (28). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16. Found: C, 60.99; H, 6.33.

Reaction of 18j with LiHMDS. After addition of methyl iodide, workup and chromatography afforded methyl 1-phenylethenyl sulfoxide (**20j**)[2] (15%) followed by methyl (*E*)-2-phenylethenyl sulfoxide (**19j**)[2] (29%). GC analysis of the crude mixture offered no indication of the presence of styrene.

Preparation of Deuterated Thiirane *S*-Oxide (18b−D). (*E*)-1-Deuterio-1-hexene[16] was oxidized with MCPBA[12] to afford the corresponding oxirane (71%) (^{1}H NMR (200 MHz), δ 2.90 (m, 1H), 2.34 (d, J = 2.6 Hz, 1H), 1.58−1.28 (m, 6H), 0.92 (t, 7.3 Hz, 3H); ^{13}C NMR (50.3 MHz), δ 52.23, 46.73 (t, J = 26.1 Hz), 32.10, 28.05, 22.46, 13.91). Treatment of the crude oxirane with KSCN in MeOH/H_2O[12] provided crude thiirane which was flash distilled at 22−24 °C (1.1 mm) into a cooled collection flask (77%). (^{1}H NMR (400 MHz), δ 2.87 (q, J = ca. 6 Hz, 1H), 2.13 (d, J = 5.7 Hz, 1H), 1.83 (m, 1H), 1.54−1.32 (m, 5H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 36.18, 35.82, 31.42, 25.50 (t, J = 25.9 Hz), 22.25, 13.89.) The thiirane was oxidized with MCPBA as described above for other alkyl thiiranes to yield (*E*)-1-deuterio-*anti*-2-*n*-butylthiirane *S*-oxide (**18b−D**) (66%). Spectral data: ^{1}H NMR (200 MHz), δ 2.92 (m, 1H), 2.00 (d, J = 9.6 Hz, 1H), 1.56−1.21 (m, 6H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50.3 MHz), δ 50.09, 41.13 (t, J = 26.0 Hz), 29.56, 28.94, 21.92, 13.60; IR (neat) cm^{-1} 2958, 2930, 1461, 1049 (s), 988.

Reaction of (*E*)-1-Deuterio-*anti*-2-*n*-butylthiirane *S*-Oxide (18b−D) with LiHMDS. The two components were reacted together at −78 °C for 10 min before addition of benzyl bromide. Workup and chromatography afforded **19b** (77%). ^{2}H NMR (61.4 MHz) of the sample of **19b** showed no resonances corresponding to the vinyl deuteriums of **19b−D**.

Reaction of (*E*)-1-Deuterio-*anti*-2-*n*-butylthiirane *S*-Oxide (18b−D) with LDA. The two components were reacted together at −78 °C for 10 min before addition of benzyl bromide. Workup and chromatography afforded benzyl *Z*-1-deuterio-2-hex-1-enyl sulfoxide (**20b−D**) (15%) followed by **19b** (56%). Spectral data for **20b−D**: ^{1}H NMR (400 MHz), δ 7.36−7.21 (m, 5H), 5.50 (t, J = 1.5 Hz, 1H), 3.92 (AB q, J = 12.8 Hz, 2H), 2.29 (ddt, J = 1.5, 7.7, 16.4 Hz, 1H), 2.09 (ddt, J = 1.5, 7.7, 16.4 Hz, 1H), 1.55 (pentet, J = ca. 7.7 Hz, 2H), 1.38 (pentet, J = ca. 7.7 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{2}H NMR (61.4 MHz), δ 5.45 (s); ^{13}C NMR (100.6 MHz), δ 152.12, 130.09, 129.96, 128.50, 128.13, 116.44 (t, J = 24.8 Hz), 58.82, 29.98, 27.85, 22.21, 13.73; IR (neat) cm^{-1} 3067, 3037, 2962, 2943, 2868, 1613, 1508, 1458, 1066 (s), 706; MS, *m/z* (%) 223 (0.7), 174 (12), 117 (12), 92 (82), 91 (100), 65 (23). Anal. Calcd for $C_{13}DH_{17}OS$: C, 69.91; H/D, 8.14. Found: C, 69.76; H/D, 8.06.

Preparation of Silylated Thiirane *S*-Oxides 21. The thiiranes were prepared as described in the supplementary material. Their oxidation was performed as outlined above of the alkyl-substituted thiiranes above. Products were purified by column chromatography unless otherwise noted.

***anti*-Triethylsilylthiirane *S*-oxide (21a):** (91%, not purified) ^{1}H NMR (400 MHz), δ 2.66 (m, 1H), 1.98 (m, 2H), 1.31 (m, 1H), 0.95 (m, 9H), 0.53 (m, 6H); ^{13}C NMR (100.6 MHz), δ 36.89, 36.83, 7.04, 2.61; IR (neat) cm^{-1} 2955, 2910, 2877, 1461, 1415, 1240, 1071 (s), 1012.

