Pergamon

Tetrahedron, Vol. 52, No. 25, pp. 8387-8396, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00406-1

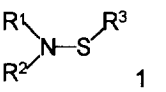
Preparation of *N,N*-Bis(trimethylsilyl)-1-alkenesulfenamides and their Desilylative Conversion to 1-Alkenesulfenimines. New Stable 1-Alkenesulfenic acid Derivatives.[1]

Mitchell D. Refvik and Adrian L. Schwan*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus,
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

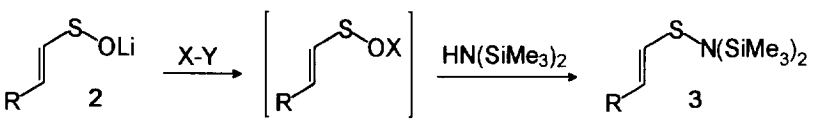
Abstract: Eight stable *N,N*-bis(trimethylsilyl)-1-alkenesulfenamides (**3**) were synthesized by the reaction of 1-alkenesulfenate anions with TMSCl and LiHMDS. Compounds **3** were isolated either by distillation or by chromatography. 1-Alkenesulfenamides (**3**) can be desilylated in the presence of aldehydes and ketones that do not bear α-hydrogens, to afford 1-alkenesulfenimines (**7**) either as single isomers or as mixtures of geometric isomers about the C=N bond. Protodesilylation of compounds **3** leads to 1-alkenesulfenamides (**8**) that have only hydrogens on the nitrogen. The parent 1-alkenesulfenamides **8** are not particularly stable, but could be characterized.

Sulfenamides (**1**), mostly recognized for their industrial uses[2] and their interesting chiroptical properties,[3] have become an important tool for the fundamental chemist.[4-9] Sulfenamides have proved valuable as a source of nitrogen radicals[4] and in the synthesis of chiral amines[5] and amino acids.[6] The sulfur of sulfenamides may behave as an electrophilic[7] or a nucleophilic atom,[8,9] as the key step in a chemical transformation.



1

While most of the sulfenamides known in the literature possess alkyl, haloalkyl or aryl groups on the sulfur, sulfenamides that bear a 1-alkenyl substituent are less common.[10-12] Baudin and co-workers have treated aminosulfenyl chlorides with vinyl Grignards to produce ethenesulfenamides.[10] The electrophilic addition of phthalimidosulfenyl chloride across alkynes constitutes an approach to 2-chloro-1-alkenesulfenamides.[11] Those two 1-alkenesulfenamide preparations both circumvent what would be the usual approach to sulfenamides, the reaction of an amine with a 1-alkenesulfenic acid derivative.[2] This is not surprising since many neutral 1-alkenesulfenic acid derivatives have very short lifetimes[13] and are not readily available for elaboration to 1-alkenesulfenamides. On the other hand, metalated 1-alkenesulfenate anions (**2**) persist in THF for several hours at room temperature.[14] Since sulfenates **2** co-exist with hexamethyldisilazane, it was believed that the sulfenate anions could be converted to their corresponding 1-alkenesulfenamides by modifying their normally nucleophilic sulfur to an electrophilic center (Scheme 1). We have accomplished that



Scheme 1

and in doing so have obtained a collection of *N,N*-bis(trimethylsilyl)-1-alkenesulfenamides (**3**).[15] This paper provides an account of that chemistry[1,15] and a description of the desilylative transformation of sulfenamides **3** into 1-alkenesulfenimines.

Results and Discussion

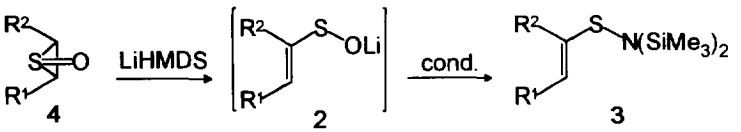
Trimethylsilyl chloride was chosen to be the reagent (XY, Scheme 1) for chemoselective oxygen substitution.[16] Quenching a solution containing lithium 1-hexenesulfenate (**2a**)[14] and hexamethyldisilazane with trimethylsilyl chloride provided a relatively clean sample of *N,N*-bis(trimethylsilyl)-1-hexenesulfenamide (**3a**, 24%). The reaction conditions were optimized on this substrate by varying temperature and the sequence of introduction of silyl chloride and additional amine source. Two sets of conditions were eventually found that brought the yields near 50%, but 1-hexenyl disulfide was often recovered as a co-product (5-10%). Serendipitously we learned that addition of excess cyclohexene to the reaction mixture eliminated any disulfide and provided rather clean sulfenamide in slightly higher yield. The initial intent of the cyclohexene was to chemically capture any transient 1-alkenesulfenyl chloride or trimethylsilyl 1-alkenesulfenate esters that may be present in solution.[17] Details of the two sets of conditions are outlined in the experimental section.

Based on the results with 1-hexenesulfenate, several other sulfenates, all generated from a thiirane *S*-oxide (**4**), were converted to their corresponding sulfenamides and the results are tabulated in Table 1. The sulfenamides were distilled where possible in the final purification step. The higher molecular weight compounds were chromatographed on basic alumina. The isolated yields of the compounds possessing smaller substituents were lowest but yields determined from calibrated ^{1}H NMR spectra of the crude mixtures indicated the chemical yields were actually higher. Although the purification was done carefully, some material was nevertheless lost, presumably due to the volatility of the lower molecular weight compounds. Sulfenamide **3h** partially decomposed during chromatography. Compound **3h** and all the sulfenamides were sufficiently pure in their crude state and purification before employing them in other reactions is an option rather than a requirement. The yields reported in Table 1 are in keeping with yields obtained for many other synthetic approaches to alkane- and arenesulfenamides.[2] Furthermore, on some occasions, particularly larger scale reactions, the sulfenamide yield may reach 70%. Consequently, the yields reported in Table 1 are the minimum consistently obtainable yields.

A few spectroscopic elements of sulfenamides **3** are noteworthy. In their mass spectra, the compounds exhibit a rather strong molecular ion peak (40-90%). Common fragments often include $(M\text{-}Me)^+$ and $(M\text{-}SiMe_3)^+$ peaks. In both the ^{1}H and ^{13}C NMR spectra, the trimethylsilyl peaks appear as a singlet with the resonance for the TMS methyls consistently in the +1.8-1.9 ppm range of the ^{13}C NMR scale. ^{13}C NMR peaks of the S-C=C double bond are usually around 130 and 123 ppm for singly substituted double bonds. The vinyl hydrogens give the expected coupling patterns in the ^{1}H NMR and in singly substituted systems (**3a**, **c-f**), the hydrogen α to the sulfur is always downfield from the other vinyl hydrogen (5.90 ppm vs. 5.38 ppm).

