Transamination Studies on *N*-(1-Alkenylthio)phthalimides and Related Compounds. Synthesis of 1-Alkenesulfenamides and 1-Alkenesulfonamides[1]

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In an attempt to develop a method for the general preparation of 1-alkenesulfenamides, some *N*,*N*-bis(trimethylsilyl)-1-alkenesulfenamides (**4**) were converted to a number of nitrogen functionalized analogs through desilylation and acylation procedures. Mono- and dibenzoylated derivatives **5a** and **6a** did not undergo transamination reactions with simple amines. Transamination reactions could be achieved once compounds **4** were converted to thiophthalimides **7**. The transamination products **8** are unstable to chromatography, but could be oxidized to 1-alkenesulfonamides **9** using MCPBA. Some of the sulfenamides **8** may be stable to distillation. 3-(Alkenylthioimino)phthalides **11**, isomers of thiophthalimides **7**, also react with amines, but the process of ring opening accompanies transamination. It was found that the transamination reactions of **11** probably involve the intermediacy of isomers **7**.

Sulfenamides **1** have long been of interest to both the fundamental chemist and the industrial chemist.[2] In industry, sulfenamides have found uses as pesticides,[2,3] rubber vulcanization accelerators,[2,4] and as spontaneously igniting rocket fuels.[5] The interesting chiroptical properties of sulfenamides, based on the S−N bond, have been studied extensively particularly by the groups of Raban and Kost.[6,7]

Sulfenamides have enjoyed a resurgence in recent years due to the development of new applications for them. For instance, a number of groups are now utilizing *S*-phenyl sulfenamides as a source of aminyl,[8] amidyl,[9] and thioaminyl[10] radicals. Sulfenamides are key intermediates in syntheses of chiral amines[11] and amino acids.[12] The Montevecchi group has utilized *S*,*N*-diaryl sulfenamides as sources of electrophilic arylthio units.[13] The sulfur of a methanesulfenamide has been used as the internal nucleophile in an iodocyclization reaction that affords inversely fused bicyclic β-lactams.[14] Also of interest is the surprising reactivity of sulfenamides with singlet oxygen as reported by Clennan and Zhang.[15]

Typical methods of synthesis of sulfenamides may involve amine or metal amide attack of sulfenic acid derived materials RSX, where X may be a halogen, phthalimide, alkoxy group, or sulfur-bearing functionality.[2] Another method involves combining an amine and a thiol in an oxidative environment.[2] Disulfides are useful starting materials and can be converted to sulfenamides when treated with chloramines or chloramides[2] or with lithium amides.[16] Davis has shown that amines and disulfides react in the presence of silver or mercuric salts to afford sulfenamides.[17]

Most of the sulfenamides known in the literature possess alkyl, haloalkyl, or aryl groups on the sulfur. Only a few groups have reported sulfenamides that retain an 1-alkenyl unit attached to the sulfur atom.[18−22] Baudin and co-workers have treated aminosulfenyl chlorides with vinyl Grignards to produce ethenesulfenamides, which can be transaminated with aromatic amines.[18] Two *N*-(1-naphthyl)ethenesulfenamides prepared by that group were converted to 1*H*-benzo[*g*]indoles upon thermolysis.[18] The Capozzi/Menichetti group has also contributed in the

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(4) Hofmann, W. *Rubber Technology Handbook*; Hanser Publishers: Munich, 1989; pp 233−255.

(5) Ayers, A. L.; Scott, C. L. US Patent 2,932,941. (*Chem. Abstr.* **1960**, *54*, 14690d)

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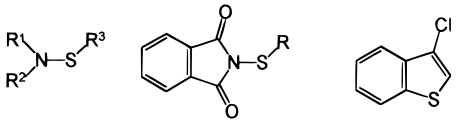
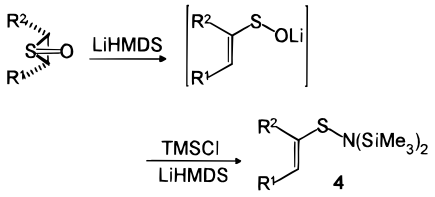


1 **2a**, R = 2-chloro-1-alkenyl **2b**, R = aryl, alkyl **3**

area; their synthesis of alkenesulfenamides represented by structure **2a** involves the electrophilic addition of phthalimidosulfenyl chloride across alkynes.[19−21] The resulting [(2-chloroalkenyl)thio]phthalimides **2a** demonstrate electrophilicity at sulfur, and the phthalimido component can be replaced by nucleophiles such as *tert*-butyllithium, hexamethyldisilazide, and acetylide.[19,20] The latter reaction represents a valuable synthesis of alkynyl alkenyl sulfides.[20] Those researchers also reported the conversions of alkenesulfenamides of the type **2a** to 3-chlorobenzo[*b*]thiophenes (**3**).[21]

Scheme 1

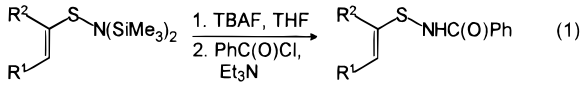


We have recently communicated a new preparation of *N*,*N*-bis(trimethylsilyl)-1-alkenesulfenamides (**4**), a new family of 1-alkenesulfenamides.[1] That chemistry was achieved through the deprotonation of thiirane *S*-oxides with LiHMDS, and quenching of the intermediate 1-alkenesulfenate with TMSCl and more LiHMDS as shown in Scheme 1.[23,24] The synthetic utility of 1-alkenesulfenamides reported above prompted us to develop a means to transform 1-alkenesulfenamides **4** into a larger family of 1-alkenesulfenamides. Previous preparations of alkane- and arenesulfenamides that employed transamination reactions on compounds **2b** were chosen as model reactions, and we sought to develop methods for the desilylation and acylation of compounds **4**. We now provide full details of our preparations and transamination attempts of various acylated 1-alkenesulfenamides.[25,26]

Results and Discussion

Initial attempts to synthesize a larger family of 1-alkenesulfenamides involved direct transamination attempts on compounds **4**. These experiments met with unsatisfactory results: either there was no reaction or significant decomposition accompanied any transaminations that did proceed. The doubly silylated nitrogen proved resolute under various conditions including those reported for transamination of other 1-alkenesulfenamides.[18]

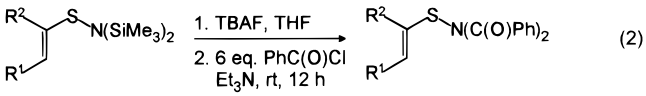
The robust behavior of sulfenamides **4** under typical transamination conditions prompted a different approach. It was decided that the nitrogen of **4** should be functionalized in order to make it a better leaving group. The strategy would also provide an opportunity to examine some of the chemistry of silylated alkenesulfenamides **4**. The first reaction explored was double desilylation of the nitrogen followed by acylation, since an acylated nitrogen would be expected to possess better leaving capability than a silylated one. It was found that the conversion could be effected in satisfactory yield when a mixture of **4** and wet TBAF in THF was treated with Et_3N and excess benzoyl chloride as indicated in reaction 1. Several attempts to transaminate *N*-benzoyl-1-hexenesulfenamide (**5a**) with piperidine under neutral and Lewis acid catalysis conditions responded with only starting materials.



