1-Alkenesulfinyl Chlorides: Synthesis, Characterization, and Some Substitution Reactions

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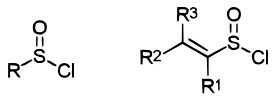
A number of 1-alkenyl sulfoxides bearing either a diphenylmethyl (DPM) or a *p*-methoxybenzyl (PMB) group have been prepared and exposed to the chlorine surrogate SO_2Cl_2. Through an oxidative fragmentation reaction, a new family of sulfur acid derivatives, 1-alkenesulfinyl chlorides, is generated. They can be characterized by IR spectroscopy before chemical capture with an alcohol. Ethenesulfinyl chloride (**2a**) and 1-propenesulfinyl chloride (**2b**), obtained from their corresponding DPM precursor, can be distilled at reduced pressure to afford ca. 90% pure material. NMR chemical shift comparison of various 1-alkenesulfinyl-containing compounds is made. 1-Alkenesulfinylmethyl phenyl(alkyl) ketones (**6**) can be prepared directly from sulfinyl chlorides **2** although decomposition and/or isomerization is sometimes extensive during purification.

Introduction

In the broad area of organosulfur chemistry, sulfinyl chlorides (**1**)[1] serve as a key starting point in numerous synthetic schemes. Sulfinyl chlorides are employed directly in the preparation of sulfoxides,[1,2] sulfines,[3] and a number of sulfinic acid derivatives.[1,4] They are also the ultimate starting position in the preparation of optically pure sulfoxides[5] and sulfinimines[6] by way of homochiral sulfinic acid esters[7] and/or amide derivatives.[8,9]

The types of sulfoxides or other species accessible through sulfinyl chloride chemistry is nevertheless limited by the number and substitution pattern of available sulfinyl chlorides. Numerous methods are available for the synthesis of arene-, alkane-, and haloalkanesulfinyl chlorides.[1,10] However, the first examples of 1-alkenesulfinyl chlorides (**2**) were only recently reported in communication form.[11] It was shown that the sulfuryl chloride treatment of diphenylmethyl or *p*-methoxybenzyl 1-alkenyl sulfoxides led to cleavage of the *S*-benzyl bond and hence generation of the sulfinic acid chloride. In this paper, we provide full details of the approach adopted for the first synthesis of 1-alkenesulfinyl chlorides.



1 **2**

Results and Discussion

Synthetic Strategy. A number of groups have been pursuing the oxidation of sulfides or sulfoxides bearing sacrificial functionality (R′) which is lost in the reaction to afford a sulfur acid derivative, as shown in eq 1. R′ may be a functional group such as *t*-Bu,[12] benzyl,[13] 2-trimethylsilylethyl,[14] or phthalimidomethyl,[15] each of which has the inherent ability to stabilize positive charge at the carbon attached to the sulfur. Under those circumstances, oxidation using a positive chlorine source

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(11) Schwan, A. L.; Kalin, M. L.; Vajda, K. E.; Xiang, T.-J.; Brillon, D. *Tetrahedron Lett.* **1996**, *37*, 2345.

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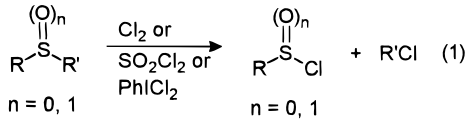
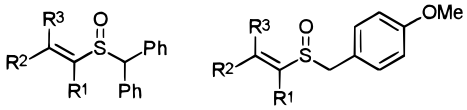
will result in scission of the S−C bond between the sulfur and R′. α-Oxidation of the R or R′ group is usually observed when neither group has a propensity for cleavage.

The approach outlined (eq 1, R = alkenyl) seemed attractive for the preparation of 1-alkenesulfinyl chlorides. It was viewed as a strategy that would differ from most other sulfinyl chloride preparations, which typically entail oxidation of thiols, thiolacetates, or disulfides.[1,10] Attempted syntheses of 1-alkenesulfinyl chlorides through the protocol of chlorine oxidation of divinyl disulfides or 1-alkenyl thiolacetates is suspected to be highly problematic: the electrophilic chlorine reagents would likely prefer to attack the nucleophilic double bond(s).



Our efforts commenced with the attempted oxidative fragmentation of 1-alkenyl 2-trimethylsilylethyl sulfoxides, which proved useful only in specialized instances.[11] Trityl and 1-phenyl-2-trimethylsilylethyl 1-alkenyl sulfoxides were found to be too labile for isolation. *tert*-Butyl 1-alkenyl sulfoxides did not undergo fragmentation but instead provided somewhat confusing, irreproducible chemistry that seemed to involve reversible dichlorination of the double bond. Benzyl 1-alkenyl sulfoxides were also unsatisfactory. The most promising candidates were diphenylmethyl (DPM) and *p*-methoxybenzyl (PMB). Hence a synthetic procedure for diphenylmethyl and *p*-methoxybenzyl 1-alkenyl sulfoxides (**3** and **4**, respectively) was required.

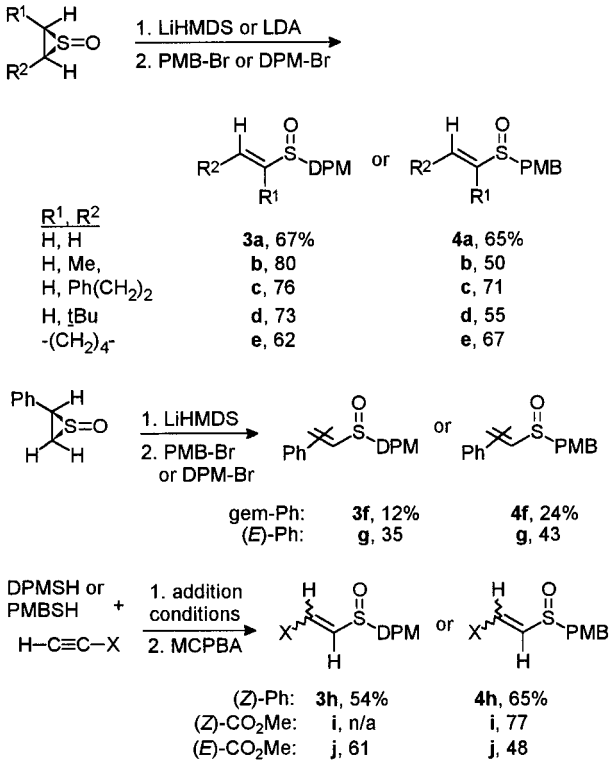


3 **4**

Preparation of Starting Materials. A method previously demonstrated for the preparation of geometrically pure benzylic vinyl sulfoxides was utilized.[16] Thus the LiHMDS-mediated regioselective deprotonation and consequent stereoselective ring opening of *anti*-thiirane *S*-oxides generate (*E*)-1-alkenesulfenate anions in solution, and these species were captured in separate experiments with diphenylmethyl bromide (DPM-Br) and *p*-methoxybenzyl bromide (PMB-Br). Yields are indicated in Scheme 1. Sulfoxides **3a** and **4a** can also be prepared by the sequence commencing with acid-induced reaction of 2-mercaptoethanol and DPM and PMB alcohols, respectively. The resulting 2-hydroxyethyl DPM and PMB sulfides were oxidized to the sulfoxide with *m*-CPBA. Mesylation and elimination steps complete this alternative synthesis.