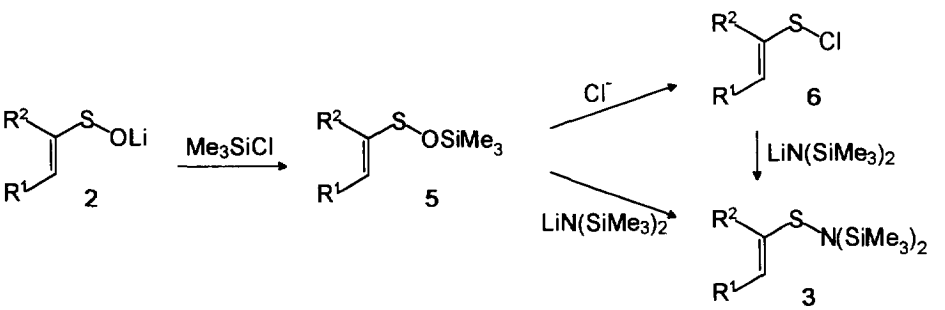
The mechanism of formation of the sulfenamide cannot be specifically identified, but two logical pathways are depicted in Scheme 2.[18] The sulfenate is expected to react with trimethylsilyl chloride at oxygen[16,19] to afford a trimethylsilyl 1-alkenesulfenate (**5**). Such a sulfenate would be expected to be electrophilic at sulfur and could show reactivity towards both lithium amide (or amine)[20] and chloride ion. The reaction of silyl sulfenate **5** affords sulfenamide **3** directly, while reaction with chloride would generate a

Table 1. Synthesis of N,N-Bis(trimethylsilyl)alkenesulfenamides (3) from Thiirane *S*-oxides (4)



entry	product	R^1; R^2	Method[a]	Yield[b]
1	**3a**	*n*-Bu; H	A	46
2	**3a**		B	51
3	**3b**	H; H	A	25(44)[c]
4	**3c**	Me; H	A	43(58)[c]
5	**3d**	$Ph(CH_2)_2$; H	A	57
6	**3d**		B	52
7	**3e**	3-butenyl; H	B	50
8	**3f**	n-$C_{11}H_{23}$; H	A	53
9	**3f**		B	64
10	**3g**	-$(CH_2)_4$-	A	49(58)[c]
11	**3g**		B	63
12	**3h**	Ph; Ph	A	(58)[c]
13	**3h**		B	34(46)[c]

a See experimental section for a description of the methods. *b* All yields are of isolated purified material unless otherwise indicated. *c* Yield in parentheses is a crude ^{1}H NMR calibrated yield.



Scheme 2

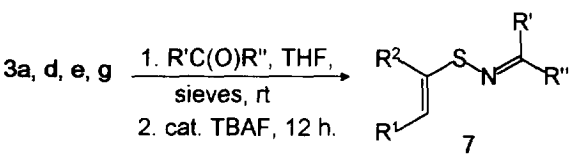
sulfenyl chloride (**6**) which should be even more reactive toward lithium amide. Clearly the isolation of sulfenamide, regardless of its means of formation, is consistent with the conversion of the nucleophilic sulfur of sulfenate anion (**2**) to an electrophilic atom, in accord with our desire outlined in the introduction.[21]

We sought to convert alkenesulfenamides **3** to 1-alkenesulfenimines, species which possess an S-N=C unit rather than the S-N$(SiMe_3)_2$ functionality of **3**. A literature report[22] stated that *N,N*-bis(trimethylsilyl)arene- and alkanesulfenamides could be converted to the corresponding sulfenimines by

treatment with a ketone or aldehyde and catalytic TBAF. The method has been used successfully by the initial authors and by others[23] and is reported to be tolerant of carbonyl compounds bearing α-hydrogens. In our hands the method proved satisfactory for aryl aldehydes and ketones to furnish 1-alkenesulfenimines **7**, but was troublesome for carbonyl compounds bearing an α-hydrogen. In those cases the desired sulfenimine was obtained in low yield and was accompanied by a material which was assigned the structure of the 1-alkenesulfenamide bearing only hydrogens on the nitrogen (**8**, *vide infra).* Based on a number of pieces of circumstantial evidence, we believe that after desilylation, the nitrogen did indeed remove α-hydrogens of ketones or aldehydes in competition with carbonyl attack, and that deprotonation is the source of sulfenamide **8**.

The evidence is as follows. First, the yield of sulfenimine formation is highest with carbonyl compounds for which there are no α-hydrogens and in those cases the presence of sulfenamide **8** is minimal. Moreover, the yield is also good with cyclopropyl ketones; the low kinetic acidity of the α-hydrogen of such ketones is well-documented.[24] Similarly, carbonyl attack of α,β-unsaturated carbonyl compounds occurred more rapidly than removal of the sp^2 hybridized α-hydrogen. The presence of **8** is best explained by rapid proton transfer from some source and numerous experiments with wet and dry TBAF sources led to little variation in the amount of **8**, indicating that the proton source was not the TBAF solution. Table 2 shows all the results for clean sulfenimine formation.[25]

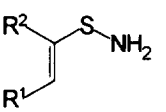
Table 2. Formation of Alkenesulfenimines 7 from Reactions of Compounds 3 with Aldehydes and Ketones.



starting material	carbonyl compound R'	carbonyl compound R"	sulfenimine (% yield)[a](ratio)[b]
3d	H	2-furyl	**7a**(82)(2.25:1)
3d	H	*t*-butyl	**7b**(75)
3e	H	*p*-$MeOC_6H_4$	**7c**(82)
3g	H	Ph	**7d**(72)
3g	H	β-styryl	**7e**(90)(3.33:1)
3g	Ph	β-styryl	**7f**(70)(1.25:1)
3a	Ph	Ph	**7g**(60)
3a	β-styryl	β-styryl	**7h**(46)
3a	2-thienyl	cyclopropyl	**7i**(68)(5:1)
3g	Ph	cyclopropyl	**7j**(64)(2:1)

a Yield of pure, chromatographed material. *b* Where a mixture of isomers was obtained the isomeric ratio (from ^1H NMR) is noted. When a single isomer was obtained its geometry was assigned to be *trans* about the C=N bond.