***anti*-Trimethylsilylthiirane *S*-oxide (21b):** (42%, chromatographed twice) ^{1}H NMR (200 MHz), δ 2.78−2.62 (m, 1H), 2.10−1.94 (m, 2H), −0.03 (s, 9H); ^{13}C NMR (50.3 MHz), δ 39.31, 37.29, −2.62; IR (neat) cm^{-1} 2956, 2891, 1263, 1071, 841.

***anti*-(Triphenylsilyl)thiirane *S*-oxide (21c):** (95%, not purified) ^{1}H NMR (200 MHz), δ 7.56−7.36 (m, 15H), 2.90 (dd, J = 12.8, 5.4 Hz, 1H), 2.67 (t, J = ca. 12.5 Hz, 1H), 2.07 (dd, J = 12.1, 5.4 Hz, 1H); ^{13}C NMR (50.3), δ 135.52, 131.11, 130.43, 128.26, 37.13, 36.07; IR (neat) cm^{-1} 3158, 3081, 3060, 3025, 1586, 1495, 1439, 1130, 1074, 912.

(*Z*)-*n*-Butyl(trimethylsilyl)thiirane *S*-oxide (21d): (76%) ^{1}H NMR (200 MHz), δ 3.02 (m, 1H), 2.05 (d, J = 12.8 Hz, 1H), 1.63−1.03 (m, 6H), 0.90 (t, J = 7.1 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (50.3 MHz), δ 55.80, 47.16, 30.94, 28.29, 22.02, 13.72, −0.46; IR (neat) cm^{-1} 2961, 2926, 2877, 1467, 1410, 1263, 1074, 997, 849.

(*Z*)-*n*-Butyl(*tert*-Butyldimethylsilyl)thiirane *S*-oxide (21e): (75%) ^{1}H NMR (200 MHz), δ 3.01 (m, 1H), 2.06 (d, J = 12.9 Hz, 1H), 1.67−1.29 (m, 6H), 1.00 (s, 9H), 0.90 (t, J = 7.0 Hz, 3H), 0.03 (s, 3H), −0.04 (s, 3H); ^{13}C NMR (100.6 MHz), δ 55.29, 44.35, 31.07, 28.61, 26.31, 22.05, 16.98, 13.74, −4.72, −4.95; IR (neat) cm^{-1} 2961, 2933, 2863, 1481, 1368, 1256, 1081, 842.

Reactions of Silylated Thiirane *S*-Oxides 21. The various thiirane *S*-oxides were treated with amide bases in the manner described for the reactions of **8a**. After a period of stirring at −78 °C, the mixtures were quenched with benzyl bromide in THF and were warmed slowly to room temperature over the course of two hours. Workup and separation were performed as described above.

Reaction of 21a with LDA. The mixture was stirred for 10 min before the addition of benzyl bromide. After workup, the crude material was chromatographed to afford benzyl 1-(triethylsilyl)ethenyl sulfoxide (**22a**) (18%) followed by benzyl (*E*)-2-(triethylsilyl)ethenyl sulfoxide (**23a**) (49%). Spectral data for **22a**: ^{1}H NMR (400 MHz), δ 7.28−7.19 (m, 5H), 6.45 (s, 1H), 6.04 (s, 1H), 3.99 (d, J = 13.0 Hz, 1H), 3.50 (d, J = 13.0 Hz, 1H), 0.94 (t, J = 7.8 Hz, 9H), 0.71 (m, 6H); ^{13}C NMR (100.6 MHz), δ 152.92, 131.20, 130.86, 130.23, 128.51, 128.11, 61.02, 7.09, 3.37; IR (neat) cm^{-1} 3062, 3031, 2954, 2877, 1597, 1496, 1458, 1415, 1278, 1230, 1237, 1050, 1010, 958, 750, 733, 697; MS, *m/z* (%) 280 (3.4), 249 (24), 115 (19), 103 (36), 92 (64), 91 (100), 87 (24), 86 (41), 84 (54), 75 (32); HRMS (*m/z*) calcd for $C_{15}H_{24}OSSi$ 280.1317, found 280.1303. Spectral data for **23a**: ^{1}H NMR (400 MHz), δ 7.35−7.23 (m, 5H), 6.65 (AB q, J = 18.0 Hz, 2H), 3.97 (AB q, J = 12.5 Hz, 2H), 0.91 (t, J = 7.9 Hz, 9H), 0.59 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100.6 MHz), δ 145.06, 135.58, 130.09, 129.35, 128.60, 128.17, 60.07, 7.08, 3.06; IR (neat) cm^{-1} 3062, 3031, 2953, 2910, 2876, 1578, 1496, 1458, 1415, 1236, 1057, 1012, 977, 777, 730, 698; MS, *m/z* (%) 280 (8), 131 (26), 115 (26), 92 (25), 91 (100), 87 (33), 59 (24); HRMS (*m/z*) calcd for $C_{15}H_{24}OSSi$ 280.1317, found 280.1305.