Phenyl-substituted sulfoxides **3f**,**g** and **4f**,**g** were both prepared from the identical reaction on phenylthiirane *S*-oxide. The other sulfoxides were prepared by the addition of a thiol to an alkyne. Reworking the experimental conditions[17,18] provided *Z*-phenyl-substituted substrates, while both *E*- and *Z*-carbomethoxy analogues could also be accessed.[19] Full experimental procedures for the preparation of these sulfoxides can be found in the Supporting Information.

Scheme 1



Fragmentation Reactions and Sulfinyl Chlorides. Preliminary studies to determine the appropriate fragmentation groups did not indicate which of the DPM or PMB sulfoxides was preferred for sulfinyl chloride synthesis. Hence both groups were employed in parallel experiments. Each of the sulfoxides was subjected to conditions previously determined to be ideal for the fragmentation of alkyl/aryl 2-trimethylsilylethyl sulfoxides: 1.2 equiv of SO_2Cl_2, −78 °C to rt.[14] As the mixture warmed to r.t., TLC indicated consumption of sulfoxide and appearance of a new more polar constituent, which moves and then stalls on the TLC plate. The evidence is consistent with sulfinyl chloride formation, but the subsequent isolation procedure was not readily obvious. Simple concentration and distillation was not a general solution due to the anticipated explosive character of the sulfinyl chlorides, particularly the nonvolatile congeners. It was decided to capture each acid chloride with an alcohol (Scheme 2). The resulting 1-alkenesulfinate esters could then be fully characterized.

Partial characterization of the 1-alkenesulfinyl chlorides was carried out through solution cell IR spectroscopy of an aliquot removed from the reaction mixtures. This approach provided diagnostic S=O stretches for the acid chlorides, regardless of the starting sulfoxide. The values are consistent with expectations as predetermined by the stretching frequencies of typical sulfinyl chlo-

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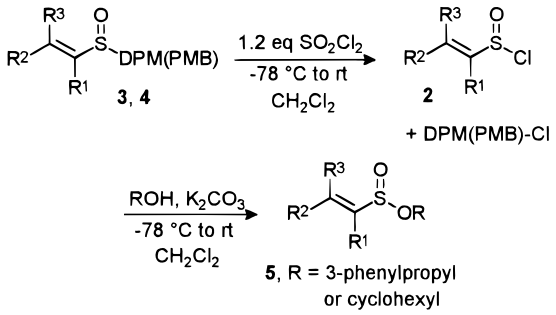
(18) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756.

(19) The preparation of DPM sulfoxide **3i** was particularly troublesome and unreliable. Hence only the PMB system **4i** could be obtained and converted to sulfinyl chloride. Full experimental details for all the starting material preparations can be found in the Supporting Information.

Scheme 2



rides.[20] The C=C stretches of compounds **2** were very weak and could not be confidently assigned.[21]

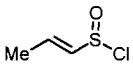
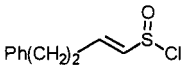
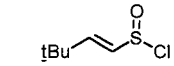
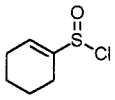
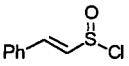
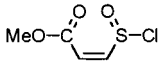
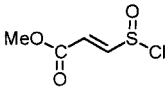
3-Phenylpropanol and cyclohexanol were chosen as appropriate alcohols for capture of the 1-alkenesulfinyl chlorides.[22] To effect the capture, the alcohol was added along with excess K_2CO_3. Flash chromatography of the mixture provided material that remained contaminated with either *p*-methoxybenzyl or diphenylmethyl alcohol, depending on the starting sulfoxide. It was concluded that some hydrolysis of the coproduct PMB (or DPM) chloride was occurring prior to or more likely during flash chromatography. That separation process transformed the nonpolar chlorides into the corresponding alcohol, a species more polar than the sulfinates and hence the sulfinates were regularly contaminated with 2−10% alcohol. A second flash chromatography treatment was usually required to afford analytically pure material in the yields indicated in the Table 1.[23] The structure of the sulfinates was confirmed through full spectroscopic analysis.

Overall, the PMB sulfoxides are the preferred source of 1-alkenesulfinate esters, based both on consistent yield of sulfinate recovered and ease of purification of those sulfinates.[24] Each sulfoxide was able to produce 1-alkenesulfinyl chloride with no evidence of double bond isomerization. Of the DPM sulfoxides that gave comparatively low yields of ester (**2f**, **2h**), it would appear that the greater steric size of the DPM group may responsible for the less efficient fragmentation reaction. Indeed the *preparation* of DPM sulfoxide **3i** was troublesome.[19] On the down side, the synthesis of the (*E*)-1-alkenyl PMB sulfoxides (**4**) from thiirane *S*-oxides is less efficient than the preparation of the corresponding DPM sulfoxides (**3**). Hence both methods have their strengths and drawbacks.

The sulfinates in general are stable indefinitely at −20 °C. The lone exception is **5i** which could be purified and partially characterized but proved to be a sensitive compound and decomposed within a few days at room temperature. Notwithstanding our difficulties with alcohol choice,[22] the capture of **2i** was effected with ethanol (34% yield) and the resulting sulfinate (**5ii**) is stable indefinitely if rigorously purified. Many of the sulfinates decompose slowly in $CDCl_3$ if that solvent has not been pretreated for its mildly acidic nature.

Attempts were made to isolate some of the lower molecular weight sulfinyl chlorides. Thus, larger scale fragmentations were performed on **3a** and **3b**. After removal of most of the solvent under reduced pressure, the mixtures were exposed to flash distillation conditions.

Table 1. Conversion of Sulfoxides to 1-Alkenesulfinates by way of 1-Alkenesulfinyl Chlorides.

#	starting sulfoxide	sulfinyl chloride		S=O stretch (cm^{-1})	yield of sulfinate **5** (%)[a]
1	**3a**		**2a**	1148	65
2	**4a**			1148	65
3	**3b**		**2b**	1145	78
4	**4b**			1146	76
5	**3c**		**2c**	1148	69
6	**4c**			1149	62
7	**3d**		**2d**	1147	78
8	**4d**			1144	68
9	**3e**		**2e**	1144	83
10	**4e**			1144	62
11	**3f**		**2f**	1151	42
12	**4f**			1152	69
13	**3g**		**2g**	1145	75
14	**4g**			1149	69
15	**3h**		**2h**	1130	56
16	**4h**			1129	65
17	**4i**		**2i**	1159	48
18	**4i**[b]				34[b]
19	**3j**		**2j**	1164	37
20	**4j**			1161	73

[a] Yield of doubly chromatographed material. [b] Yield of product (**5ii**) when EtOH was employed for the esterification.

(20) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: New York, 1983; p I225.

(21) Peaks near 1610 cm^{-1} originally attributed to 1-alkenesulfinyl chloride (ref 11) have since been determined to arise from PMB-Cl.