(1)

4a, R¹, R² = *n*-Bu, H **4b**, R¹, R² = -$(CH_2)_4$- **5a**, 68% **5b**, 41%

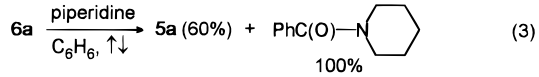
Since the single acyl group on the nitrogen provided insufficient activation for the reaction, we searched for an approach to the installation of two acyl groups on a single sulfenamide nitrogen. Two concepts immediately came to mind: the desilylation and double acylation of **4** using 2 equiv of a monofunctional acid chloride and the introduction of a phthalimido group by some means. The double acylation was achieved first by treating compounds **4a** and **4b** with TBAF followed by 6 equiv of benzoyl chloride as shown in reaction 2. Compounds **6a** and **6b** could be isolated in good yield,[27] and **6a** was



(2)

4a, **4b** **6a**, 84%; **6b**, 66%

subjected to transamination conditions of piperidine in refluxing benzene. The result was consumption of **6a**, but the product arose through amine substitution at a carbonyl carbon rather than at sulfur (reaction 3). Such a reaction is consistent with the instability of compounds



(3)

6 with respect to loss of a benzoyl unit.[27] It was felt that the desired transamination chemistry may occur more

(23) For details of the conversion of thiirane *S*-oxide to 1-alkenesulfenate, see 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.

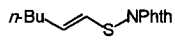
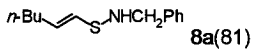
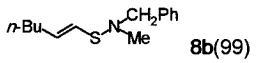
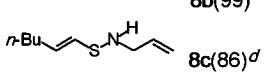
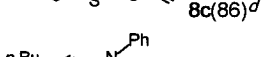
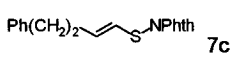
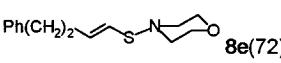
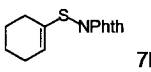
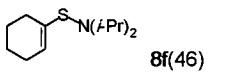
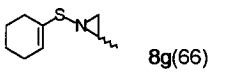
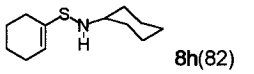
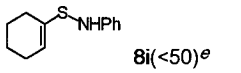
(24) Full practical details of the preparation of compounds **4** will presented elsewhere.

(25) (a) Harpp, D. N.; Back, T. G. *Tetrahedron Lett.* **1971**, 4953. (b) Boustany, K. *Chimia* **1970**, 396.

(26) One possible method of preparing 1-alkenesulfenamides with nitrogen substituents other than silicons would be to have the appropriate amine or amide present during the TMSCl quenching of the 1-alkenesulfenate. We have tried such experiments, but even with 10 equiv of dialkylamine present, the silylated sulfenamide is still the major product. The use of LDA rather than LiHMDS to deprotonate the thiirane *S*-oxide, is not a viable means of preparing pure sulfenamide bearing non-silicon substituents on nitrogen, since that chemistry yields two isomeric 1-alkenesulfenates (see ref 23). Hence, we treated *anti*-*n*-butylthiirane *S*-oxide (**4a**) with excess LDA and TMSCl. Analysis of the mixture by ^{1}H NMR and GC/MS revealed two isomeric *N*,*N*-bis(1-methylethyl)hexenesulfenamides in an expected ratio.

(27) Compounds **6** are not particularly stable: they have a limited lifetime in the freezer and do not exhibit ideal chromatographic behavior. Loss of a benzoyl unit is one of their fates. For this reason, satisfactory elemental analysis could not be obtained. A referee has suggested that compounds **6** may not have the structures that we have assigned to them, but that they could possess C=O and C=N bonds rather than two C=O bonds. Indeed, based on our synthetic method, structures such as 1-alkenyl-SN=C(Ph)OC(O)Ph would also conform with the measured spectral data. The alternative isomers would also be expected to undergo chemistry consistent with our experimental observations.

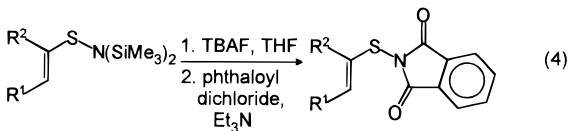
Table 1. Transamination Reactions of Thiophthalimides 7

entry	starting thiophthalimide	amine[a]	conditions[a]	transamination products (crude yields, %)[b]	sulfonamide # (%)[c]
1	 **7a**	benzylamine	PhH, rt, 2 h	 **8a**(81)	**9a**(67)
2		benzylmethylamine	PhH, rt, 2 h	 **8b**(99)	**9b**(73)
3		allyltrimethyl-silylamine	PhH, reflux 4 h	 **8c**(86)[d]	**9c**(53)
4		*N*-allylaniline	EtOH reflux 16 h	 **8d**(<68)	**9d**(35)
5	 **7c**	morpholine	PhH, rt, 2 h	 **8e**(72)	**9e**(63)
6	 **7b**	LDA	THF, -78 °C-rt	 **8f**(46)	**9f**(25)
7		2-methylaziridine	PhH, rt, 2 h	 **8g**(66)	**9g**(60)
8		cyclohexylamine	PhH, rt, 2 h	 **8h**(82)	**9h**(67)
9		aniline	EtOH reflux 16 h	 **8i**(<50)[e]	--[e]

[a] See Experimental Section for full details. [b] ^{1}H and ^{13}C NMR data were acquired for most of these compounds. Yields are estimated from the ^{1}H NMR spectra. [c] Yield of isolated, pure 1-alkenesulfonamides **9**. [d] Protodesilylation occurred prior to analysis of the sulfenamide. [e] Oxidation of **8i** was unsuccessful. Spectral data acquired for **8i** was consistent with the assigned structure, but not particularly diagnostic. No further structural proof was obtained.

readily if the doubly acylated nitrogen was part of a phthalimide ring,[25] so the conversion of compounds **4** to alkenylthiophthalimides became our focus.

Using alkenesulfenamide **4a** as a model compound, the desilylation of the nitrogen and ensuing introduction of the phthaloyl moiety was extremely difficult. Several experiments showed that phthaloyl dichloride was the preferred phthalic acid derivative and that more than 2 equiv of fluoride were required; the reaction was eventually realized, and three thiophthalimides **7** were obtained (70−78%, reaction 4). Transaminations with various amines proceeded smoothly in benzene[25] for monoalkyl-

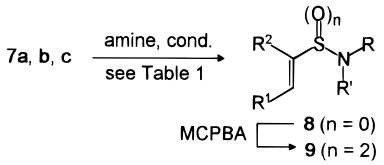


(4)

4a, R^1, R^2 = *n*-Bu, H
4b, R^1, R^2 = -(CH$_2$)$_4$-
4c, R^1, R^2 = CH$_2$CH$_2$Ph, H

7a, 78%
7b, 73%
7c, 70%

and dialkylamines, but arylamines required heating in ethanol (reaction 5). Workup included addition of pentane and filtration of the solid phthalimide. Concentra-



(5)

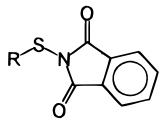
tion of the pentane/reaction solvent mixture afforded crude 1-alkenesulfenamides **8**. The sulfenamides did not behave well on silica gel nor alumina (basic or neutral). On alumina, pure material could be obtained but with <50% mass recovery. Hence, after concentration and acquisition of a crude yield and NMR data, 1-alkenesulfenamides **8** were oxidized to their corresponding 1-alkenesulfonamides **9** for full characterization. Conditions similar to those adopted previously for a sulfinamide to sulfonamide conversion[28] were employed (3 equiv of MCPBA/K_2CO_3/rt/1−3 days). The crude yields of sulfenamide **8** and isolated yields of sulfonamide **9** are recorded in Table 1.