Reaction of 21a with LiHMDS. The mixture was stirred for 10 min before the addition of benzyl bromide. After workup, the crude material was passed through a silica gel plug to afford **22a** (58%).

Reaction of 21a with NaHMDS. The mixture was stirred for 10 min before the addition of benzyl bromide. After workup, the crude material was chromatographed to afford **22a** (59%) followed by benzyl vinyl sulfoxide (**19a**) (3%).

Reaction of 21a with KHMDS. The mixture was stirred for 10 min before the addition of benzyl bromide. After workup, the crude material was chromatographed to afford **22a** (36%) followed by **19a** (15%).

Reaction of 21b with LiHMDS. The mixture was stirred for 1 h before the addition of benzyl bromide. After workup, the crude material was passed through a silica plug to afford benzyl 1-(trimethylsilyl)-ethenyl sulfoxide (**22b**) (35%). Spectral data for **22b**: ^{1}H NMR (400 MHz), δ 7.36−7.24 (m, 5H), 6.33 (s, 1H), 6.09 (s, 1H), 4.06 (d, J = 13.0 Hz, 1H), 3.66 (d, J = 13.0 Hz, 1H), 0.29 (s, 9H); ^{13}C NMR (100.6 MHz), δ 155.61, 130.48 (2 C's), 130.33, 128.47, 128.12, 60.79, −0.79; IR (neat) cm^{-1} 3065, 3032, 1508, 1468, 1421, 1256, 1051, 852; MS, *m/z* (%) 238 (3), 221 (17), 205 (10), 92 (52), 91 (100), 75 (50), 73 (70), 65 (45), 58 (17); HRMS (*m/z*) calcd for $C_{12}H_{18}OSSi$ 238.0848, found 238.0842.

Reaction of 21c with LiHMDS. The mixture was stirred for 30 min before the addition of benzyl bromide. After workup, the crude material was passed through a silica plug to afford benzyl 1-(triphenylsilyl)ethenyl sulfoxide (**22c**) (36%), mp 120−121 °C. Spectral data: ^{1}H NMR (400 MHz), δ 7.61 (m, 6H), 7.52−7.42 (m, 9H), 7.25 (m, 3H), 6.98 (s, 1H), 6.88 (m, 2H), 6.38 (s, 1H), 3.65 (d, J = 13.0 Hz, 1H), 3.16 (d, J = 13.0 Hz, 1H); ^{13}C NMR (100.6 MHz), δ 150.67, 136.28, 135.39, 131.47, 131.11, 130.53, 130.12, 128.35, 128.00, 60.65; IR (neat) cm^{-1} 3081, 3046, 3031, 1593, 1509, 1116, 1060, 744; MS *m/z* (%) 424 (1), 365 (17), 335 (17), 334 (34), 333 (100), 260 (25), 259 (93), 215 (15), 91 (31). Anal. Calcd for $C_{27}H_{24}OSSi$: C, 76.37; H, 5.70. Found: C, 76.47; H, 5.56.

Reaction of 21d with LiHMDS. The mixture was stirred for 30 min before the addition of benzyl bromide. After workup, the crude material was passed through an alumina plug to afford benzyl (*E*)-1-(trimethylsilyl)-1-hex-1-enyl sulfoxide (**22d**) (57%). Spectral data for **22d**: ^{1}H NMR (400 MHz), δ 7.36−7.20 (m, 5H), 6.65 (t, J = 7.8 Hz, 1H), 4.06 (d, J = 12.8 Hz, 1H), 3.53 (d, J = 12.8 Hz, 1H), 2.27 (m, 2H), 1.36−1.21 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (100.6 MHz), δ 149.13, 140.53, 130.39, 130.21, 128.21, 127.87, 60.84, 31.45, 30.90, 22.22, 13.78, −0.20; IR (neat) cm^{-1} 3095, 3073, 3039, 2961, 2926, 2870, 1600, 1509, 1460, 1251, 1053, 856, 702; MS *m/z* (%) 294 (10), 251 (11), 171 (15), 161 (16), 91 (100), 75 (19), 73 (31); HRMS (*m/z*) calcd for $C_{16}H_{26}OSSi$ 294.1493, found 294.1474.