(22) The choice of alcohol was initially thought to be trivial. It was soon learned that the sulfinates are rather volatile and the use of an alcohol with substantial molecular weight would be beneficial. Further, an alcohol possessing an aromatic group would provide a strong chromophore enabling UV-visualization during TLC analysis of reaction mixtures and chromatography fractions. Benzyl alcohol seemed like the logical choice until the products were found to be unstable. Specifically, the characteristic AB quartet of the geminal benzylic hydrogens would revert to a singlet upon standing over a few days in an NMR solvent. The literature indicated that isomerization to sulfone via ionic O−C fragmentation and S−C recombination was likely occurring. The process would be most prevalent when the alcoholic carbon was benzylic or tertiary. The choice of 3-phenylpropanol meets our demands and lacks the shortcomings of other alcohols. In other related studies, we observed occasional Michael addition of 3-phenylpropanol to compounds similar to **2j**. With such substrates that contain a particularly electrophilic double bond, cyclohexanol was employed so that addition to the double bond is retarded by the increased hindrance of the 2° alcoholic carbon.

(23) Difficulties in the purification of a sulfinate ester prepared through the fragmentation of a PMB sulfoxide have been encountered previously. See ref 12a.

(24) Other oxidative conditions were employed in an effort to increase the yield of the sulfoxide to sulfinate conversion. However, use of excess SO_2Cl_2 gave lower yields, as did NCS or NBS in the presence of the alcohol. The use of trimethylsilyl-protected alcohols in place of the alcohol/base combination (see ref 4b) did provide sulfinate esters **5**, but the purification was more difficult and the yields were lower.

Table 2. ^{1}H and ^{13}C NMR Data for Selected Sulfinyl Compounds

	vinyl resonances[a,b]			
	^{1}H NMR (ppm)		^{13}C NMR (ppm)	
compd	α to S=O	β to S=O	α to S=O	β to S=O
3a	6.37 (dd)	6.01 (d) 5.81 (d)	139.7	122.5
2a	7.24 (dd)	6.31 (d) 6.12 (d)	146.8	128.5
5a	6.64 (dd)	6.13 (d) 5.99 (d)	142.8	124.8
ethene[c]	5.25		123.3	
MVK[c]	5.85	6.40 (*E*-H)	138.3	129.1
3b	5.99 (d)	6.31 (dq)	132.3	137.1
2b	6.91 (d)	6.72 (dq)	140.9, 138.3	
5b	6.31 (d)	6.54 (dq)	136.5	138.5
propene	4.96[d]	5.73[d]	114.7[e]	135.0[e]

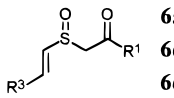
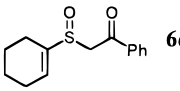
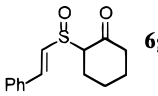
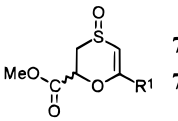
[a] Assignments of some hydrogen and carbons were made with the assistance of DEPT and HETCOR acquisitions. [b] No solvent was provided for the literature chemical shifts, except where indicated. [c] From ref 25a. [d] From ref 25b. [e] Acquired in CS_2; from ref 25c.

Sulfinyl chlorides **2a** and **2b** with >90% purity could be realized, and spectroscopic data (^{1}H and ^{13}C NMR, IR) were acquired. The identity of the distillation products was confirmed by adding base and 3-phenylpropyl alcohol to the NMR sample. The formation of the sulfinate ester therein and IR spectroscopy confirmed that sulfinyl chloride rather than sulfonyl chloride had distilled. The distillation of **2a** from the fragmentation of **4a** was attempted on two occasions, and the contents of the distillation pot decomposed before any sulfinyl chloride could be distilled.

The availability of NMR data of **2a** and **2b** provided an opportunity to glean some information pertaining to the electronic properties of the sulfinyl chloride moiety. Table 2 lists a series of ^{1}H and ^{13}C NMR data for related sulfoxides, sulfinyl chlorides, 1-alkenesulfinate esters, and model compounds.[25] Clearly the sulfinyl chloride is the most electron withdrawing of the three sulfinyl-containing groups, as both α-carbons and hydrogens on those α-carbons were shifted the farthest downfield in compounds **2a** and **2b**. Whereas the chemical shift of β-carbons of simples enones are downfield compared to the α-carbons, as exemplified by MVK, the trend is the opposite for sulfinyl groups. Indeed, in all sulfinyl compounds possessing the simple vinyl group, the relative chemical shifts of the α- and β-carbons and the hydrogens on them reaffirm that the net electron withdrawing effect of sulfinyl-containing functionalities is dominated by induction rather than by resonance.[26] These data clearly demonstrate the additional electron-withdrawing strength of the chloride over that of the ester oxygen of **5** and the carbon of sulfoxides **3**.

Carbon Capture of 1-Alkenesulfinyl Chlorides 2. β-Keto sulfoxides have varied uses in organic synthesis. For instance, they have been employed in the synthesis of oxirane-2-carboxamides,[27] for the formation of highly substituted 4*H*-pyrans through Michael addition chemistry,[28] and a number of other asymmetric and achiral transformations.[29] A survey of the literature revealed no examples of β-keto sulfoxides holding simple 1-alkenyl groups on the sulfur. We took the opportunity to probe the utility of these alkenesulfinyl chlorides for the preparation of such compounds, adopting methodology from the reactions of methane- and benzenesulfinyl chlorides with TMS enol ethers.[2c]

Table 3. Preparation of 1-Alkenylsulfinylmethyl Ketones (6)

S.M.	R^1, R^2 of 	Products (% yields)[a]
4a	Ph, H	 **6a**, R^3 = H (59)
3d	Ph, H	**6d**, R^3 = t-Bu (72)
3d	Me, H	**6dd**, R^3 = t-Bu (17)
3e	Ph, H	 **6e** (41)
3g	-$(CH_2)_4$-	 **6g** (35)
4j	Ph, H	 **7j** (49)[b]
4j	Me, H	**7jj** (12)[b]

[a] Yield was calculated from starting sulfoxide. [b] Compounds **6j** and **6jj** could be observed in the ^{1}H NMR of the crude reaction mixture, but cyclic isomers **7** were obtained after chromatography.

A number of fragmentations were carried out using DPM and PMB sulfoxides, and one-pot sulfoxide formation could be effected with or without Lewis acid catalyst.[30] Isolation proved difficult in virtually all cases, as the products demonstrated some instability during purification. Hence, rapid chromatography was performed on neutral alumina to minimize decomposition yet allow recovery of some pure β-keto sulfoxide **6**. The best yields were obtained when α-styryl trimethylsilyl ether was employed, while 1-cyclohexenyl trimethylsilyl ether proved less useful. Only in one instance was pure product obtained using propenyl trimethylsilyl ether; this nucleophile was found to be very sluggish for the reaction at hand. Moreover, once compounds **6** derived from propenyl trimethylsilyl ether were formed in the reaction, they were particularly predisposed to decomposition during isolation. 1-Cyclohexenesulfinyl chloride (**2e**) demonstrated reduced responsiveness to the method. Table 3 shows some representative results. There was no evidence that DPM-Cl or PMB-Cl underwent a reaction with the silyl enol ethers.

In the attempted synthesis of the β-keto sulfoxides through reactions of **2j** with two trimethylsilyl ethers,

(25) (a) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw-Hill: London, 1995; pp 72−73. (b) Sohár, P. *Nuclear Magnetic Resonance Spectroscopy, Vol. III*; CRC Press: Boca Raton, 1983; p 51. (c) Savitzky, G. B.; Ellis, P. O.; Namikawa, K.; Maciel, G. E. *J. Chem. Phys.* **1968**, *49*, 2395.