The reaction works reasonably well for primary and secondary alkylamines but not for aniline or *N*-allylaniline. In those cases, the transamination was very sluggish and yields were lower. Furthermore, the subsequent oxidation to *N*-aryl 1-alkenesulfonamide involved significant losses, and the oxidation of **8i** did not provide any sulfonamide. The use of LDA as a nucleophile resulted in sulfenamide **8f** in 46% yield; thiophthalimide **7b** proved inert when treated with diisopropylamine.

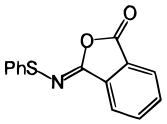
The utility of this transamination approach is accentuated when compared to previous work. It has been shown that the reaction of cyclohexylamine with sulfenamide **10**, the saturated analog of **7b**, proceeds via attack at a phthalimido carbonyl followed by ring opening, rather than by transamination.[29] In contrast, cyclohexylamine effected clean transamination on **7b**. The reason for this is not entirely clear; steric hindrance to attack at sulfur, perhaps slightly smaller in **7b** than in **10**, is essentially identical. However, the conjugation of the sulfur electrons with the double bond make the sulfur a more electrophilic atom and it is possible that this renders the sulfur of **7b** more prone to attack by amine.

The chemistry shown in entry 3 of Table 1 is also of note. Although allyltrimethylsilylamine was the starting

(28) Baudin, J.-B.; Julia, S. A.; Wang, Y. *Synlett* **1992**, 911.
(29) Boustany, K.; Vander Kooi, J. P. *Tetrahedron Lett.* **1970**, 4983.



7b, R = 1-cyclohexenyl
10, R = cyclohexyl



12

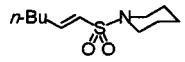
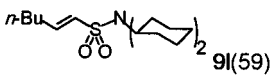
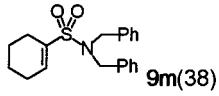
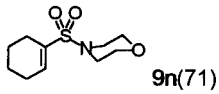
amine, the product recovered (**8c**, **9c**) had lost the TMS group. Since there is no reason to expect the loss of the TMS group before the reaction of the amine, it follows that the silyl group is lost at some point during the isolation of **8c**. The good yield of **8c** indicates that the protodesilylation occurs both readily and cleanly. This is noteworthy since previous attempts to transaminate *S*-aryl- and *S*-alkylthiophthalimides (**2b**) with primary amines have met with limited success. The reaction is problematic since ring opening of the thiophthalimide by the amine is a competitive process, as discussed in the preceding paragraph.[25] From our observations it would appear that the use of silylalkylamines for the synthesis of *N*-monoalkyl arene- and alkanesulfenamides through transamination chemistry of the corresponding thiophthalimides (**2b**) may be a method to circumvent the ring opening reaction. The silylalkylamine would effect transamination like a dialkylamine but would provide the product containing a lone alkyl group on nitrogen. The unwanted ring opening reaction is expected to be sterically deterred by the presence of the silyl and alkyl groups on the amine.

In the reaction of **7b** with 2-methylaziridine, the crude ^{1}H NMR indicated two sets of peaks consistent with the transamination product **8g**. These were originally thought to be pairs of diastereomers due to the asymmetric carbon of the heterocycle and to either a torsional or inversional barrier as previously observed for sulfenyl aziridines.[30] Consistent with this assignment was the fact that the oxidation of this material afforded a single isomer (**9g**), since sulfonamides have reduced isomerization barriers compared to sulfenamides. A sample of **8g** was subjected to variable temperature ^{1}H NMR analysis in an attempt to confirm the presence of two diastereomers. However, there was no coalescence of the cyclohexenyl vinyl hydrogens up to 185 °C.[31] In light of this result and the known low barriers for sulfenyl aziridine isomerization, there were probably not two diastereomers present in the original mixture. Rather, the minor component was more likely an impurity that did not survive the oxidation.

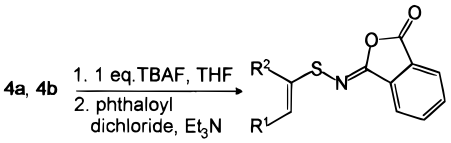
A transamination was performed on a larger scale using thiophthalimide **7b** and dimethylamine in benzene. The crude yield was found to be 96% and the material was subjected to a short-path distillation at reduced pressure. The crude mixture (1.40 g) yielded 1.02 g (78%) of *N*,*N*-dimethyl-1-cyclohexenesulfenamide (**8j**). Distillation of other, heavier systems provided sulfenamide, but some decomposition was also evident.

During our studies toward the preparation of thiophthalimides **7** using phthaloyl dichloride, 3-(thioimino)phthalide **11** was often observed as a byproduct and was occasionally obtained as the major product. The thioiminophthalide represents an isomer of **7** and is presumably the kinetic product of the reaction under certain experimental conditions. Upon standing for several days at room temperature, a small amount of a solid sample of compound **11a** had isomerized to **7a**. For reasons discussed in the next paragraph, deliberate effort was made to prepare thioiminophthalides **11a** and **11b**. Their synthesis was eventually realized through the use of only 1 equiv of fluoride followed by addition of phthaloyl dichloride (reaction 6).

Table 2. Transamination Reactions of Thiooximes 11[a]

#	11	amine[b]	cond.[c]	sulfonamide # (%)
1	**11a**	benzyl-methylamine	rt, 16 h	**9b**(47)
2		piperidine	rt, 16 h	 **9k**(50)
3		dicyclohexyl-amine	↑↓ 16 h	 **9l**(59)
4	**11b**	dibenzyl-amine	↑↓ 8 h	 **9m**(38)
5		morpholine	rt, 16 h	 **9n**(71)

[a] Transaminations were immediately followed by oxidation; yields of sulfonamide are reported. [b] See discussion for chemistry involving primary amines. [c] Solvent was benzene in each instance.