For the first time we demonstrate that the method is suitable for α,β-unsaturated aldehydes and ketones and for cyclopropyl ketones. Mixtures of isomers were obtained in several instances, usually when the substituents attached to the imino carbon are close in size. These were postulated to be pairs of geometric isomers about the C=N double bond. Support for this assignment was obtained through variable temperature experiments on isomers **7f**. Heating a 1:1 mixture of those isomers in DMSO-d_6 led to coalescence of the cyclohexenyl hydrogens at 96 °C. This translates into a $\Delta G_c^{\ddagger}$ for inversion about the C=N bond of 19.2 ± 0.2 kcal mol^{-1},[26] which is within the range reported for arene- and alkanesulfenimines.[27]



8 a, R^1, R^2 = *n*-Bu, H
d, R^1, R^2 = CH_2CH_2Ph, H
g, R^1, R^2 = $-(CH_2)_4-$

In order to gain proper evidence for our assignment of structures **8**, we set out to deliberately prepare those compounds through a double protodesilylation reaction of alkenesulfenamides **3**. It was quickly learned that the parent 1-alkenesulfenamides were similar to most other nitrogen unsubstituted sulfenamides: they were not very stable in neat form.[2] Conditions were finally found whereby reasonably reliable spectral data for some examples of **8** could be acquired. Data for sulfenamides **8a**, **d** and **g** were obtained through the following means. The silylated sulfenamide **3** in MeCN with a trace of water was treated with 4 equiv. of TBAF freshly adsorbed onto basic alumina (I).[28] After 10 min., the sulfenamide was extracted into pentane. After removal of most of the pentane on the rotary evaporator,[29] ^{1}H NMR, ^{13}C NMR, IR and GCMS data consistent with the assigned structure, could be obtained.

The ^{13}C NMR data of the vinyl carbons of compounds **8** are similar to their doubly silylated counterparts **3**. The ^{1}H NMR resonances of the vinyl hydrogens of **8** are shifted downfield from those of **3**. The hydrogens on the carbon α to the sulfur move 0.14-0.18 ppm while the vinyl protons on the β-carbon are shifted by 0.22-0.23 ppm. The IR spectra of sulfenamides **8** show peaks indicative of NH_2 groups, while the mass spectra afford significant molecular ion peaks. Comparison of the NMR data to those acquired during our investigations into the preparation of 1-alkenesulfenimines **7** validated our initial assignment of the impurity in some of those syntheses. The unwanted, unfunctionalized product was indeed the simple 1-alkenesulfenamide **8**.

We have demonstrated a method for the conversion of nucleophilic 1-alkenesulfenate anions into a species that can be attacked by hexamethyldisilazide. The result is a preparation of silicon substituted 1-alkenesulfenamides (**3**), which have potential for a number of desilylative transformations. One of those reactions has been presented here: sulfenamides **3** can be desilylated in the presence of carbonyl compounds that do not bear α-hydrogens, to yield 1-alkenesulfenimines **7**. We have also learned that like most sulfenamides, the parent 1-alkenesulfenamides are sensitive species although spectroscopic characterization of them was achieved. We will describe other desilylative reactions of compounds **3** elsewhere.

Experimental

General. Most of our general experimental methods have been reported previously.[14,30] Elemental analyses were performed by M-H-W Labs, Phoenix, Arizona. Thiirane *S*-oxides **4** were prepared as described previously.[14] LiHMDS was purchased from Aldrich as a 1.0 M solution in THF. TMSCl was purchased from Aldrich and used without purification. The TBAF used was 1.0 M in THF unless otherwise indicated. All aldehydes and ketones were purified before use.

Synthesis of *N,N*-Bis(trimethylsilyl)-1-alkenesulfenamides (3).

Method A. Thiirane *S*-oxide (**4**, 6-80 mmol) dissolved in cold dry THF (4-15 mL) was added to a solution of LiHMDS (1.1 eq.) in dry THF (30-400 mL) at -78 °C as described previously.[14] Cyclohexene (2 mL/g of **4**) was added and the solution was stirred for 15 min. TMSCl (0.8 eq.) in dry THF (4-10 mL) was added, followed by LiHMDS (1.0 eq.). The solution was warmed to rt over 1 h and was stirred for 16 h. Water was added (30-100 mL) and the layers were separated and the aq. layer was extracted with hexanes (3 X 30 mL). The combined organic extracts were washed with water, brine and were dried over $MgSO_4$. Filtration and concentration afforded crude sulfenamide **3** contaminated with hexamethyldisilazane. Pure sulfenamide **3** was obtained by fractional distillation or chromatography on basic alumina (I) with light petroleum as eluent.

Method B. Thiirane *S*-oxide (**4**, 6-80 mmol) dissolved in cold dry THF (4-15 mL) was added to a solution of LiHMDS (2.2 eq.) in dry THF (30-400 mL) at -78 °C. Cyclohexene (2 mL/g of **4**) was added and the solution was stirred for 15 min. TMSCl (0.8 eq.) in dry THF (4-10 mL) was added. The solution was warmed to rt over 1 h and was stirred for 16 h. Workup and isolation as described for Method A provided pure **3**. The yields obtained by either method are reported in Table 1.

N,N-Bis(trimethylsilyl)-(E)-1-hexenesulfenamide (3a). Colorless liquid, bp 98-102 °C (1.4 mm). ^{1}H NMR (400 MHz), δ 5.89 (dt, *J* = 14.7, 1.3 Hz, 1H), 5.37 (dt, *J* = 14.7, 7.0 Hz, 1H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.36-1.26 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.18 (s, 18H); ^{13}C NMR (100.6 MHz), δ 130.3, 123.9, 32.2, 31.8, 22.1, 13.9, 1.8; IR (neat) 3016, 2959, 2928, 2877, 1626, 1465, 1256, 947, 922, 891, 840 cm^{-1}; GCMS, *m/z* 275, 260, 178, 177, 162, 147, 146, 130, 100, 73, 59; Anal. Calcd for $C_{12}H_{29}NSSi_2$: C, 52.30; H, 10.61; N, 5.08. Found: C, 52.20; H, 10.79; N, 5.23.

N,N-Bis(trimethylsilyl)ethenesulfenamide (3b). Colorless liquid, bp 36-38 °C (1.4 mm); lit.[23b] bp 38-40 °C (0.5 mm).