(26) Sheppard, W. A.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 1919.

(27) García Ruano, J. L.; Martín Castro, A. M.; Rodríguez Ramos, J. H.; Rubio Flamarique, A. C. *Tetrahedron: Asymmetry* **1997**, *8*, 3503.

(28) Marco, J. L. *J. Org. Chem.* **1997**, *62*, 6575.

(29) (a) Nokami, J.; Osafune, M.; Shiraishi, K.; Sumida, S.-i.; Imai, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2947. (b) Solladie, G.; Carreño, M. C. *in Organosulfur Chemistry: Synthetic Aspects*; Page, P., Ed.; Academic Press: Toronto, 1995; Chapter 1.

(30) Catalytic $TiCl_4$ was found to be the most effective reagent. Other Lewis acids or greater quantities were less effective and decomposed the substrate. The use of F^- provided product but in reduced yield. In the case of **6g**, the use of K_2CO_3 as the only additive proved to be the most efficient.

decomposition was again substantial. Close monitoring of the reaction allowed ^{1}H NMR detection of β-keto sulfoxides **6j** and **6jj**, but chromatography induced the formation of a rearranged product, whose spectral data were consistent with structures **7**. Characteristic data included an ABX pattern in the ^{1}H NMR spectra and the absence of a ketone stretching frequency in the IR spectra. 1,4-Oxathiin *S*-oxides **7** are presumably formed through enol or enolate addition to the highly electrophilic Michael acceptor portion of the molecule. Hence, it is possible the decomposition problems encountered herein have their origin in the tendency of the β-keto sulfoxides to readily enolize. Acidity of hydrogens between two strong electron withdrawing groups is well-documented.

Conclusions

The first preparation of 1-alkenesulfinyl chlorides is achieved through the oxidative fragmentation of diphenylmethyl or *p*-methoxybenzyl alkenyl sulfoxides. Low molecular weight sulfinyl chlorides from DPM sulfoxides can be distilled and characterized with IR and NMR, while the S=O stretch of all sulfinyl chlorides could be assigned by IR. Full characterization can be achieved through reaction with an alcohol in the presence of base. The resulting sulfinate esters could be purified, and their structure provided trustworthy, though indirect, evidence for the structure of the proposed sulfinyl chlorides. β-Keto sulfoxides derived from the sulfinyl chlorides were difficult to purify and seem to demonstrate a propensity to enolize.

Functionalization of 1-alkenesulfinyl chlorides represents a new direction for the organic chemistry of sulfur acids, and we are currently pursuing optically active sulfinate esters and functionalization reactions of the double bond of various 1-alkenesulfinic acid derivatives.

Experimental Section

General. Melting points are uncorrected. Infrared (IR) spectra were obtained either neat or in a solution cell (CH_2Cl_2 or $CDCl_3$). NMR spectra for ^{1}H and ^{13}C were recorded at 400 and 100.6 MHz, respectively, in $CDCl_3$. Mass spectra (MS) were obtained using chemical ionization and electron impact techniques. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl before use. Methylene chloride and toluene were distilled from calcium hydride. Air and water sensitive reagents were transferred via oven-dried nitrogen-purged syringes. Analytical thin-layer chromatography (TLC) was performed using 0.25 mm Merck Kieselgel 60 F_{254} precoated silica gel plates. Analytical GC was performed on a Varian 3400 capillary gas chromatograph. Sulfuryl chloride was purchased from Aldrich as a 1.0 M solution in CH_2Cl_2. Older solutions were discarded before complete consumption of their contents. *m*-CPBA was obtained from Acros. Elemental analyses were performed by MHW Labs of Phoenix, AZ. The procedures for the preparation of sulfoxides **3** and **4** are part of the Supporting Information.

Fragmentation Reactions of Alkenyl Sulfoxides 3 and 4. General Method for Synthesis of 1-Alkenesulfinates 5 via Fragmentation Chemistry. To a solution of sulfoxide (1.0 equiv) in dry CH_2Cl_2 (15 mL) at −78 °C was added SO_2Cl_2 (usually 1.1−1.5 equiv, as 1 M solution in CH_2Cl_2) via syringe. The mixture was stirred for 10 min and allowed to warm to room temperature over 30 min, and a sample (500−900 μL) was taken for IR analysis. Upon cooling to −78 °C, the alcohol (0.7−1.0 equiv) was added via a syringe immediately followed by addition of K_2CO_3 (5.0 equiv). Stirring continued for another 10 min, followed by warming to room temperature over the next 3 h. Filtration through Celite and concentration under reduced pressure (aspirator) provided crude product. Two consecutive flash chromatography columns on silica gel (unless otherwise noted) with EtOAc and hexanes as eluent afforded the pure alkenesulfinate.

Synthesis of 3-Phenylpropyl Ethenesulfinate 5a from DPM Ethenyl Sulfoxide 3a. The reaction of sulfoxide **3a** (183 mg, 0.753 mmol) with SO_2Cl_2 (904 μL, 0.904 mmol) yielded sulfinyl chloride **2a**. IR (CH_2Cl_2), cm^{-1}: 1338, 1148. Addition of 3-phenylpropanol (103 mg, 0.753 mmol) and K_2CO_3 (520 mg, 3.77 mmol) afforded sulfinate **5a** (103 mg, 65%) as an oil after chromatography (10% EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 7.24 (m, 5H), 6.64 (dd, J = 9.9 and 16.9 Hz, 1H), 6.13 (d, J = 16.9 Hz, 1H), 5.99 (d, J = 9.9 Hz, 1H), 3.99 (t of ABq, J = 6.3 and 9.9 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 2.01 (m, 2H). ^{13}C NMR (100.6 MHz), δ: 142.8, 140.9, 128.4 (2 C's), 126.0, 124.8, 65.2, 31.8, 31.4. Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. Found: C, 62.72; H, 6.56.

Synthesis of 3-Phenylpropyl Ethenesulfinate (5a) from PMB Ethenyl Sulfoxide (4a). The reaction of sulfoxide **4a** (179 mg, 0.911 mmol) with SO_2Cl_2 (1.09 mL, 1.09 mmol) yielded sulfinyl chloride **2a**, IR (CH_2Cl_2), cm^{-1}: 1338, 1148. Addition of 3-phenylpropanol (124 mg, 0.911 mmol) and K_2CO_3 (630 mg, 4.56 mmol) afforded sulfinate **5a** (125 mg, 65%) as an oil after chromatography (10% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl (*E*)-1-Propenesulfinate (5b) from DPM (*E*)-1-Propenyl Sulfoxide (3b). The reaction of sulfoxide **3b** (289 mg, 1.13 mmol) with SO_2Cl_2 (1.35 mL, 1.35 mmol) yielded sulfinyl chloride **2b**. IR (CH_2Cl_2), cm^{-1}: 1450, 1338, 1145. Addition of 3-phenylpropanol (153 mg, 1.13 mmol) and K_2CO_3 (778 mg, 5.63 mmol) afforded sulfinate **5b** (197 mg, 78%) as an oil after chromatography (10% EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 7.24 (m, 5H), 6.54 (dq, J = 6.8 and 15.6 Hz, 1H), 6.31 (d, J = 15.6 Hz, 1H), 3.98 (t of ABq, J = 6.4 and 10.1 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 2.01 (m, 2H), 1.93 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100.6 MHz), δ: 141.0, 138.5, 136.5, 128.4 (2 C's), 126.0, 65.0, 31.8, 31.5, 17.5. Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19. Found: C, 64.44; H, 7.40.