4a, **4b** → 1. 1 eq. TBAF, THF; 2. phthaloyl dichloride, Et_3N → **11a**, 61%; **11b**, 67% (6)

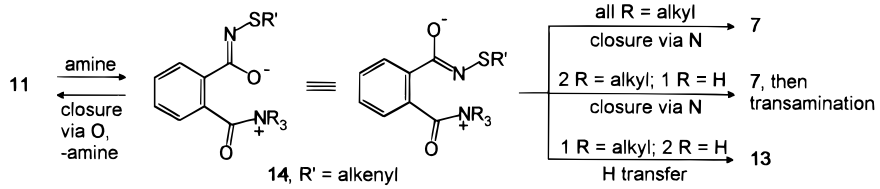
Phthalide-derived compounds **11** are intriguing compounds; they appear yellow (UV/vis: λ_{max} = 356 nm) while thiophthalimides **7** are colorless. Another distinguishing feature is a more complicated aromatic region in their ^{1}H and ^{13}C NMR spectra. To our knowledge, only one 3-(thioimino)phthalide has been reported previously: 3-[(phenylthio)imino]phthalide (**12**) was obtained in low yield from the reaction of tribenzenesulfenamide with phthalic anhydride.[32] No chemistry of **12** was reported and since we had developed a route to a rare pair of sulfenamides, it was decided to explore their ability to act as alkenylthio transfer agents.

Some initial reactions indicated that species **11** were prone to substitution at sulfur and hence may act as surrogates for the thiophthalimides as intervening compounds in the overall transamination of silylated sulfenamides **4**. Once again the transamination products were characterized and quantitated through oxidation to the sulfonamide. Only secondary amines provided clean transamination products; Table 2 indicates the products and yields. Yields are lower compared to transaminations of thiophthalimides **7**.

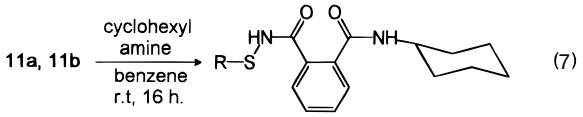
Primary amines proved troublesome and did not effect efficient transaminations. Only with cyclohexylamine were stable products obtained (reaction 7).[33] The prod-

(30) Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1976**, *98*, 8333.
(31) The solvent was DMSO. The sample decomposed rapidly above 185 °C.
(32) Almog, J.; Barton, D. H. R.; Magnus, P. D.; Norris, R. K. *J. Chem. Soc., Perkin Trans. 1* **1974**, 853.
(33) Other primary amines afforded mixtures containing a number of constituents whose identity changed thoughout workup. One component, isolated from a transamination attempt with *n*-hexylamine, was determined to be *N*,*N*′-di(1-hexyl)phthalamide (19%).

Scheme 2



ucts **13** appear to arise from a ring opening reaction that occurs through attack at the carbonyl of **11**. Acyl



15a, R = 1-hexenyl, 63%
b, R = 1-cyclohexenyl, 63%

sulfenamides **13** belong to a family of sulfenamides prepared previously by the reaction of primary amine with *S*-alkyl and *S*-aryl thiophthalimides (**2b**).[25a,29] Indeed, aid in assigning the structure of compounds **13** was found through review of the data previously reported. Particularly diagnostic were the two broad NH resonances, providing ^{1}H NMR chemical shifts of δ 8.17 and 6.36 (for **13a**) and δ 8.12 and 6.41 (for **13b**) which are consistent with the analogous chemical shifts of the *S*-alkyl congeners.[29,34,35]

Clearly, 3-[(alkenylthio)imino]phthalides **11** are more predisposed to ring opening than are thiophthalimides **7**. However, the iminophthalides react similarly to (*S*-alkyl- and (*S*-arylthio)phthalimides[25,29] in that secondary amines execute clean transamination, whereas primary amines are more prone to carbonyl attack and ring opening. Important mechanistic evidence was uncovered in the reaction of dibenzylamine with **11b**. When TLC indicated complete consumption of **11b**, the mixture was found to contain dibenzylamine, transamination product **8m**, *and thiophthalimide* ***7b***. Since the transamination reactions of iminophthalides **11** were significantly slower than those of **7**, it became apparent that the amine was involved in a rate-determining isomerization of **11** to **7** *before* consummating a transamination reaction. To find support for the premise, **11b** was exposed to triethylamine, a nucleophile that would bring about neither transamination nor irreversible ring opening, but could induce isomerization. After 16 h, analysis of the mixture showed 28% conversion to **7**. Further supporting evidence for the isomerization before transamination premise is the identity of the byproduct of the "iminophthalide" transaminations: in each case the phthaloyl-containing moiety was found to be phthalimide, the same material obtained from the transaminations of compounds **7**. There is precedent for an aprotic nucleophile inducing the iminophthalide to phthalimide conversion in a system that does not contain a sulfur.[36]

It would seem that the role of amine is not that of simple substitution at the sulfur of iminophthalides **11** to afford transaminated products **8**. On the basis of the evidence, we prefer to invoke an initial amine induced isomerization of **11** to **7**, followed by amine substitution at the sulfur of **7**. If this mechanism is indeed operable, then at some point, there must be differentiation between secondary and primary amines that accounts for the observed reaction products. The isomerization most likely occurs by reversible amine attack at the carbonyl carbon. From this point, Scheme 2 demonstrates the three options available for the ionic species **14**. Tertiary amine provides **7** and nothing more; secondary amine also affords **7** but subsequently reacts with **7**. In the instance where primary amine has opened **11**, the fate of **14** involves a hydrogen transfer on the way to **13**.

The different fates of **14** and their relation to the type of amine attached are presumably due to a number of reasons. Factors that should favor closure to **7** over proton transfer may include the fewer hydrogens on the amine and the reduced ability of the nitrogen to adopt the proper conformation for loss of a proton.[37] There are certainly other steric and conformational factors at play in this system.

Conclusions

There are a few published reports of the synthesis and useful transformations of certain 1-alkenesulfenamides. Prompted in part by that previous work, we have prepared various *N*-acylated 1-alkenesulfenamides through derivatization of *N*,*N*-bis(trimethylsilyl)-1-alkenesulfenamides (**4**). Through the agency of some of these acylated sulfenamides and thiophthalimides **7** in particular, we have demonstrated a synthetic approach to a number of 1-alkenesulfenamides bearing different alkyl groups on nitrogen (**8**). Indeed, it would seem that compounds **7** are more prone to transamination than their saturated analogs. The *N*-alkylated sulfenamides **8** are not very stable to chromatography, but can be distilled if they possess a low molecular weight. 1-Alkenesulfenamides **8** were oxidized to their corresponding sulfonamides, and this chemistry also serves as one of the few synthetic approaches to 1-alkenesulfonamides.[28] Overall, our work provides a method for the synthesis of a large number of 1-alkenesulfenamides bearing nonspecialized substituents on sulfur or nitrogen. Moreover our study has

(34) The δ 6.41 resonance of **13b** appears a doublet, allowing it to be assigned as the hydrogen on the nitrogen attached to the cyclohexyl group. The 6.36 ppm resonance of **13a** appeared as a doublet in crude ^{1}H NMR spectra, but not in the spectrum of pure material.

(35) The isolation and structural assignment of compounds **13** prompted a reexamination of the crude ^{1}H NMR spectra of the alkenesulfenamides **8** generated from transaminations of thiophthalimides **7**. Only in the synthesis of sulfenamide **8a** did we observe a ring-opening product of the type **13** (ca. 10%). Other experiments have shown that the ring-opened product would not survive the oxidation process.

