Novel Synthesis of Sulfonimidoyl Halides and Sulfonimidates from N-Silylated Sulfonamides and Dihalophosphoranes

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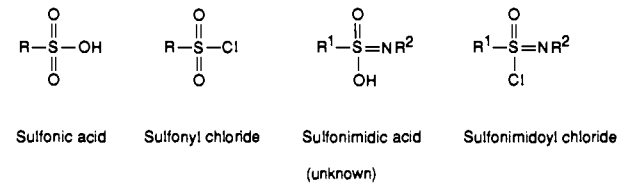
Abstract: In the past, general methods for the preparation of sulfonimidoyl chlorides have involved oxidation of sulfur(IV) compounds with various oxidizing agents. For the purpose of studying the thermal decomposition of suitably substituted sulfonimidates to sulfur–nitrogen based polymeric materials, a simple method was developed for the synthesis of sulfonimidoyl halides from readily available sulfur(VI) starting materials. Unsubstituted sulfonamides are known to react with Ph_3P–CCl_4 to produce only *N*-phosphoranylidenesulfonamides. In contrast, we have found that the reaction of N-silylated sulfonamides [$RSO_2NHSiMe_3$ (**6**), $RSO_2N(SiMe_3)_2$ (**7**)] with Ph_3PCl_2 in $CHCl_3$ yields *N*-trimethylsilylsulfonimidoyl chlorides, $Me_3SiN{=}S(O)(R)Cl$, **11**, except when the group R is strongly electronegative, like CF_3. Further, the reaction of **7** (R = Me) with Ph_3PBr_2 in CH_2Cl_2 produced the first detectible sulfonimidoyl bromide, $Me_3SiN{=}S(O)(Me)Br$, **12**. The sulfonimidoyl chlorides **11** were converted (in one-pot reactions) to 2,2,2-trifluoroethyl-, phenyl-, or ethyl *N*-trimethylsilylsulfonimidates **3** (R = Me, Et, ClCH32CH_2CH_2, PhCH=CH, Ph, 4-F-C_6H_4). In preliminary reactions, it was found that the *N*-silylsulfonimidates can in turn be derivatized by taking advantage of the susceptibility of the Si–N bond to cleavage.

Introduction

Sulfonimidoyl chlorides are aza analogs of the better-known and more-utilized sulfonyl chlorides (Chart I). As acid chlorides, sulfonimidoyl chlorides are important intermediates for the synthesis of the corresponding esters and amides, sulfonimidates and sulfonimideamides, respectively. In addition, the substituent at nitrogen allows for greater synthetic scope in sulfonimidoyl compounds.

Arenesulfonimidoyl chlorides with dichlorophosphoryl and arenesulfonyl substitution at nitrogen were first prepared by Levchenko and co-workers.[1] Later, a variety of arenesulfonimidoyl chlorides containing acyl and alkyl substituents at nitrogen were synthesized by Levchenko's group from arenesulfinyl chlorides and sodium (or tertiary amine) salts of *N*-chloro amides/carbamates or *N,N*-dichloro amines.[2] Following these, Johnson et al. developed a fairly general procedure for the synthesis of *N*-alkyl, *N*-aryl, and *N*-sulfonyl-alkane- and arenesulfonimidoyl chlorides from sulfinamides via oxidation with chlorine, *N*-chlorobenzotriazole, or *tert*-butyl hypochlorite.[3] While a variety of sulfonimidoyl chlorides can be synthesized by one or both of the above methods, the accessibility and ease of handling of sulfinyl chlorides and sulfinamides are poor compared to the corresponding sulfur(VI) compounds sulfonyl chlorides and sulfonamides. Sulfinyl chlorides, in particular, also suffer from relatively poor chemical stability.[4] Further, many of the oxidizing agents used to convert sulfur(IV) to sulfur(VI) are either not readily accessible or are high-energy or unstable compounds requiring special care in handling. In connection with our interests in sulfur–nitrogen based polymeric materials, one of our objectives was to develop a convenient method for the synthesis of sulfonimidoyl halides from readily available or accessible sulfur(VI) compounds, namely, sulfonic acids, sulfonyl chlorides, and sulfonamides.