Synthesis of 3-Phenylpropyl (*E*)-1-Propenesulfinate (5b) from PMB (*E*)-1-Propenyl Sulfoxide (4b). The reaction of sulfoxide **4b** (158 mg, 0.751 mmol) with SO_2Cl_2 (902 μL, 0.902 mmol) yielded sulfinyl chloride **2b**. IR (CH_2Cl_2), cm^{-1}: 1338, 1146. Addition of 3-phenylpropanol (102 mg, 0.751 mmol) and K_2CO_3 (519 mg, 3.76 mmol) afforded sulfinate **5b** (128 mg, 76%) as an oil after chromatography (10% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl (*E*)-4-Phenyl-1-butenesulfinate (5c) from DPM (*E*)-4-Phenyl-1-butenyl Sulfoxide (3c). The reaction mixture of sulfoxide **3c** (116 mg, 0.335 mmol) with SO_2Cl_2 (502 μL, 0.502 mmol) yielded sulfinyl chloride **2c**. IR (CH_2Cl_2), cm^{-1}: 1338, 1148, 1031. Addition of 3-phenylpropanol (45.6 mg, 0.335 mmol) and K_2CO_3 (231 mg, 1.67 mmol) afforded sulfinate **5c** (72.6 mg, 69%) as an oil after chromatography (10% EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 7.23 (m, 10H), 6.56 (dt, J = 6.7 and 15.6 Hz, 1H), 6.26 (dt, J = 1.5 and 15.6 Hz, 1H), 3.88 (t of ABq, J = 6.4 and 10.1 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.7 Hz, 2H), 2.58 (br q, J = ca. 7.1 Hz, 2H), 1.97 (m, 2H). ^{13}C NMR (100.6 MHz), δ: 142.0, 141.1, 140.4, 135.6, 128.5, 128.4 (2 C's), 128.3, 126.3, 122.0, 64.7, 34.2, 33.3, 31.9, 31.4. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 71.49; H, 7.33. Found: C, 71.68; H, 7.31.

Synthesis of 3-Phenylpropyl (*E*)-4-Phenyl-1-butenesulfinate (5c) from PMB (*E*)-4-Phenyl-1-butenyl Sulfoxide (4c). The reaction mixture of sulfoxide **4c** (168 mg, 0.558 mmol) with SO_2Cl_2 (669 μL, 0.669 mmol) yielded sulfinyl chloride **2c**. IR (CH_2Cl_2), cm^{-1}: 1338, 1149, 1033. Addition of 3-phenylpropanol (75.9 mg, 0.558 mmol). and K_2CO_3 (385 mg, 2.79 mmol) afforded sulfinate **5c** (109 mg, 62%) as an oil after chromatography (10% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl (*E*)-3,3-dimethyl-1-butenesulfinate (5d) from DPM (*E*)-(3,3-Dimethyl-1-butenyl) Sulfoxide (3d). The reaction mixture of sulfoxide **3d** (196 mg, 0.656 mmol) with SO_2Cl_2 (787 μL, 0.787 mmol)

yielded sulfinyl chloride **2d**. IR (CH_2Cl_2), cm^{-1}: 1338, 1147. Addition of 3-phenylpropanol (89.3 mg, 0.656 mmol) and K_2CO_3 (453 mg, 3.28 mmol) afforded sulfinate **5d** (136 mg, 78%) as an oil after chromatography (7% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.24 (m, 5H), 6.51 (d, $J = 15.6$ Hz, 1H), 6.17 (d, $J = 15.6$ Hz, 1H), 3.98 (t of ABq, $J = 6.4$ & 10.1 Hz, 2H), 2.72 (t, $J = 7.6$ Hz, 2H), 2.02 (m, 2H), 1.10 (s, 9H); ^{13}C NMR (100.6 MHz), δ: 153.0, 141.0, 131.0, 128.4 (2 C's), 126.0, 64.9, 34.0, 31.9, 31.5, 28.7; Anal. Calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32. Found: C, 67.51; H, 8.08.

Synthesis of 3-Phenylpropyl (*E*)-3,3-Dimethyl-1-butenesulfinate (5d) from PMB (*E*)-(3,3-Dimethyl-1-butenyl) Sulfoxide (4d). The reaction mixture of sulfoxide **4d** (200 mg, 0.792 mmol) with SO_2Cl_2 (950 μL, 0.950 mmol) yielded sulfinyl chloride **2d**. IR (CH_2Cl_2), cm^{-1}: 3052, 2967, 1338, 1144, 1033. Addition of 3-phenylpropanol (108 mg, 0.792 mmol) and K_2CO_3 (547 mg, 3.96 mmol) afforded sulfinate **5d** (143 mg, 68%) as an oil after chromatography (7% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl 1-Cyclohexenesulfinate (5e) from DPM 1-Cyclohexenyl Sulfoxide (3e). The reaction mixture of sulfoxide **3e** (161 mg, 0.542 mmol) with SO_2Cl_2 (651 μL, 0.651 mmol) yielded sulfinyl chloride **2e**. IR (CH_2Cl_2), cm^{-1}: 1451, 1338, 1144. Addition of 3-phenylpropanol (73.8 mg, 0.542 mmol) and K_2CO_3 (375 mg, 2.71 mmol) afforded sulfinate **5e** (119 mg, 83%) as an oil after chromatography (7% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.24 (m, 5H), 6.51 (m, 1H), 3.94 (t of ABq, $J = 6.4$ & 10.1 Hz, 2H), 2.71 (t, $J = 7.7$ Hz, 2H), 2.27 (m, 4H), 2.01 (m, 2H), 1.70 (m, 4H); ^{13}C NMR (100.6 MHz), δ: 144.6, 141.0, 133.8, 128.4 (2 C's), 126.0, 65.3, 31.9, 31.5, 25.2, 21.8, 21.7, 20.3. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.15; H, 7.62. Found: C, 67.97; H, 7.78.

Synthesis of 3-Phenylpropyl 1-cyclohexenesulfinate (5e) from PMB 1-Cyclohexenyl Sulfoxide (4e). The reaction mixture of sulfoxide **4e** (150 mg, 0.597 mmol) with SO_2Cl_2 (717 μL, 0.717 mmol) yielded sulfinyl chloride **2e**. IR (CH_2Cl_2), cm^{-1}: 1338, 1249, 1144, 1034. Addition of 3-phenylpropanol (81.3 mg, 0.597 mmol) and K_2CO_3 (413 mg, 2.99 mmol) afforded sulfinate **5e** (97.9 mg, 62%) as an oil after chromatography (7% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl 1-Phenylethenesulfinate (5f) from DPM 1-Phenylethenyl Sulfoxide (3f). The reaction mixture of sulfoxide **3f** (150 mg, 0.471 mmol) with SO_2Cl_2 (565 μL, 0.565 mmol) yielded sulfinyl chloride **2f**. IR (CH_2Cl_2), cm^{-1}: 1452, 1338, 1216, 1151. Addition of 3-phenylpropanol (64.2 mg, 0.471 mmol) and K_2CO_3 (326 mg, 2.36 mmol) afforded sulfinate **5f** (56.7 mg, 42%) as an oil after chromatography (5% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.24 (m, 10H), 6.17 (s, 1H), 6.05 (s, 1H), 3.87 (t of ABq, $J = 6.3$ & 10.1 Hz, 2H), 2.51 (t, $J = 7.7$ Hz, 2H), 1.85 (m, 2H). ^{13}C NMR (100.6 MHz), δ: 140.9, 133.6, 129.1, 128.8, 128.4, 128.4 (2 C's), 126.9, 125.9, 119.8, 64.3, 31.7, 31.2. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.53; H, 6.19.