N,N-Bis(trimethylsilyl)-(E)-1-propenesulfenamide (3c). Colorless liquid, bp 55-57 °C (1.8 mm). ^{1}H NMR (400 MHz), δ 5.91 (dd, *J* = 14.2, 1.4 Hz, 1H), 5.39 (dq, *J* = 14.2, 6.7 Hz, 1H), 1.74 (dd, *J* = 6.7, 1.4 Hz, 3H), 0.18 (s, 18H); ^{13}C NMR (100.6 MHz), δ 131.4, 118.6, 17.9, 1.9; IR (neat) 3027, 2963, 2912, 2855, 1633, 1447, 1409, 1261, 942, 884, 839, 762 cm^{-1}; GCMS, *m/z* 233, 218, 178, 146, 130, 100, 99, 74, 73; Anal. Calcd for $C_9H_{23}NSSi_2$: C, 46.29; H, 9.93; N, 6.00. Found: C, 46.13; H, 9.89; N, 6.14.

N,N-Bis(trimethylsilyl)-4-phenyl-(E)-1-butenesulfenamide (3d). Colorless oil purified by chromatography. ^{1}H NMR (400 MHz), δ 7.28-7.16 (m, 5H), 5.93 (d, *J* = 14.8 Hz, 1H), 5.38 (dt, *J* = 14.8, 7.0 Hz, 1H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.41 (dt, *J* = 8.0, 7.0 Hz, 2H), 0.15 (s, 18H); ^{13}C NMR (100.6 MHz), δ 141.7, 131.3, 128.4, 128.3, 125.8, 122.2, 36.1, 34.2, 1.8; IR (neat) 3086, 3068, 3030, 2956, 2894, 2856, 1644, 1619, 1253, 936, 880, 842 cm^{-1}; GCMS, *m/z* 323, 234, 233, 232, 158, 144, 91, 73, 59; Anal. Calcd for $C_{16}H_{29}NSSi_2$: C, 59.38; H, 9.03; N, 4.33. Found: C, 59.50; H, 9.21; N, 4.59.

N,N-Bis(trimethylsilyl)-(E)-1-hexa-1,5-dienesulfenamide (3e). Colorless liquid purified by chromatography. ^{1}H NMR (400 MHz), δ 5.93 (d, *J* = 14.7 Hz, 1H), 5.86-5.76 (m, 1H), 5.38 (dt, *J* = 14.7, 6.7 Hz, 1H), 5.02 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.97 (dd, *J* = 10.1, 1.9 Hz, 1H), 2.23-2.11 (m, 4H), 0.18 (s, 18H); ^{13}C NMR (100.6 MHz), δ 138.1, 130.9, 122.4, 114.9, 34.0, 31.9, 1.8; IR (neat) 3079, 3014, 2959, 2928, 2903, 2846, 1641, 1629, 1452, 1402, 1256, 928, 884, 840, 821, 758 cm^{-1}; GCMS, *m/z* 273, 233, 232, 158, 146, 144, 130, 100, 73, 59; Anal. Calcd for $C_{12}H_{27}NSSi_2$: C, 52.68; H, 9.95; N, 5.12. Found: C, 52.47; H, 10.06; N, 5.53.

N,N-Bis(trimethylsilyl)-(E)-1-tridecenesulfenamide (3f). Colorless oil which solidifies at ca. -20 °C, purified by chromatography. ^{1}H NMR (400 MHz), δ 5.88 (d, *J* = 14.7 Hz, 1H), 5.37 (dt, *J* = 14.7, 6.7 Hz, 1H), 2.07 (q, *J* = 6.7 Hz, 2H), 1.37-1.30 (m, 2H), 1.26 (s(br), 16H), 0.88 (t, *J* = 6.1 Hz, 3H), 0.18 (s, 18H); ^{13}C NMR (100.6 MHz), δ 130.3, 123.9, 32.6, 32.0, 29.7 (2 C's), 29.7 (2 C's), 29.5, 29.4, 29.1, 22.7, 14.1, 1.9; IR (neat) 3015, 2963, 2931, 2861, 1633, 1473, 1402, 1261, 942, 884, 846, 762 cm^{-1}; GCMS, *m/z* 373, 358, 232, 178, 177, 162, 146, 130, 73, 59, 55; Anal. Calcd for $C_{19}H_{43}NSSi_2$: C, 61.05; H, 11.60; N, 3.75. Found: C, 61.09; H, 11.49; N, 3.94.

N,N-Bis(trimethylsilyl)-1-cyclohexenesulfenamide (3g). Colorless liquid, bp 72-74 °C (0.4 mm). ^{1}H NMR (400 MHz), δ 5.34 (s(br), 1H), 2.08 (m, 2H), 1.90 (m, 2H), 1.64 (m, 4H), 0.16 (s, 18 H); ^{13}C NMR (100.6

MHz), δ 138.5, 114.7, 25.6, 25.2, 23.1, 22.9, 1.8; IR (neat) 3027, 2938, 2861, 2836, 1645, 1453, 1409, 1338, 1255, 929, 884, 846, 762 cm^{-1}; GCMS, *m/z* 273, 258, 184, 178, 177, 170, 146, 130, 100, 79, 73, 59; Anal. Calcd for $C_{12}H_{27}NSSi_2$: C, 52.68; H, 9.95; N, 5.12. Found: C, 52.59; H, 9.93; N, 5.37.

N,N-Bis(trimethylsilyl)-(E)-1,2-diphenylethenesulfenamide (3h). Colorless oil which solidifies at ca. -20 °C, purified by chromatography. ^1H NMR (400 MHz), δ 7.49-7.26 (m, 5H), 7.17-7.00 (m, 3H), 6.92 (d, *J* = 7.3 Hz, 2H), 6.22 (s, 1H), 0.31 (s, 18H); ^{13}C NMR (100.6 MHz), δ 145.4, 136.7, 135.7, 129.3, 128.8, 128.4, 128.0, 127.9, 125.6, 117.2, 1.8; IR (neat) 3092, 3079, 3057, 3026, 2960, 2901, 1624, 1598, 1499, 1446, 1257, 920, 880, 848, 755 cm^{-1}; GCMS, *m/z* 371, 211, 210, 179, 178, 177, 146, 130, 73; HRMS Calcd for $C_{20}H_{29}NSSi_2$: 371.1559; Found: 371.1542.

General Preparation of 1-Alkenesulfenimines 7. To a thoroughly flame-dried flask, continuously protected with dry N_2, was added dry THF (10 mL), 4Å molecular sieves (1 g), alkenesulfenamide **3** (122-199 mg, 0.447-0.722 mmol) and the aldehyde or ketone (1 eq.). After stirring at rt for 0.5 h, TBAF in THF (0.1 eq.),[31] was added all at once. The mixture was stirred for 12 h and then was filtered. The sieves were washed with ether (2 X 10 mL). The combined organics were concentrated and chromatographed on basic alumina (I) to afford pure 1-alkenesulfenimines **7**.