(36) Azide ion was the nucleophile, (*tert*-butylimino)phthalide was the substrate, see: Keung Au, T.; Baydar, A. E.; Boyd, G.V. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2884.

(37) Expeditious proton removal from the quaternary nitrogen of **14** requires that the lone pair left behind is in conjugation with the carbonyl, see: Perrin, C. L. *Acc. Chem. Res.* **1989**, *22*, 268. It would seem logical that with more hydrogens on the nitrogen, the required conformation will be more achievable and the hydrogen transfer more rapid.

provided valuable information regarding the physical properties of such sulfenamides.

Experimental Section

General. Most of our general experimental methods have been reported previously.[23,38] Elemental analyses were performed by M-H-W Labs, Phoenix, AZ. The synthesis of sulfenamides **4** has been reported previously.[1] TMSCl and phthaloyl dichloride were purchased from Aldrich and used without purification. Piperidine (Fisher) was distilled before use, while the other amines were used as received from commercial sources. The TBAF used was 1.0 M in THF.

Desilylation and Monobenzoylation of Alkenesulfenamides 4. To a solution of alkenesulfenamide **4** (62−74 mg, 0.22−0.27 mmol) in THF (10 mL) stirring at 0 °C was added TBAF (1 M in THF, 1.0 equiv) followed by Et_3N (neat, 2 equiv) and benzoyl chloride (neat, 2 equiv). The solution was stirred for 15 min at 0 °C and for 1 h at rt. Water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic extracts were washed with water and brine and were dried over Na_2SO_4. Filtration and concentration afforded crude *N*-benzoyl sulfenamide **5**. The crude material was chromatographed on basic alumina (I) (15% EtOAc in hexanes) to afford pure **5**.

***N*-Benzoyl-(*E*)-1-hexenesulfenamide (5a):** 68%, oil. ^{1}H NMR (400 MHz), δ 7.82 (d, 7.0 Hz, 2H), 7.56−7.44 (m, 3H), 7.09 (s(br), 6.14 (d, J = 14.9 Hz, 1H), 5.82 (dt, J = 14.9, 7.0 Hz, 1H), 2.10 (q, J = 7.0 Hz, 2H), 1.40−1.25 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 168.8, 133.5, 133.1, 132.2, 128.7, 127.5, 124.2, 32.2, 31.0, 22.1, 13.8. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95. Found: C, 66.47; H, 7.39; N, 5.94.

***N*-Benzoyl-1-cyclohexenesulfenamide (5b):** 41%, oil. ^{1}H NMR (400 MHz), δ 7.83 (d, J = 7.8 Hz, 2H), 7.55 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.04 (s(br), 1H), 5.83 (s(br), 1H), 2.18−2.14 (m, 2H), 2.12−2.08 (m, 2H), 1.72−1.65 (m, 2H), 1.63−1.55 (m, 2H); ^{13}C NMR (100.6 MHz), δ 169.0, 134.8, 133.5, 132.2, 128.7, 127.5, 123.8, 26.7, 25.9, 22.9, 21.8. Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00. Found: C, 65.72; H, 6.68; N, 5.86.

Desilylation and Dibenzoylation of Alkenesulfenamides 4. To a solution of alkenesulfenamide **4** (256−301 mg, 0.93−1.10 mmol) in THF (15 mL) stirring at 0 °C was added TBAF (1 M in THF, 1.0 equiv) followed by Et_3N (neat, 6 equiv) and benzoyl chloride (neat, 6 equiv). The solution was stirred for 10 min at 0 °C and overnight at rt. Water (30 mL) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic extracts were washed with water and brine and were dried over Na_2SO_4. Filtration and concentration afforded crude *N*,*N*-dibenzoyl sulfenamide **6**. The crude material was chromatographed on basic alumina (I) (15% EtOAc in hexanes) to afford compounds **6**.

***N*,*N*-Dibenzoyl-(*E*)-1-hexenesulfenamide (6a):** 84%, pale yellow oil. ^{1}H NMR (400 MHz), δ 8.23 (d, J = 7.3 Hz, 2H), 7.78−7.34 (m, 8H), 6.50 (d, J = 15.9 Hz, 1H), 5.93 (dt, J = 15.9, 7.0 Hz, 1H), 2.17 (q, J = 7.0 Hz, 2H), 1.44−1.26 (m, 4H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 161.9, 147.4, 134.2, 131.6, 131.0, 130.6, 130.4, 128.8, 128.5, 127.9, 126.7, 124.3, 32.5, 31.1, 22.1, 13.9. HRMS Calcd for $C_{20}H_{21}NO_2S$: 339.1293. Found: 339.1287.

***N*,*N*-Dibenzoyl-1-cyclohexenesulfenamide (6b):** 66%, pale yellow oil. ^{1}H NMR (200 MHz), δ 8.25 (m, 2H), 7.79−7.33 (m, 8H), 6.09 (m, 1H), 2.48−2.44 (m, 2H), 2.21−2.13 (m, 2H), 1.86−1.49 (m, 4H); ^{13}C NMR (50.3 MHz), δ 162.3, 146.9, 134.3, 132.7, 132.1, 130.6 (2 C's), 129.3, 128.9, 128.7, 126.9, 125.6, 27.5, 25.9, 23.0, 21.8. HRMS Calcd for $C_{20}H_{20}NO_2S$, $(M + H)^+$: 338.1215. Found: 338.1221.

Reaction of *N*,*N*-Dibenzoyl-(*E*)-1-hexenesulfenamide (6a) with Piperidine. A mixture of sulfenamide **6a** (187 mg, 0.55 mmol) and piperidine (47 mg, 0.55 mmol) in benzene was refluxed for 2 h. The mixture was concentrated and chromatographed (silica gel, 15% EtOAc in hexanes and then 100% EtOAc) to afford sulfenamide **5a** (78 mg, 60%) followed by *N*-benzoylpiperidine (104 mg, 100%).

Preparation of (*S*-Alkenylthio)phthalimides 7. To a flame-dried flask under N_2 was added sulfenamide **6** (1−3 g, 3−11 mmol) and dry ether (200 mL). The flask was cooled to 0 °C and TBAF (2 molar equiv, 1 M in THF, freshly opened bottle) was added. The mixture was allowed to come to rt over 20 min and then was cooled to −78 °C for the addition of Et_3N (6 equiv) and phthaloyl dichloride (3 equiv). The mixture was transferred to an ice bath for 1 h and then was stirred at rt for 2 h. After suction filtration through Celite with the aid of EtOAc, the filtrate was transferred to a separatory funnel and saturated aqueous NH_4Cl (80 mL) was added. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic extracts were washed with saturated aqueous Na_2CO_3 (4 × 60 mL), saturated aqueous NH_4Cl (3 × 60 mL), water (2 × 60 mL), and brine (60 mL). The organic layer was dried over Na_2SO_4. Filtration, concentration, and flash chromatography (silica gel, 10% EtOAc in hexanes) afforded stable solids which could be recrystallized from EtOAc/hexanes to afford analytically pure thiophthalimides **7**.