Synthesis of 3-Phenylpropyl 1-Phenylethenesulfinate (5f) from PMB 1-Phenylethenyl Sulfoxide (4f). The reaction mixture of sulfoxide **4f** (150 mg, 0.551 mmol) with SO_2Cl_2 (826 μL, 0.826 mmol) yielded sulfinyl chloride **2f**. IR (CH_2Cl_2), cm^{-1}: 1338, 1152. Addition of 3-phenylpropanol (75.0 mg, 0.551 mmol) and K_2CO_3 (381 mg, 2.75 mmol) afforded sulfinate **5f** (109 mg, 69%) as an oil after chromatography (5% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl (*E*)-2-Phenylethenesulfinate (5g) from DPM (*E*)-2-Phenylethenyl Sulfoxide (3g). The reaction mixture of sulfoxide **3g** (186 mg, 0.584 mmol) with SO_2Cl_2 (701 μL, 0.701 mmol) yielded sulfinyl chloride **2g**. IR (CH_2Cl_2), cm^{-1}: 3055, 1338, 1145. Addition of 3-phenylpropanol (79.6 mg, 0.584 mmol) and K_2CO_3 (404 mg, 2.92 mmol) afforded sulfinate **5g** (126 mg, 75%) as an oil after chromatography (10% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.34 (m, 10H), 7.29 (d, $J = 15.9$ Hz, 1H), 6.86 (d, $J = 15.9$ Hz, 1H), 4.04 (t of ABq, $J = 6.4$ & 9.9 Hz, 2H), 2.73 (t, $J = 7.6$ Hz, 2H), 2.04 (m, 2H). ^{13}C NMR (100.6 MHz), δ: 140.9, 139.3, 133.2, 132.5, 130.3, 129.0, 128.4 (2 C's), 128.1, 126.0, 64.9, 31.9, 31.5. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.16; H, 6.24.

Synthesis of 3-Phenylpropyl (*E*)-2-Phenylethenesulfinate (5g) from PMB (*E*)-2-Phenylethenyl Sulfoxide (3g). The reaction mixture of sulfoxide **3g** (174 mg, 0.640 mmol) with SO_2Cl_2 (768 μL, 0.768 mmol) yielded sulfinyl chloride **2g**. IR (CH_2Cl_2), cm^{-1}: 3054, 1338, 1176, 1149. Addition of 3-phenylpropanol (87.1 mg, 0.640 mmol) and K_2CO_3 (442 mg, 3.20 mmol) afforded sulfinate **5g** (126 mg, 69%) as an oil after chromatography (10% EtOAc/hexanes).

Synthesis of 3-Phenylpropyl (*Z*)-2-Phenylethenesulfinate (5h) from DPM (*Z*)-2-Phenylethenyl Sulfoxide (3h). The reaction mixture of sulfoxide **3h** (195 mg, 0.611 mmol) with SO_2Cl_2 (733 μL, 0.733 mmol) yielded sulfinyl chloride **2h**. IR (CH_2Cl_2), cm^{-1}: 1338, 1130. Addition of 3-phenylpropanol (83.2 mg, 0.611 mmol) and K_2CO_3 (422 mg, 3.05 mmol) afforded sulfinate **5h** (97.5 mg, 56%) as an oil after chromatography (10% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.27 (m, 10H), 7.10 (d, $J = 11.2$ Hz, 1H), 6.45 (d, $J = 11.2$ Hz, 1H), 4.09 (t of ABq, $J = 6.4$ & 9.9 Hz, 2H), 2.71 (t, $J = 7.7$ Hz, 2H), 2.04 (m, 2H). ^{13}C NMR (100.6 MHz), δ: 140.9, 138.6, 138.4, 133.7, 129.6, 129.5, 128.6, 128.4 (2 C's), 126.0, 65.7, 31.8, 31.5. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.46; H, 6.47.

Synthesis of 3-Phenylpropyl (*Z*)-2-Phenylethenesulfinate (5h) from PMB (*Z*)-2-Phenylethenyl Sulfoxide (4h). The reaction mixture of sulfoxide **4h** (116 mg, 0.426 mmol) with SO_2Cl_2 (511 μL, 0.511 mmol) yielded sulfinyl chloride **2h**. IR (CH_2Cl_2), cm^{-1}: 1338, 1129, 1033. Addition of 3-phenylpropanol (58.0 mg, 0.426 mmol) and K_2CO_3 (294 mg, 2.13 mmol) afforded sulfinate **5h** (79.3 mg, 65%) as an oil after chromatography (10% EtOAc/hexanes).

Synthesis of Cyclohexyl (*Z*)-2-Carbomethoxyethenesulfinate (5i) from PMB (*Z*)-2-Carbomethoxyethenyl Sulfoxide (4i). The reaction of sulfoxide **4i** (201 mg, 0.791 mmol) with SO_2Cl_2 (870 μL, 0.870 mmol) yielded sulfinyl chloride **2i**. IR (CH_2Cl_2), cm^{-1}: 1724, 1339, 1227, 1159, 1133. Addition of cyclohexanol (79.2 mg, 0.791 mmol) and K_2CO_3 (328 mg, 2.37 mmol) afforded sulfinate **5i** (89 mg, 48%) as an unstable oil after chromatography (10% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 6.80 (d, $J = 10.7$ Hz, 1H), 6.29 (d, $J = 10.7$ Hz, 1H), 4.35 (m, 1H), 3.82 (s, 3H), 2.00 (m, 2H), 1.82−1.21 (m, broad, 8H). ^{13}C NMR (100.6 MHz), δ: 164.1, 153.5, 124.6, 79.5, 52.4, 33.9, 33.1, 25.1, 23.7.

Synthesis of Ethyl (*Z*)-2-Carbomethoxyethenesulfinate (5ii) from PMB (*E*)-2-carbomethoxyethenyl Sulfoxide (4i). The reaction mixture of sulfoxide (0.500 g, 1.97 mmol) with SO_2Cl_2 (2.36 mL, 2.36 mmol) yielded sulfinyl chloride **2i**. After addition of absolute ethanol (91 mg, 1.97 mmol) and K_2CO_3 (1.36 g, 9.85 mmol), the solution was stirred at −50 °C for 20 h to afford sulfinate **5ii** (119 mg, 34%) as an oil after chromatography on basic alumina (10−20% EtOAc/hexanes). Kugelrohr distillation of a different sample gave bp 130 °C/0.5 Torr. ^1H NMR (400 MHz), δ: 6.84 (d, $J = 10.4$ Hz, 1H), 6.33 (d, $J = 10.4$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100.6 MHz), δ: 164.1, 153.3, 125.5, 64.7, 52.5, 15.9. Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66. Found: C, 40.57; H, 5.52.