N-(2-Furylmethylene)-4-phenyl-(E)-1-butenesulfenamide (7a). 2.25:1 mixture of isomers, 82%, oil. ^1H NMR (400 MHz), major isomer: δ 8.12 (s, 1H) 7.49 (d, *J* = 1.6 Hz, 1H), 7.31-7.17 (m, 5H), 6.62 (d, *J* = 3.4 Hz, 1H), 6.57 (dt, *J* = 15.3, 1.3 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.04 (dt, *J* = 15.3, 7.0 Hz, 1H), 2.78 (m, 2H), 2.52 (m, 2H); minor isomer: δ 8.20 (s, 1H), 7.55 (dd, *J* = 1.8, 0.6, 1H), 7.31-7.17 (m, 5H), 7.01 (d, *J* = 3.3 Hz, 1H), 6.62 (dt, *J* = 15.4, 1.4 Hz, 1H), 6.59 (m, 1H), 5.98 (dt, *J* = 15.4, 6.9 Hz, 1H), 2.78 (m, 2H), 2.52 (m, 2H); ^{13}C NMR (100.6 MHz) δ 151.7, 149.5, 144.7, 144.5, 144.1, 142.6, 141.3, 141.1, 134.2, 129.3, 128.3, 128.3, 127.6, 126.0, 125.9, 124.4, 116.2, 112.5, 112.4, 111.7, 35.4, 35.1, 34.7, 34.6; IR (neat) 3059, 3033, 2927, 2855, 1624, 1604, 1572, 1499, 1486, 1453, 1150, 1078, 1018, 940, 755, 702 cm^{-1}; MS, *m/z* 257, 166, 129, 96, 94, 91, 73, 71, 65, 55; Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44. Found: C, 69.88; H, 5.78; N, 5.38.

N-(2,2-Dimethyl-1-propylidene)-4-phenyl-(E)-1-butenesulfenamide (7b). (*E*)-isomer, 75%, oil. ^1H NMR (400 MHz), δ 7.68 (s, 1H), 7.30-7.17 (m, 5H), 6.43 (d, *J* = 15.0 Hz, 1H), 5.93 (dt, *J* = 15.0, 7.0 Hz, 1H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.49 (dt, *J* = 7.7, 7.0 Hz, 2H), 1.06 (s, 9H); ^{13}C NMR (100.6 MHz), δ 169.4, 141.4, 130.9, 128.4, 128.3, 125.9, 124.8, 38.6, 35.4, 34.8, 26.7; IR (neat) 3092, 3065, 3033, 2967, 2927, 2868, 1618, 1506, 1460, 1368, 953, 749, 703 cm^{-1}; MS, *m/z* 247, 163, 156, 129, 91, 86, 73, 57; HRMS Calc'd for $C_{15}H_{21}NS$ 247.1395, found 247.1391.

N-(4-Methoxyphenyl)methylene-(E)-1-hexa-1,5-dienesulfenamide (7c). (*E*)-isomer, 82%, oil. ^1H NMR (400 MHz), δ 8.35 (s, 1H), 7.59 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.56 (dt, *J* = 15.1, 1.4 Hz, 1H), 6.01 (dt, *J* = 15.1, 6.7, 1H), 5.90-5.80 (m, 1H), 5.07 (ddt, *J* = 18.8, 1.9, 1.6 Hz, 1H), 5.01 (ddt, *J* = 10.2, 1.9, 1.2 Hz, 1H), 3.83 (s, 3H), 2.35-2.20 (m, 4H); ^{13}C NMR (100.6 MHz), δ 161.3, 156.3, 137.7, 132.3, 129.5, 128.8, 124.6, 115.2, 114.0, 55.3, 33.1, 32.4; IR (neat) 3079, 2927, 2841, 1611, 1512, 1308, 1256, 1170, 1032, 946, 920, 834 cm^{-1}; GCMS, *m/z* 247, 174, 147, 136, 135, 134, 133, 103, 92, 90, 85, 77, 76, 74, 73, 72, 71, 64; Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66. Found: C, 67.79; H, 6.78; N, 5.66.

N-(Phenylmethylene)-1-cyclohexenesulfenamide (7d). (*E*)-isomer, 72%, oil. ^1H NMR (400 MHz), δ 8.44 (s, 1H), 7.65-7.63 (m, 2H), 7.41-7.36 (m, 3H), 6.16 (m, 1H), 2.43 (m, 2H), 2.22 (m, 2H), 1.81 (m, 2H), 1.68 (m, 2H); ^{13}C NMR (100.6 MHz), δ 156.1, 136.5, 134.2, 130.0, 128.6, 127.7, 127.2, 28.2, 26.3, 23.2, 22.0; IR (neat) 3060, 3024, 2930, 2858, 1630, 1594, 1565, 1494, 1446, 1435, 1358, 1335, 1308, 1263, 1216, 1170, 1136, 1073, 1022, 949, 916, 833, 799 cm^{-1}; GCMS, *m/z* 217, 114, 106, 103, 81, 79, 77, 76, 71; Anal. Calcd for $C_{13}H_{18}NS$: C, 71.85; H, 6.96; N, 6.44. Found: C, 71.95; H, 7.00; N, 6.27.

N-[3-phenyl-(E)-2-propen-1-ylidene]-1-cyclohexenesulfenamide (7e). 3.33:1 mixture of isomers, 90%, oil. ^1H NMR (400 MHz), major isomer: δ 8.23 (d, *J* = 8.7 Hz, 1H), 7.46-7.32 (m, 5H), 6.89 (ddd, *J* = 15.9, 8.7, 0.6 Hz, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.14 (m, 1H), 2.39 (m, 2H), 2.19, (m, 2H), 1.77 (m, 2H), 1.65 (m,

2H); minor isomer: δ 7.97 (d, J= 9.0 Hz, 1H), 7.53-7.27 (m, 5H), 7.04 (dd, J= 15.6, 9.0 Hz, 1H), 6.78 (d, J = 15.6 Hz, 1H), 6.11 (m, 1H), 2.39 (m, 2H), 2.19, (m, 2H), 1.77 (m, 2H), 1.65 (m, 2H); ^{13}C NMR (100.6 MHz), δ 158.4, 156.0, 141.6, 138.7, 135.9, 135.5, 134.5, 134.1, 129.6, 128.9, 128.8, 128.8, 128.6, 128.0, 127.6, 127.0, 126.4, 121.1, 28.4, 28.0, 26.3, 26.2, 23.2, 23.1, 22.0, 21.6; IR (neat) 3057, 3027, 2929, 2856, 2833, 1619, 1597, 1576, 1534, 1492, 1447, 1435, 1335, 1263, 1238, 1132, 1073, 1052, 1022, 972, 916, 838, 799, 750 cm^{-1}; GCMS, *m/z* 243, 152, 138, 129, 117, 116, 115, 112, 104, 91; Anal. Calcd for $C_{15}H_{17}NSSi_2$: C, 74.03; H, 7.04; N 5.76. Found: C, 73.98; H, 7.07; N, 5.52.