***N*-[(*E*)-1-Hexenylthio]phthalimide (7a):** 78%, mp 37−38 °C. ^{1}H NMR (400 MHz), δ 7.95−7.90 (m, 2H), 7.81−7.75 (m, 2H), 6.20−6.11 (m, 2H), 2.09 (m, 2H), 1.47−1.22 (m, 4H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 167.7, 140.0, 134.6, 132.1, 123.9, 121.3, 32.2, 30.5, 22.1, 13.8. Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.52; H, 6.00; N, 5.43.

***N*-(1-Cyclohexenylthio)phthalimide (7b):** 73%, mp 83.5−84 °C. ^{1}H NMR (400 MHz), δ 7.98−7.92 (m, 2H), 7.82−7.77 (m, 2H), 6.11 (s(br), 1H), 2.15−2.08 (m, 4H), 1.68-1.60 (m, 2H), 1.59−1.53 (m, 2H); ^{13}C NMR (100.6 MHz), δ 168.2, 134.6, 133.0, 131.9, 129.5, 124.0, 27.8, 26.1, 22.8, 21.4. Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.70; H, 5.08; N, 5.44.

***N*-[(4-Phenyl-(*E*)-1-butenyl)thio]phthalimide (7c):** 70%, mp 123−123.5 °C. ^{1}H NMR (400 MHz), δ 7.95−7.93 (m, 2H), 7.80−7.78 (m, 2H), 7.23−7.19 (m, 2H), 7.14−7.10 (m, 3H), 6.17−6.11 (m, 2H), 2.68 (t, J = 7.3 Hz, 2H), 2.40 (m, 2H); ^{13}C NMR (100.6 MHz), δ 167.6, 140.8, 137.8, 134.6, 132.1, 128.4, 128.3, 126.0, 124.0, 122.3, 34.9, 34.3. Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53. Found: C, 69.69; H, 5.00; N, 4.57.

1-Alkenesulfenamides 8 via Transaminations of Thiophthalimides 7. Aliphatic Amines. A mixture of thiophthalimide **7** (205−248 mg, 0.66−0.95 mmol) and alkyl- or dialkylamine (1 equiv) was stirred in benzene (5 mL) at rt for 2 h. The mixture was diluted with pentane (5 mL) and was suction filtered. The solid was rinsed with pentane (3 × 10 mL). The filtrate and the pentane washes were combined and concentrated to afford crude alkenesulfenamide **8**. The crude yields reported in Table 1 were obtained from the mass of the crude material and analysis of the ^{1}H and ^{13}C NMR spectra. Residual benzene or pentane that was present in some cases was taken into account.

Allyltrimethylsilylamine. A mixture of thiophthalimide **7a** (238 mg, 0.91 mmol) and allyltrimethylsilylamine (95% pure, 124 mg, 0.91 mmol) was refluxed in benzene (5 mL) for 4 h. After cooling, workup as above for aliphatic amines provided *N*-allyl-(*E*)-1-hexenesulfenamide (86% crude yield).

Aromatic Amines. A mixture of thiophthalimide **7** (219−334 mg, 0.84−1.28 mmol) and aniline or *N*-allylaniline (1 equiv) was refluxed in ethanol (5 mL) for 16 h. The mixture was diluted with ether (20 mL) and aqueous Na_2CO_3 solution (20 mL). The aqueous layer was extracted with ether (3 × 15 mL). The organic layers were combined and washed with aqueous Na_2CO_3 solution (20 mL), water (3 × 20 mL), and brine. After drying (Na_2SO_4), the mixture was filtered and concentrated to afford crude *N*-aryl-1-alkenesulfenamide **8**. Oxidation of these compounds was difficult and was only pursued for **8d**.

(38) (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.

LDA. To a solution of LDA (0.96 mmol, 1.1 equiv) in THF (5 mL) was added thiophthalimide **7b** (227 mg, 0.88 mmol) in THF (2 mL) at −78 °C. The mixture was warmed to rt over 0.5 h. At this time water (10 mL) and ether (20 mL) were added. The layers were separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were washed with water (3 × 10 mL) and brine and were dried over Na_2SO_4. Filtration and concentration of the mixture afforded crude alkenesulfenamide **8f** (46%). Crude yields for all systems are reported in Table 1.

MCPBA Oxidation of Crude 1-Alkenesulfenamides 8. The following is based on a method previously reported for sulfinamide to sulfonamide oxidation.[28] To a solution of sulfenamide **8** in CH_2Cl_2 (15 mL) at 0 °C was added anhydrous K_2CO_3 (3 equiv), followed by dried MCPBA (3 equiv) in CH_2Cl_2 (5−10 mL). The mixture was warmed to rt and was stirred for 3 days. At this time, the mixture was impinged with anhydrous NH_3[23,39] at rt, and the mixture was suction filtered through Celite to remove some ammonium *m*-chlorobenzoate. The NH_3 treatment and filtration was repeated at −78 °C. The filtrate was concentrated and chromatographed on basic alumina (I) (EtOAc in hexanes and/or EtOAc only) to afford pure alkenesulfonamide.

***N*-Benzyl-(*E*)-1-hexenesulfonamide (9a):** 67%, oil. ^{1}H NMR (400 MHz), δ 7.36−7.27 (m, 5H), 6.74 (dt, J = 15.0, 6.8 Hz, 1H), 6.11 (d, J = 15.0 Hz, 1H), 4.71 (t(br), J = 6.0 Hz, 1H), 4.18 (d, J = 6.0 Hz, 2H), 2.18 (q, J = 6.8 Hz, 2H), 1.44−1.28 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 146.2, 136.7, 128.7 (2 C's), 127.9 (2 C's), 47.0, 30.9, 29.8, 22.1, 13.7. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.66; H, 7.58; N, 5.77.

***N*-Benzyl-*N*-methyl-(*E*)-1-hexenesulfonamide (9b):** 73%, oil. ^{1}H NMR (400 MHz), δ 7.38−7.29 (m, 5H), 6.78 (dt, J = 15.1, 7.0 Hz, 1H), 6.11 (dt, J = 15.1, 1.2 Hz, 1H), 4.22 (s, 2H), 2.66 (s, 3H), 2.27 (dq, J =7.0, 1.2 Hz, 2H), 1.46 (m, 2H), 1.36 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 147.2, 135.8, 128.6, 128.4, 127.9, 124.8, 53.8, 34.1, 31.2, 30.0, 22.1, 13.7. Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.89; H, 7.92; N, 5.24. Found: C, 62.65; H, 7.76; N, 5.26.

***N*-Allyl-(*E*)-1-hexenesulfonamide (9c):** 53%, oil. ^{1}H NMR (400 MHz), δ 6.77 (ddt, J = 15.1, 7.0, 2.2 Hz, 1H), 6.18 (d, J = 15.1, 1H), 5.84 (m, 1H), 5.26 (dt, J = 17.1, 1.3 Hz, 1H), 5.18 (dt, J = 11.1, 1.2 Hz, 1H), 4.41 (s(br), 1H), 3.64 (s, 2H), 2.26 (q, J = 7.0 Hz, 2H), 1.50−1.42 (m, 2H), 1.40−1.31 (m, 2H), 0.92, (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 146.2, 133.4, 127.9, 117.6, 45.5, 31.0, 29.9, 22.1, 13.7. HRMS Calcd for $C_9H_{17}NO_2S$: 203.0980. Found: 203.0961.