Synthesis of Cyclohexyl (*E*)-2-Carbomethoxyethenesulfinate (5j) from DPM (*E*)-2-Carbomethoxyethenyl Sulfoxide (3j). The reaction of sulfoxide **3j** (199 mg, 0.661 mmol) with SO_2Cl_2 (793 μL, 0.793 mmol) and warming to −30 °C and stirring overnight yielded sulfinyl chloride **2j**. IR (CH_2Cl_2), cm^{-1}: 1736, 1338, 1225, 1164. Addition of cyclohexanol (66.2 mg, 0.661 mmol) and K_2CO_3 (457 mg, 3.31 mmol) afforded sulfinate **5j** (57.2 mg, 37%) as an oil after chromatography (7% EtOAc/hexanes). ^1H NMR (400 MHz), δ: 7.41 (d, $J = 15.3$ Hz, 1H), 6.58 (d, $J = 15.3$ Hz, 1H), 4.29 (m, 1H), 3.78 (s, 3H), 1.91 (m, 2H), 1.73 (m, 2H), 1.53 (m, 3H), 1.37−1.17 (m, 3H). ^{13}C NMR (100.6 MHz), δ: 164.4, 149.8, 127.9, 79.3, 52.4, 33.6, 33.4, 25., 23.7, 23.7. Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.93; H, 6.54. Found: C, 52.17; H, 6.79.

Synthesis of Cyclohexyl (*E*)-2-Carbomethoxyethenesulfinate (5j) from PMB (*E*)-2-Carbomethoxyethenyl Sulfoxide (4j). The reaction of sulfoxide **4j** (332 mg, 1.31 mmol) with SO_2Cl_2 (1.57 mL, 1.57 mmol) and warming to room temperature yielded sulfinyl chloride **2j**. IR (CH_2Cl_2), cm^{-1}:

1734, 1338, 1301, 1226, 1162, 1145. Addition of cyclohexanol (131 mg, 1.31 mmol) and K_2CO_3 (288 mg, 2.09 mmol) afforded sulfinate **5j** (222 mg, 73%) as an oil after chromatography (10% EtOAc/hexanes).

Isolation of Ethenesulfinyl Chloride (2a) from DPM Ethenyl Sulfoxide (3a). The reaction of sulfoxide **3a** (2.54 g, 10.5 mmol) with SO_2Cl_2 (12.6 mL, 12.6 mmol) afforded a mixture containing ethenesulfinyl chloride (**2a**). The bulk of the solvent was removed under reduced pressure (aspirator w/ drying tube), and distillation yielded the highly reactive ethenesulfinyl chloride **2a** (734 mg, 63%, >90%) as a light orange liquid: Bp 28−29 °C/0.35 Torr; bath temperature rt−60 °C. ^{1}H NMR (400 MHz), δ: 7.24 (dd, J = 9.8 & 16.7 Hz, 1H), 6.31 (d, J = 16.7 Hz, 1H), 6.12 (d, J = 9.8 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 146.79 (−CH), 128.49 (−CH_2). The contents of the NMR tube were then subjected to excess 3-phenylpropanol to yield 3-phenylpropyl ethenesulfinate **5a**.

Isolation of (*E*)-1-Propenesulfinyl Chloride (2b) from DPM (*E*)-2-Methylethenyl Sulfoxide (3b). The reaction of sulfoxide **3b** (2.96 g, 11.5 mmol) with SO_2Cl_2 (13.8 mL, 13.8 mmol) afforded a mixture containing (*E*)-1-propenesulfinyl chloride (**3a**). The bulk of the solvent was removed under reduced pressure (aspirator w/ drying tube), and distillation yielded the highly reactive (*E*)-1-propenesulfinyl chloride **2b** (705 mg, 49%, >95%) as a pale yellow liquid: bp 28 °C/0.70 Torr; bath temperature rt−48 °C. ^{1}H NMR (400 MHz), δ: 6.91 (d, J = 15.5 Hz, 1H), 6.72 (dq, J = 6.9 & 15.5 Hz, 1H), 2.01 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100.6 MHz), δ: 140.94, 138.29, 17.44. The contents of the NMR tube were then subjected to excess 3-phenylpropanol to yield 3-phenylpropyl (*E*)-1-propenesulfinate **5b**.

General Method for the Synthesis of β-Keto Vinyl Sulfoxides 6. A 2−3 mmol solution of sulfinyl chloride **2** was prepared in CH_2Cl_2 as described above. Upon recooling to −78 °C a solution of (trimethylsilyl) vinyl ether (1.0 equiv) in dry CH_2Cl_2 was added via syringe followed by the immediate addition of $TiCl_4$ (0.1 equiv, as 1 M solution in CH_2Cl_2). The reaction was allowed to stir at −78 °C for 30−60 min. The reaction mixture was then quenched with 1 mL of deionized water, and the mixture was warmed to rt. The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The β-keto sulfoxide product was then isolated using a short neutral alumina plug using 20−80% EtOAc/hexanes (gradient).

Ethenesulfinylmethyl Phenyl Ketone (6a). Sulfinyl chloride **2a** from ethenyl PMB sulfoxide (**4a**) (606 mg, 3.09 mmol) was treated with 1-(trimethylsiloxy)styrene (594 mg, 3.07 mmol) and $TiCl_4$ (310 μL, 0.31 mmol) to afford β-keto sulfoxide **6a** (356 mg; 59%) as a solid after a neutral alumina plug. Mp: 54−55 °C (EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 7.95 (m, 2H), 7.64 (m, 1H), 7.50 (m, 2H), 6.92 (dd, J = 9.8 & 16.5 Hz, 1H), 6.19 (d, J = 16.5 Hz, 1H), 6.01 (d, J = 9.8 Hz, 1H), 4.40 (ABq, J = 14.5 Hz, 2H). ^{13}C (100.6 MHz), δ: 191.7, 140.5, 135.8, 134.3, 128.9, 128.8, 122.4, 62.3. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.78; H, 5.15. Found: C, 61.74; H, 5.13.

3,3-Dimethyl-1-butenesulfinylmethyl Phenyl Ketone (6d). Sulfinyl chloride **2d** from 3,3-dimethylbutenyl PMB sulfoxide (**3d**) (223 mg, 0.75 mmol) was treated with 1-(trimethylsiloxy)styrene (143 mg, 0.75 mmol) and $TiCl_4$ (75 μL, 0.07 mmol) to afford β-keto sulfoxide (135 mg, 72%) as a solid after a neutral alumina plug. Mp: 59−61 °C (EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 7.96 (m, 2H), 7.62 (m, 1H), 7.51 (m, 2H), 6.45 (d, J = 15.4 Hz, 1H), 6.28 (d, J = 15.4 Hz, 1H), 4.37 (ABq, J = 13.7 Hz, 2H), 1.03 (s, 9H). ^{13}C (100.6 MHz), δ: 191.4, 151.3, 136.2, 134.2, 128.9, 128.8, 127.6, 62.4, 34.2, 28.6. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.21; H, 7.19. Found: C, 67.23; H, 7.40.