Reaction of 21d with LDA. The mixture was stirred for 30 min before the addition of benzyl bromide. After workup, the crude material was passed through an alumina plug to afford **22d** (58%) and benzyl (*E*)-1-(trimethylsilyl)-2-hex-1-enyl sulfoxide (**23d**) (12%) as an inseparable mixture. The following spectral information for **23d** was obtained from the mixture containing **22d** and **23d**: partial ^{1}H NMR (400 MHz), δ 7.36−7.15 (m, 5H, aryl H's), 6.02 (s, 1H, vinyl H), 3.96 (d, J = 13.3 Hz, 1H, benzyl H), 3.73 (d, J = 13.3 Hz, 1H, benzyl H), 2.51 (m, 1H), 1.97 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H, butyl Me H's), 0.09 (s, 9H, $(Me)_3Si$ H's); partial ^{13}C NMR (100.6 MHz), δ 157.03, 130.12, 129.78, 129.60, 128.13, 58.16, 32.47, 30.07, 22.62, 13.64, −0.51.

Reaction of 21e with LiHMDS. The mixture was stirred for 1 h before the addition of benzyl bromide. After workup, the crude material was passed through an alumina plug to afford benzyl (*E*)-1-(*tert*-butyldimethylsilyl)-1-hex-1-enyl sulfoxide (**22e**) (54%). Spectral data for **22e**: ^{1}H NMR (400 MHz), δ 7.36−7.21 (m, 5H), 6.78 (t, J = 7.7 Hz, 1H), 4.07 (d, J = 13.0 Hz, 1H), 3.53 (d, J = 13.0 Hz, 1H), 2.25 (m, 2H), 1.25 (m, 4H), 0.95 (s, 9H), 0.87 (m, 3H), 0.31 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (100.6 MHz), δ 150.90, 138.86, 130.49, 130.47, 128.24, 127.89, 61.49, 32.23, 30.99, 26.72, 22.33, 18.48, 13.83, −3.68, −4.34; IR (neat) cm^{-1} 3095, 3074, 3032, 2968, 2933, 2856, 1600, 1502, 1460, 1249, 1046, 842, 709; MS *m/z* (%) 336 (5), 279 (9), 181 (22), 92 (26), 91 (100), 86 (16), 84 (25), 75 (39), 73 (22); HRMS (*m/z*) calcd for $C_{19}H_{32}OSSi$ 336.1943, found 336.1929.

Reaction of 21e with LDA. The mixture was stirred for 1 h before the addition of benzyl bromide. After workup, the crude material was passed through an alumina plug to afford **22e** (26%) and benzyl (*E*)-1-(*tert*-butyldimethylsilyl)-2-hex-1-enyl sulfoxide (**23e**) (29%) as an inseparable mixture. The following spectral information for **23e** was obtained from the mixture containing **22e** and **23e**: partial ^{1}H NMR (400 MHz), δ 7.35−7.18, (m, 5H, aryl H's), 6.10 (s, 1H, vinyl H), 3.99 (d, J = 13.0 Hz, 1H, benzyl H), 3.75 (d, J = 13.0 Hz, 1H, benzyl H), 2.54 (m, 1H), 2.00 (m, 1H), 0.81 (s, 9H, *t*Bu), 0.09 (s, 3H, Me), 0.06 (s, 3H, Me); ^{13}C NMR (100.6 MHz), δ 158.19, 130.09, 129.75, 128.33, 127.93, 127.27, 58.21, 32.52, 30.50, 26.21, 22.81, 16.88, 13.70, −4.62, −4.86.

Theoretical Predictions. Theoretical studies were carried out with the Gaussian90 and Gaussian92 program packages[6] on Silicon Graphics 4D-340 or 4D-380 workstations. Hartree−Fock methods[22] with a 6-31+G(d) basis set[23] were used. Minima were located using analytic energy gradient methods and the algorithms of Schlegel.[24] No symmetry constraints were placed on the molecules. All stationary points located were characterized by determining the harmonic vibrational frequencies using analytic second-derivative[25] methods at the SCF level and found to be minima. Structures also were optimized at a level including electron correlation, namely Møller−Plesset perturbation theory at the second order (MP2).[7] Analytic MP2 gradients[26] using the frozen core approximation were employed in these geometry optimizations.

Acknowledgment. R.D.J.F. acknowledges the Natural Sciences and Engineering Research Council of Canada (NSERC) for support in the form of a postgraduate scholarship. J.D.G. and A.L.S. acknowledge NSERC for support in the form of research grants.

Supplementary Material Available: Syntheses of the thiiranes or references to their synthesis, LIS data for some vinyl sulfoxides, independent synthesis of **17** and tables of SCF- and MP2-optimized geometries for the compounds **8b−8d**, **9b−9d**, **10b−10d**, **11b−11d**, **12b−12c**, and **13b−13c** compiled both in Z-matrix and standard orientation form are available (the atomic charges are also listed for SCF structures) (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JA942381K

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