***N*-Allyl-*N*-phenyl-(*E*)-1-hexenesulfonamide (9d):** 35%, oil. ^{1}H NMR (400 MHz), δ 7.37−7.27 (m, 5H), 6.65 (dt, J = 15.1, 7.0 Hz, 1H), 6.19 (d, J = 15.1 Hz, 1H), 5.81 (m, 1H), 5.14 (d, J = 17.1 Hz, 1H), 5.09 (d, J = 10.2 Hz, 1H), 4.20 (d, J = 6.1 Hz, 1H), 2.20 (q, J = 7.0 Hz, 1H), 1.42 (m, 2H), 1.32 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 146.9, 139.4, 133.1, 129.0, 128.7, 127.7, 126.1, 118.7, 53.5, 31.1, 29.9, 22.0, 13.7. Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.31; H, 7.48; N, 4.94.

***N*-(4-Phenyl-(*E*)-1-butenesulfonyl)morpholine (9e):** 63%, mp 96−96.5 °C. ^{1}H NMR (400 MHz), δ 7.33−7.16 (m, 5H), 6.75 (dt, J = 15.2, 6.8 Hz, 1H), 6.03 (d, J = 15.2 Hz, 1H), 3.70 (t, J = 4.6 Hz, 4H), 2.94 (t, J = 4.6 Hz, 4H), 2.83 (t, J = 7.3 Hz, 2H), 2.62 (dt, J = 7.3, 6.8 Hz, 2H); ^{13}C NMR (100.6 MHz), δ 147.5, 139.8, 128.6, 128.3, 126.5, 124.1, 66.1, 45.5, 34.0, 33.0. Anal. Calcd for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98. Found: C, 59.89; H, 6.67; N, 4.97.

***N*,*N*-Bis(2-methylethyl)-1-cyclohexenesulfonamide (9f):** 25%, oil. ^{1}H NMR (400 MHz), δ 6.81 (m, 1H), 3.58 (septet, J = 6.7 Hz, 2H), 2.31 (m, 2H), 2.23 (m, 2H), 1.74−1.68 (m, 2H), 1.63−1.58 (m, 2H), 1.30 (d, J = 6.7 Hz, 12H); ^{13}C NMR (100.6 MHz), δ: 138.8, 136.7, 48.0, 25.3, 23.1, 22.3, 22.1, 21.1. HRMS Calcd for $C_{12}H_{23}NO_2S$: 245.1450. Found: 245.1446.

***N*-(1-Cyclohexenesulfonyl)-2-methylaziridine (9g):** 60%, oil. ^{1}H NMR (400 MHz), δ 6.88 (s(br), 1H), 2.74 (m, 1H), 2.56 (d, J = 7.1 Hz, 1H), 2.49 (m, 2H), 2.28 (m, 2H), 2.02 (d, J = 4.6 Hz, 1H), 1.76 (m, 2H), 1.67 (m, 2H), 1.31 (d, J = 5.8 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 138.3, 137.6, 35.1, 34.2, 25.3, 23.5, 21.8, 20.8, 16.9. Anal. Calcd for $C_9H_{15}NO_2S$: C, 53.70; H, 7.51; N, 6.96. Found: C, 53.86; H, 7.32; N, 6.98.

***N*-Cyclohexyl-1-cyclohexenesulfonamide (9h):** 67%, mp 90−90.5 °C. ^{1}H NMR (400 MHz), δ 6.81 (m, 1H), 4.61 (d, J = 7.6 Hz, 1H), 3.07 (m, 1H), 2.32 (m, 2H), 2.24 (m, 2H), 1.89 (m, 2H), 1.76−1.53 (m, 6H), 1.38−1.17 (m, 6H); ^{13}C NMR (100.6 MHz), δ 138.5, 136.2, 52.3, 34.1, 25.2, 25.1, 24.7, 23.0, 21.9, 21.0. Anal. Calcd for $C_{12}H_{21}NO_2S$: C, 59.22; H, 8.70; N, 5.76. Found: C, 59.40; H, 8.88; N, 5.79.

***N*,*N*-Dimethyl-1-cyclohexenesulfenamide (8j).** A mixture of thiophthalimide **7g** (2.15 g, 8.30 mmol) and dimethylamine (0.7 mL, 10.6 mmol) was stirred in benzene (50 mL) at rt for 2 h. The mixture was suction filtered, and the solid was rinsed with pentane (3 × 10 mL). The filtrate and the pentane washes were combined and concentrated. The residue was triturated into pentane (20 mL) and was suction filtered. The solid as rinsed with pentane (3 × 10 mL). The filtrate and the pentane washes were combined and concentrated to afford crude alkenesulfenamide **8j** (96% crude). Distillation (42−46 °C/1.2 mm) afforded pure sulfenamide **8j** (1.02 g, 78%). ^{1}H NMR (400 MHz), δ 5.84 (m, 1H), 2.76 (s, 6H), 2.18−2.10 (m, 4H), 1.69 (m, 2H), 1.59 (m, 2H); ^{13}C NMR (100.6 MHz), δ 135.1, 125.6, 48.8, 29.4, 26.1, 23.1, 22.0. HRMS Calcd for $C_9H_{15}NS$: 157.0925. Found: 157.0926.

Preparation of [(Alkenylthio)imino]phthalides 11. To a flame-dried flask under N_2 were added sulfenamide **4** (4.09−4.28 g, 15−15.5 mmol), 4 Å molecular sieves (2 g), and dry THF (110 mL). The flask was cooled to 0 °C, and TBAF (1 mol equiv, 1 M in THF) was added dropwise over 5 min. Then Et_3N (4 equiv) was added followed by phthaloyl dichloride (2 equiv) over 5 min. The mixture turns bright yellow, and a precipitate forms. After 5 min, saturated aqueous NH_4Cl (100 mL) and ether (50 mL) were added. After transfer to a separatory funnel, the layers were separated and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic extracts were washed with water (2 × 30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4. Filtration, concentration, and immediate flash chromatography (silica gel, 30% EtOAc in hexanes) afforded compounds **11** followed by isomers **7** (10−12%). Recrystallization from EtOAc/hexanes afforded analytically pure thioiminophthalides **11**.

3-[(*E*)-(1-Hexenylthio)imino]phthalide (11a): 61%, oil. ^{1}H NMR (400 MHz), δ 7.90 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.76 (dt, J = 7.6, 0.9 Hz, 1H), 7.64 (dt, J = 7.6, 0.9 Hz, 1H), 6.52 (dt, J = 15.3, 1.4 Hz, 1H), 6.01 (dt, J = 15.3, 7.2 Hz, 1H), 2.21 (dq, J = 7.2, 1.4 Hz, 2H), 1.45 (m, 2H), 1.37 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 163.6, 145.4, 135.3, 135.1, 131.9, 131.8, 126.9, 125.3, 124.5, 122.2, 32.4, 31.0, 22.1, 13.8; UV/vis (95% ethanol), λ_{max}: 356 nm (log ϵ = 3.0). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.59; H, 5.68; N, 5.27.