N-[1,3-Diphenyl-(E)-2-propen-1-ylidene]-1-cyclohexenesulfenamide (7f). 1.25:1 mixture of isomers, 70%, oil. ^{1}H NMR (400 MHz), major isomer: δ 7.63-7.24 (m, 10H), 7.14 (d, J= 16.2, 1H), 6.37 (d, J= 16.2, 1H), 6.08 (m, 1H), 2.34 (m, 2H), 2.17 (m, 2H), 1.77 (m, 2H), 1.64 (m, 2H); minor isomer: δ 7.63-7.24 (m, 10H), 7.19 (d, J= 16.3, 1H), 6.89 (d, J= 16.3, 1H), 6.13 (m, 1H), 2.48 (m, 2H), 2.17 (m, 2H), 1.77 (m, 2H), 1.64 (m, 2H); ^{13}C NMR (100.6 MHz), δ 164.9, 161.1, 139.3, 138.9, 136.8, 136.2, 135.9, 135.8, 135.2, 130.6, 129.2, 129.0, 128.9, 128.8, 128.6, 128.5, 128.1, 127.4, 127.2, 127.1, 124.9, 124.8, 122.0, 27.8, 27.7, 26.1, 23.2, 22.1, 22.1; IR (neat) 3058, 3028, 2931, 2858, 2834, 1708, 1610, 1575, 1558, 1491, 1445, 1334, 1264, 1206, 1176, 1136, 1074, 1025, 967, 910, 736 cm^{-1}; MS, *m/z* 319, 217, 114, 106, 91, 84, 81, 79, 77, 71, 55, 51; Anal. Calcd for $C_{21}H_{21}NS$: C, 78.98; H, 6.63; N, 4.38. Found: C, 79.04; H, 6.62; N, 4.31.

N-(Diphenylmethylene)-(E)-1-hexenesulfenamide (7g). 60%, oil. ^{1}H NMR (400 MHz), δ 7.59-7.23 (m, 10H), 6.60 (d, J= 15.3 Hz, 1H), 5.87 (dt, J= 15.3, 7.0 Hz, 1H), 2.17 (q, J= 7.0 Hz, 2H), 1.45-1.29 (m, 4H), 0.90 (t, J= 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 163.8, 138.9, 137.9, 129.6, 129.2, 129.2, 128.9, 128.3, 127.8, 127.5, 126.8, 32.5, 31.1, 22.0, 13.7; IR (neat) 3065, 3033, 1657, 1618, 1578, 1506, 1453, 973, 755 cm^{-1}; GCMS, *m/z* 295, 212, 183, 182; Anal. Calcd for $C_{19}H_{21}NS$: C, 77.24; H, 7.16; N, 4.74. Found: C, 77.23; H, 7.30; N, 4.82.

N-{1-[(E)-2-Phenylethenyl]-3-phenyl-[E]-2-propen-1-ylidene}-(E)-1-hexenesulfenamide (7h). 46%, oil. ^{1}H NMR (400 MHz), δ 7.56-7.25 (m, 10 H), 7.11 (d, J= 16.1 Hz, 1H), 7.05 (d, J= 17.5 Hz, 1H), 7.01 (d, J= 17.5 Hz, 1H), 6.96 (d, J= 16.1 Hz, 1H), 6.61 (dt, J= 15.6, 1.2 Hz, 1H) 5.96 (dt, J= 15.6, 7.0 Hz, 1H), 2.20 (q, J= 7.0 Hz, 2H), 1.55-1.25 (m, 4H), 0.92 (t, J= 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 163.5, 138.7, 137.6, 132.3, 130.0, 129.4, 129.1, 129.0, 128.7, 128.2, 128.1, 127.6 (2 C's), 127.3, 126.7, 32.6, 31.3, 22.1, 13.9; IR (neat) 3085, 3033, 2960, 2927, 2861, 1690, 1657, 1631, 1611, 1572, 1499, 1453, 1348, 979, 775 cm^{-1}; MS, *m/z* 347, 234, 233, 232, 187, 186, 117, 104, 103, 91, 77, 73; Anal. Calcd for $C_{23}H_{25}NS$: C, 79.49; H, 7.25; N, 4.03. Found: C, 79.59; H, 7.20; N, 4.10.

N-[(2-Thienyl)cyclopropylmethylene]-(E)-1-hexenesulfenamide (7i). 5:1 mixture of isomers, 68%, oil. ^{1}H NMR (400 MHz), major isomer: δ 7.36 (dd, J= 3.6, 1.2 Hz, 1H), 7.27 (dd, J= 5.1, 1.2 Hz, 1H), 6.97 (dd, J= 5.1, 3.6 Hz, 1H), 6.52 (dt, J= 15.5, 1.4 Hz, 1H), 5.90 (dt, J= 15.5, 7.0 Hz, 1H), 2.18 (m, 2H), 1.74 (m, 1H), 1.46-1.31 (m, 4H), 1.07-1.01 (m, 2H), 0.94-0.83 (m, 2H), 0.91 (t, J= 7.1, 3H); minor isomer δ 7.70 (dd, J= 3.7, 1.0 Hz, 1H), 7.49 (dd, J= 5.1, 1.0 Hz, 1H), 7.14 (dd, J= 5.1, 3.7 Hz, 1H), 6.41 (dt, J= 15.3, 1.2 Hz, 1H), 5.87 (dt, J= 15.3, 7.0 Hz, 1H), 2.18 (m, 2H), 2.12 (m, 1H), 1.46-1.31 (m, 4H), 1.07-1.01 (m, 2H), 0.94-0.83 (m, 2H), 0.93 (m, 3H); ^{13}C NMR (100.6 MHz), δ 158.1, 155.8, 144.6, 139.7, 129.6, 128.5, 128.4, 128.3, 128.1, 127.3, 127.2, 127.0, 126.5, 126.3, 32.6, 32.5, 31.3, 31.3, 22.2, 20.5, 15.3, 13.9, 7.7, 6.7; IR (neat) 3085, 3013, 2954, 2927, 2861, 1624, 1565, 1545, 1473, 1433, 1368, 1256, 1236, 1052, 1038, 946, 709 cm^{-1}; MS, *m/z* 265, 152, 150, 110, 91, 81, 73, 55; Anal. Calcd for $C_{14}H_{19}NS_2$: C, 63.35; H, 7.21; N, 5.28. Found: C, 63.58; H, 6.98; N, 5.23.