3,3-Dimethyl-1-butenesulfinylmethyl Methyl Ketone (6dd). Sulfinyl chloride **2d** from 3,3-dimethylbutenyl PMB sulfoxide (**3d**) (370 mg,1.29 mmol) was treated with 2-(trimethylsiloxy)propene (207μL,1.24 mmol) and $TiCl_4$ (124 μL, 0.12 mmol) to afford β-keto sulfoxide **6dd** (39 mg, 17%) as an oil after a neutral alumina plug. ^{1}H NMR (400 MHz), δ: 6.49 (d, J = 15.4 Hz, 1H), 6.18 (d, J = 15.4 Hz, 1H), 3.73 (ABq, J = 13.4 Hz, 2H), 2.29 (s, 3H), 1.09 (s, 9H). ^{13}C (100.6 MHz), δ: 199.5, 151.4, 127.0, 62.4, 34.2, 32.4, 28.7. Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57. Found: C, 58.00; H, 8.03

1-Cyclohexenesulfinylmethyl Phenyl Ketone (6e). Sulfinyl chloride **2e** from 3,3-dimethylbutenyl PMB sulfoxide (**3e**) (283 mg, 0.96 mmol) was treated with α-(trimethylsiloxy)-styrene (184 mg, 0.96 mmol) and $TiCl_4$ (100 μL, 0.10 mmol) to afford β-keto sulfoxide **6e** (98 mg; 41%) as a semisolid after a neutral alumina plug. ^{1}H NMR (400 MHz), δ: 7.97 (m, 2H), 7.63 (m, 1H), 7.54 (m, 2H), 6.37 (m, 1H), 4.31 (ABq, J = 13.1 Hz, 2H), 2.42 (m, 1H), 2.15 (m, 3H), 1.73 (m, 3H), 1.56 (m, 1H). ^{13}C (100.6 MHz), δ: 191.4, 140.6, 136.4, 134.0, 134.0, 128.9, 128.8, 59.9, 25.5, 22.0, 21.7, 20.3. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.74; H, 6.45. Found: C, 67.98; H, 6.65.

2-([*E*]-2-Phenylethenesulfinyl)cyclohexanone (6g). Sulfinyl chloride **2g** from 2-phenylethenyl DPM sulfoxide (**3g**) (274 mg, 0.80 mmol) was treated with 1-cylcohexenyloxytrimethylsilane (251 μL, 1.29 mmol) and K_2CO_3 (595 mg, 4.31 mmol) to afford β-keto sulfoxide **6g** (76 mg, 35%) as an oil after a neutral alumina plug. ^{1}H NMR (400 MHz), δ: 7.45 (m, 2H), 7.36 (m, 3H), 7.28 (d, J = 15.5 Hz, 1H), 7.05 (d, J = 15.5 Hz, 1H), 3.51 (dd, J = 5.9 & 10.1 Hz, 1H), 2.56−2.37 (m, 3H), 2.25−2.06 (m, 3H), 1.91−1.70 (m, 2H). ^{13}C (100.6 MHz), δ: 206.2, 137.5, 133.8, 129.6, 129.5, 128.8, 127.6, 73.1, 42.4, 27.2, 26.4, 23.4. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H 6.49. Found: C, 67.54; H, 6.21.

Attempted Synthesis of [*E*]-2-Carbomethoxyethenesulfinylmethyl Phenyl Ketone (6j). Sulfinyl chloride **2j** from (*E*)-2-carbomethoxyethenyl PMB sulfoxide (**4j**) (388 mg; 1.53 mmol) was treated with 1-(trimethylsiloxy)styrene (345 μL, 1.79 mmol) and $TiCl_4$ (150 μL, 0.15 mmol) to afford β-keto sulfoxide **6j**. ^{1}H NMR (400 MHz, partial spectrum from crude reaction mixture), δ: 7.90−7.84 (m, 2H), 7.81 (d, J = 15.4 Hz, 1H), 7.77−7.34 (m, 3H), 6.66 (d, J = 15.4 Hz, 1H), 4.44 (ABq, J = 15.0, 2H), 3.80 (s, 3H). Chromatography on a neutral alumina plug afforded the cyclized product, oxathiin S-oxide **7j** (189 mg, 49%) as a partially separable 6:1 ratio of diastereomers, which could not be further purified. **Major Isomer**. ^{1}H NMR (400 MHz), δ: 7.70 (m, 2H), 7.51−7.41 (m, 3H), 6.62 (s, 1H), 5.39 (dd, J = 8.8 & 5.3 Hz, 1H), 3.82 (s, 3H), 3.32 (center of ABX pattern, J_{AB} = 17.6 Hz, J_{AX} = 8.8 Hz, J_{BX} = 5.3 Hz, 2H). ^{13}C (100.6 MHz), δ: 169.5, 167.0, 131.8, 128.8, 127.8, 127.3, 102.0, 94.1, 52.5, 30.4. **Minor Isomer**. ^{1}H NMR (400 MHz) δ: 7.70 (m, 2H), 7.51−7.41 (m, 3H), 6.52 (s, 1H), 5.88 (dd, J = 6.6 & 8.0 Hz, 1H), 3.79 (s, 3H), 2.85 (center of ABX pattern, J_{AB} = 16.5 Hz, J_{AX} = 8.0 Hz, J_{BX} = 6.6 Hz, 2H). ^{13}C (100.6 MHz), assignable signals only, δ: 131.9, 127.4, 100.9, 100.1, 52.5, 34.8. HRMS (EI), *m*/*z* (mixture of isomers): calcd for $C_{12}H_{12}O_4S$ 252.0456, found 252.0458.

Attempted Synthesis of [*E*]-2-Carbomethoxyethenesulfinylmethyl Methyl Ketone (6jj). Sulfinyl chloride **2j** from (*E*)-2-carbomethoxyethenyl PMB sulfoxide (**4j**) (231 mg, 0.91 mmol) was treated with 2-(trimethylsiloxy)propene (178 μL, 1.07 mmol) and $TiCl_4$ (100 μL, 0. 09 mmol) to afford β-keto sulfoxide **6jj**. ^{1}H NMR (200 MHz, crude reaction mixture), δ: 7.69 (d, J = 15.0 Hz, 1H), 6.66 (d, J = 15.0 Hz, 1H), 3.95 (ABq, J = 14.7 Hz, 2H), 3.78 (s, 3H), 2.29 (s, 3H). Chromatography on a neutral alumina plug afforded the cyclized product, oxathiin *S*-oxide **7jj** (20 mg, 12%) as a 20:1 ratio of diastereomers which could not be further purified. Data for major isomer only: ^{1}H NMR (400 MHz), δ: 6.02 (s, 1H), 5.18 (dd, J = 8.1 & 5.7 Hz, 1H), 3.78 (s, 3H), 3.18 (center of ABX pattern, J_{AB} = 17.6 Hz, J_{AX} = 8.1 Hz, J_{BX} = 5.7 Hz, 2H), 2.11 (s, 3H). ^{13}C (100.6 MHz) δ: 169.6, 168.8, 104.8, 94.0, 52.5, 30.3, 15.2.

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Supporting Information Available: Full preparative procedures and spectra data for sulfoxides **3** and **4**, IR and MS data for 1-alkenesulfinates, *β*-ketosulfoxides, and oxathiin *S*-oxides, and NMR spectra of compounds for which no or unsuitable elemental analysis was obtained (30 pages). This material is contained in 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.

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