3-[(1-Cyclohexenylthio)imino]phthalide (11b): 67%, oil. ^{1}H NMR (400 MHz), δ 7.90 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.75 (dt, J = 7.6, 1.0 Hz, 1H), 7.64 (dt, J = 7.6, 1.0 Hz, 1H), 6.17 (m, 1H), 2.48 (m, 2H), 2.20 (m, 2H), 1.82 (m, 2H), 1.69 (m, 2H); ^{13}C NMR (100.6 MHz), δ 163.8, 144.9, 135.3, 135.2, 134.1, 131.6, 126.9, 126.8, 125.3, 122.2, 27.4, 26.1, 23.0, 21.8. UV/vis (95% ethanol), λ_{max}: 357 nm (log ϵ = 3.7). Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.64; H, 4.95; N, 5.35.

Reactions of [(Alkenylthio)imino]phthalides 11 with Amines. A mixture of thioiminophthalide **11** (205−248 mg, 0.66−0.95 mmol) and alkyl- or dialkylamine (1 equiv) was stirred in benzene (5 mL) under the conditions indicated in Table 2.

Transaminations. The mixture was diluted with pentane (5 mL) and was suction filtered. The solid was rinsed with pentane (3 × 10 mL). The filtrate and the pentane washes were combined and concentrated to afford crude 1-alkenesulfenamide **8** which was oxidized as above to afford 1-alkenesulfonamides **9**.

Ring-Openings. The mixture was diluted with pentane (5 mL) and was suction filtered. The solid was recrystallized

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or chromatographed on basic alumina (I) to afford pure *N*,*N*′-disubstituted phthalamides **13**. In the synthesis of **13b**, the filtrate was chromatographed to afford additional pure product.

***N*-Benzyl-*N*-methyl-(*E*)-1-hexenesulfonamide (9b):** 47%.

***N*-[(*E*)-1-Hexenesulfonyl]piperidine (9k):**[28] 50%, mp 30.5−31.0 °C. ^{1}H NMR (400 MHz), δ 6.72 (dt, J = 15.0, 7.1 Hz, 1H), 6.08 (d, J = 15.0 Hz, 1H), 3.08 (t, J = 5.5 Hz, 4H), 2.26 (q, J = 7.1 Hz, 2H), 1.66 (pentet, J = 5.6 Hz, 4H), 1.53 (m, 2H), 1.46 (m, 2H), 1.37 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 147.4, 124.1, 46.4, 31.1, 29.9, 25.2, 23.6, 22.0, 13.6. Anal. Calcd for $C_{11}H_{21}NO_2S$: C, 57.11; H, 9.15; N, 6.05. Found: C, 57.00; H, 9.03; N, 5.99.

***N*,*N*-Dicyclohexyl-(*E*)-1-hexenesulfonamide (9l):** 59%, oil. ^{1}H NMR (400 MHz), δ 6.65 (dt, J = 14.6, 7.2 Hz, 1H), 6.07 (d, J = 14.6 Hz, 1H), 3.20 (pentet, J = 7.7 Hz, 2H), 2.19 (q, J = 7.2 Hz, 2H), 1.82−1.06 (m, 24H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 142.6, 131.3, 57.5, 32.6, 30.9, 30.1, 26.5, 25.2, 22.1, 13.7. HRMS Calcd for $C_{18}H_{33}NO_2S$: 327.2232. Found: 327.2219.

***N*,*N*-Dibenzyl-1-cyclohexenesulfonamide (9m):** 38%, mp 46−47 °C. ^{1}H NMR (200 MHz), δ 7.36−7.20 (m, 10H), 6.83 (m, 1H), 4.31 (s, 4H), 2.24−2.21 (m, 4H), 1.70−1.55 (m, 4H); ^{13}C NMR (50.3 MHz), δ 139.1, 137.2, 136.1, 128.8, 128.6, 127.8, 49.9, 25.1, 23.0, 21.7, 20.7. HRMS Calcd for $C_{13}H_{16}NO_2S$, $(M - C_7H_7)^+$: 250.0902. Found: 250.0910.

***N*-(1-Cyclohexenesulfonyl)morpholine (9n):** 71%, mp 108.5−109.0 °C. ^{1}H NMR (400 MHz), δ 6.78 (s(br), 1H), 3.74 (t, J = 4.6 Hz, 4H), 3.17 (t, J = 4.6 Hz, 4H), 2.29 (m, 4H), 1.72 (m, 2H), 1.65 (m, 2H); ^{13}C NMR (100.6 MHz), δ 139.1, 136.2, 66.6, 45.6, 25.4, 24.4, 21.9, 21.0. Anal. Calcd for $C_{10}H_{17}NO_2S$: C, 51.93; H, 7.41; N, 6.06. Found: C, 52.18; H, 7.16; N, 6.11.

***N*-[(*E*)-1-Hexenylthio]-*N*′-cyclohexylphthalamide (13a):** 63%, mp 142−143 °C. ^{1}H NMR (400 MHz), δ 8.17 (s(br), 1H), 7.63 (m, 1H), 7.51−7.45 (m, 3H), 6.36 (s(br), 1H), 6.12 (d, J = 15.0 Hz, 1H), 5.84 (dt, J = 15.0, 7.0 Hz, 1H), 3.86 (m, 1H), 2.10 (q, J = 7.0 Hz, 2H), 1.95 (m, 2H), 1.76−1.62 (m, 3H), 1.43−1.15 (m, 9H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.6 MHz), δ 170.6, 168.3, 135.0, 133.4, 133.0, 130.8, 130.1, 129.0, 128.1, 124.0, 49.2, 32.7, 32.3, 31.0, 25.4, 24.8, 22.2, 13.8. Anal. Calcd for $C_{20}H_{28}N_2O_2S$: C, 57.11; H, 9.15; N, 6.05. Found: C, 57.00; H, 9.03; N, 5.99.

***N*-(1-Cyclohexenylthio)-*N*′-cyclohexylphthalamide (13b):** 63%, mp 120−121 °C. ^{1}H NMR (400 MHz), δ 8.12 (s(br), 1H), 7.64 (m, 1H), 7.52−7.46 (m, 3H), 6.41 (d, J = 7.6 Hz, 1H), 5.82 (s(br), 1H), 3.86 (m, 1H), 2.16 (m, 2H), 2.10 (m, 2H), 1.95 (m, 2H), 1.76−1.58 (m, 6H), 1.39 (m, 2H), 1.21 (m, 4H); ^{13}C NMR (100.6 MHz), δ 170.9, 168.4, 134.9, 134.4, 133.4, 130.7, 130.1, 129.1, 128.2, 23.7, 49.2, 32.7, 26.7, 25.9, 25.4, 24.8, 22.9, 21.8. HRMS Calcd for $C_{14}H_{13}NO_2S$, $(M - C_6H_{13}N)^+$: 259.0667. Found: 259.0640.

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Supporting Information Available: Infrared and mass spectral data of most compounds and copies of ^{1}H NMR and/or ^{13}C NMR spectra of compounds for which satisfactory elemental analyses could not be obtained (20 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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