N-(Phenylcyclopropylmethylene)-1-cyclohexenesulfenamide (7j). 2:1 mixture of isomers, 64%, oil. ^{1}H NMR (400 MHz), major isomer: δ 7.70 (m, 2H), 7.44-7.29 (m, 3H), 6.10 (s(br), 1H), 2.46 (m, 2H), 2.17 (m, 2H), 1.81-1.60 (m, 5H), 1.05 (m, 2H), 0.72 (m, 2H); minor isomer: δ 7.70 (m, 2H), 7.44-7.29 (m, 3H), 5.96.(s(br), 1H), 2.29 (m, 2H), 2.13 (m, 2H), 1.93 (m, 1H), 1.81-1.60 (m, 4H), 0.93 (m, 2H), 0.82 (m, 2H); ^{13}C NMR (100.6 MHz), δ 167.7, 163.4, 138.6, 135.5, 135.2, 128.8, 128.6, 128.4, 127.8, 127.2, 126.4, 123.7, 122.2, 30.3, 27.6, 27.4, 26.0, 25.9, 23.4, 23.2, 23.1, 22.3, 22.2, 21.8, 20.9, 15.1, 7.8, 7.1; IR (neat) 3085, 3059, 3006, 2934, 2855, 2835, 1677, 1591, 1499, 1453, 1361, 1335, 1025, 920, 762, 696 cm^{-1}; GCMS, *m/z* 257,

216, 146, 144, 113, 104, 79, 77, 71, 55; Anal. Calcd for $C_{16}H_{19}NS$: C, 74.66; H, 7.44; N, 5.44. Found: C, 74.52; H, 7.30; N, 5.28.

General Procedure for Protodesilylation of 1-Alkenesulfenamides 3. To a solution of **3** (228-285 mg, 0.832-0.967 mmol), MeCN (10 mL) and water (ca. 0.5 mL) stirring at rt, was added TBAF (4 equiv.) previously adsorbed on basic alumina (I). After 10 min, the mixture was filtered with the aid of suction. The solid residue was washed with MeCN (10 mL) and pentane (3 X 5 mL). All organics were transferred to a separatory funnel and the pentane layer was removed. The MeCN layer was extracted with more pentane (3 X 5 mL). The combined pentane layers were dried over Na_2SO_4. The solution was concentrated on the rotary evaporator (water aspiration) to afford 1-alkenesulfenamide **8**, contaminated with some solvent residues.[32] Solutions for NMR analysis were quickly prepared using deacidified $CDCl_3$.

(E)-1-Hexenesulfenamide (8a). ^{1}H NMR (200 MHz), δ 6.12 (d, *J*= 14.9 Hz, 1H), 5.51 (dt, *J*= 14.9, 7.0 Hz, 1H), 2.40 (s(br), 2H), 2.10 (q, *J*= 7.0 Hz, 2H), 1.32 (m, 4H), 0.87 (t, *J*= 7.0 Hz, 3H); ^{13}C NMR (50.3 MHz), δ 130.2, 125.6, 32.1, 31.4, 22.0, 13.7; IR (neat) 3379, 3294, 3006, 2962, 2932, 2866, 1689, 1623, 1472, 1382, 1261, 1104, 1050, 947, 917, 736 cm^{-1}; GCMS, *m/z* 131, 99, 88, 85, 81, 73, 71, 61, 55.

4-Phenyl-(E)-1-butenesulfenamide (8d). ^{1}H NMR (200 MHz), δ 7.32-7.15 (m, 5H), 6.16 (dt, *J*= 14.9, 1.4 Hz, 1H), 5.55 (dt, *J*= 14.9, 6.8 Hz, 1H), 2.71 (t, *J*= 6.8 Hz, 2H), 2.43 (m, 2H), 2.37 (s(br), 2H); ^{13}C NMR (50.3 MHz), δ 141.7, 131.2, 128.6, 128.5, 126.0, 123.9, 35.8, 34.1; IR (neat) 3374, 3293, 3164, 3023, 2926, 2854, 1606, 1495, 1456, 1379, 1260, 1069, 928, 737 cm^{-1}; MS, *m/z* 179, 131, 91, 89, 88, 71, 57.

1-Cyclohexenesulfenamide (8g). ^{1}H NMR (200 MHz), δ 5.56 (m, 1H), 2.40 (s(br), 2H), 2.08 (m, 4H), 1.63 (m, 4H); ^{13}C NMR (50.3 MHz), δ 139.2, 117.5, 25.7, 25.5, 22.7, 22.3; IR (neat) 3391, 3306, 3038, 3011, 2930, 2857, 2834, 1686, 1638, 1569, 1441, 1333, 1263, 1136, 1051, 1022, 918, 834, 798 cm^{-1}; GCMS, *m/z* 129, 113, 81, 80, 79, 77, 71, 69, 53.

References and Notes

1. Presented in part at the 16th International Symposium on the Organic Chemistry of Sulfur, Merseburg, Germany, July 10-15, 1994 and at the 78th Canadian Chemical Conference, Guelph, Ontario, May 28-June 1, 1995. The authors wish to thank the Natural Sciences and Engineering Council of Canada for their generous funding of this research.
2. (a) Craine, L.; Raban, M. *Chem. Rev.* **1989**, *89*, 689. (b) Capozzi, G.; Modena, G.; Pasquato, L. In *The Chemistry of Sulfenic Acids and their Derivatives*; Patai, S., Ed.; J. Wiley & Sons: New York, 1990; p. 487.
3. Kost, D.; Raban, M. In *The Chemistry of Sulfenic Acids and their Derivatives*; Patai, S., Ed.; J. Wiley & Sons: New York, 1990; Chapt. 2.
4. (a) Bowman, W.R.; Clark, D.N.; Marmon, R.J. *Tetrahedron Lett.* **1992**, *33*, 4993. (b) Beckwith, A.L.J.; Maxwell, B.J.; Tsanaktsidis, J. *Aust. J. Chem.* **1991**, *44*, 1809. (c) Esker, J.L.; Newcomb, M. *Tetrahedron Lett.* **1993**, *34*, 6877. (d) Miura, Y.; Yamano, E. *J. Org. Chem.* **1995**, *60*, 1070. (e) Miura, Y.; Oka, H.; Yamano, E.; Teki, Y.; Takui, T.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1187.
5. (a) Yan, L.; Guishu, Y.; Yaozhong, J.; Tengkui, Y. *Synth. Commun.* **1995**, *25*, 1551. (b) Yang, T.-K.; Chen, R.-Y.; Lee, D.-S.; Peng, W.-S.; Jiang, Y.-Z.; Mi, A.-Q.; Jong, T.-T. *J. Org. Chem.* **1994**, *59*, 914.
6. Lovey, R.G.; Cooper, A.B. *Synlett* **1994**, 167.
7. Benati, L.; Capella, L.; Montevecchi, P.C.; Spagnolo, P. *Tetrahedron* **1994**, *50*, 12395.
8. Ren, X.F.; Konaklieva, M.I.; Turos, E. *J. Org. Chem.* **1995**, *60*, 4980.
9. Clennan, E.L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809.
10. Baudin, J.-B; Julia, S.A.; Ruel, O. *Tetrahedron* **1987**, *43*, 881.
11. (a) Capozzi, G.; Gori, L.; Menichetti, S.; Nativi, C. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1923. (b) Busi, E.; Capozzi, G.; Menichetti, S.; Nativi, C. *Synthesis* **1992**, 643. (c) Capozzi, G.; De Sio, F.; Menichetti, S.; Nativi, C.; Pacini, P.L. *Synthesis* **1994**, 521.
12. Barton, T.J.; Zika, R.G. *J. Org. Chem.* **1970**, *35*, 1729.
13. Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135.

14. Refvik, M.D.; Froese, R.D.J.; Goddard, J.D.; Pham, H.H.; Pippert, M.F.; Schwan, A.L. *J. Am. Chem. Soc.* **1995**, *117*, 184.
15. Aspects of this project have been published in communication form. See: Schwan, A.L.; Refvik, M.D. *J.C.S. Chem. Commun.* **1995**, 1949.
16. Sulfenate anions can be functionalized at either oxygen or sulfur, see Hogg, D.R.; Robertson, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1125.
17. The exact role that cyclohexene plays in eliminating the formation of disulfide is unclear especially since no byproducts were detected. One possibility is that small amounts of sulfenyl chloride or silyl sulfenate ester that would normally be the source of disulfide are captured by electrophilic addition across cyclohexene. The β-chlorosulfide that results has an electron rich vinyl sulfide double bond which would be expected to react faster with more sulfenyl chloride than would cyclohexene. Thus, a series of sequential additions of sulfenyl chloride to a single molecule would furnish an oligomer that may not survive the work-up procedure. To test this theory, dihydropyran was used instead of cyclohexene as an electron rich alkene that would be more competitive with vinyl sulfide in the reaction with sulfenyl chloride and hence would reduce the amount and size of any oligomer. However, no addition products to dihydropyran could be detected.
18. Other mechanisms can also be envisioned and are under investigation, as are the reactions of the sulfenates with other TMSX reagents.
19. (a) Davis, F.A.; Rizvi, S.Q.A.; Ardecky, R.; Gosciniak, D.J.; Friedman, A.J.; Yocklovich, S.G. *J. Org. Chem.* **1980**, *45*, 1650. (b) Chou, T.S. *Tetrahedron Lett.* **1974**, 725.
20. We ,suggest amide substitution rather than amine substitutions since both of our idealized reactions conditions involve the addition of excess LiHMDS.
21. It should be noted that the yields reported in Table 1 are based on starting thiirane *S*-oxide (**4**). We have previously reported that the thiirane *S*-oxides are converted to the alkenesulfenates in 70±10% yield (Ref. 14). Hence the yields of the silylation and subsequent amide substitution as shown in Scheme 2 are really more accurately quantitated as (50-60%)/(ca. 0.7) = 71-86%. Moreover, the yield calculations are based on sulfur containing substrate, even though TMSCl is the limiting reagent.
22. Morimoto, T.; Nezu, Y.; Achiwa, K.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1584.
23. (a) Boivin, J.; Fouquet, E.; Zard, S.Z. *Tetrahedron* **1994**, *50*, 1757. (b) Ruel, O.; Baudin, J.-B.; Julia, S.A. *Synth. Commun.* **1990**, *20*, 2151.
24. Boche, G.; Walborsky, H.M. In *Cyclopropane Derived Reactive Intermediates* Patai, S.; Rappoport, Z. Eds.; John Wiley & Sons: Chichester, 1990; pp. 68-76.
25. Reactions were attempted with carbonyl substrates such as butyraldehyde, acetophenone and cyclohexanone, but the reactions always contained **8** and usually contained sulfenimine **7**. Crude ^{1}H NMR spectra of the reactions showed that the **7**:**8** ratio ranged from 0:100 to 50:50. Purification of these mixtures was difficult and was not pursued.
26. For calculation method, see: Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH: Deerfield Beach, 1985; p. 5.
27. (a) Claus, P.K. In *The Chemistry of Sulfenic Acids and their Derivatives*: Patai, S., Ed.; J. Wiley & Sons: New York, 1990; p. 726. (b) See ref. 26, p. 359.
28. If the TBAF is not adsorbed on a solid substrate, then the sulfenamide sample is contaminated by significant amounts of $(n\text{-Bu})_3$N.
29. Any further concentration leads to decomposition of the sulfenamide.
30. (a) Schwan, A.L.; Pippert, M.F. *Tetrahedron: Asymmetry* **1995**, *6*, 131. (b) Schwan, A.L.; Brillon, D.; Dufault, R. *Can. J. Chem.* **1994**, *72*, 325.
31. For this set of experiments the TBAF in THF solution was prepared as follows. Solid TBAF·$3H_2O$ (ca. 140 mg) in a vessel was pumped on under high vacuum for 1h. After cooling the vessel to 0 °C and flushing with N_2, THF (10 mL) was added. The solution was transferred to a second vessel containing 4Å molecular sieves which had been thoroughly flame-dried. After stirring for 0.5 h, this solution was ready for use.
32. The yields were not obtained since the sulfenamides contained solvent and mass recovery appeared to be very low (ca. 10-20%). An unfavorable partition into pentane (vs. MeCN) may account for the low recovery. Other approaches to sulfenamides **8** did not provide discernible spectroscopic data.

(*Received in USA* 13 *March* 1996; *accepted* 26 *April* 1996)