Chart I



Over the last decade, Neilson, Wisian-Neilson, and co-workers have developed polycondensation of suitably substituted *N*-silylphosphoranimines as a general procedure for the synthesis of poly(alkyl/aryl phosphazenes), $(N{=}PR_2)_n$, which are a relatively new class of inorganic backbone polymers.[5] The method involves 1,2-elimination of a suitable silyl ether from a N-silylated phosphorus(V) ester imide **1** (eq 1). It seemed plausible, therefore, that sulfur(VI)–nitrogen backbone polymers based on the repeat unit [N=S(O)R] might be accessible via analogous polycondensation of *N*-silylsulfonimidates **3** (eq 2). Hence, the need arose to develop a convenient route to *N*-silylsulfonimidoyl halides which, as acid halides, would serve as intermediates for the synthesis of the corresponding sulfonimidates.

In this paper, we describe a covenient, one-pot synthesis of a variety of *N*-silylsulfonimidates starting from readily accessible N-silylated sulfonamides and Ph_3PCl_2.[6] In addition, we report the first spectroscopic detection of a sulfonimidoyl bromide, previously only postulated as intermediates. Preliminary results have also been obtained on the derivatization of *N*-silylsulfonimidates by taking advantage of the reactivity of the Si–N bond. It turns out that one such reaction, the desilylation of *N*-silylsulfonimidates to free sulfonimidates, is of paramount importance in the synthesis of the targeted sulfur–nitrogen polymers. However, because of this relevance, this aspect of the Si–N

(1) (a) Levchenko, E. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1960**, *30*, 1553. (b) Levchenko, E. S.; Derkach, N. Ya.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1960**, *30*, 1971. (c) Levchenko, E. S.; Derkach, N. Ya.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1961**, *31*, 1971.

(2) (a) Levchenko, E. S.; Kozlov, E. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1961**, *31*, 2381. (b) Levchenko, E. S.; Berzina, I. N.; Kirsanov, A. V. *Zh. Org. Khim.* **1965**, *1*, 1251. (c) Levchenko, E. S.; Markovskii, L. N.; Kirsanov, A. V. *Zh. Org. Khim.* **1967**, *3*, 1273. (d) Pinchuk, A. M.; Markovskii, L. N.; Levchenko, E. S.; Shevchenko, V. I. *Zh. Obshch. Khim.* **1967**, *37*, 852.

(3) (a) Jonsson, E. U.; Bacon, C. C.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5306. (b) Johnson, C. R.; Jonsson, E. U.; Bacon, C. C. *J. Org. Chem.* **1979**, *44*, 2055. (c) Johnson, C. R.; Wambsgans, A. *J. Org. Chem.* **1979**, *44*, 2278.

(4) Douglass, I. B.; Farah, B. S. *Organic Syntheses*; Wiley: New York, 1960; Collect. Vol. V, p 709.

(5) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541 and references therein.

(6) Roy, A. K. US Patent 5,068,379, 1991.

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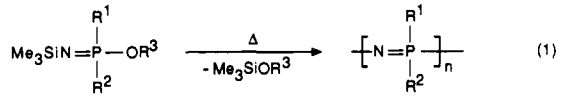
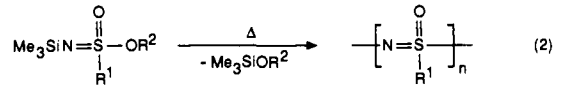


1 2

$R^3 = CH_2CF_3$, aryl (1)



3 4

$R^2 = CH_2CF_3$, aryl (2)

chemistry in *N*-silylsulfonimidates has been discussed in the accompanying paper on the condensation synthesis of polymers **4**.

Results and Discussion

Synthesis of N-Silylated Sulfonamides. Two general methods are available for the synthesis of *N*-silylsulfonamides. One involves the reaction of sulfonyl chlorides, sulfonamides, or sulfonic anhydrides with hexaalkyldisilazanes.[7] In the second method, sulfonamides are silylated using trialkylchlorosilanes in the presence of a suitable base.[8] The latter procedure also yields *N,N*-disilylsulfonamides when excess chlorosilane and base are used. For our studies, we used only trimethylsilylated sulfonamides. Their synthesis is depicted in Scheme I.

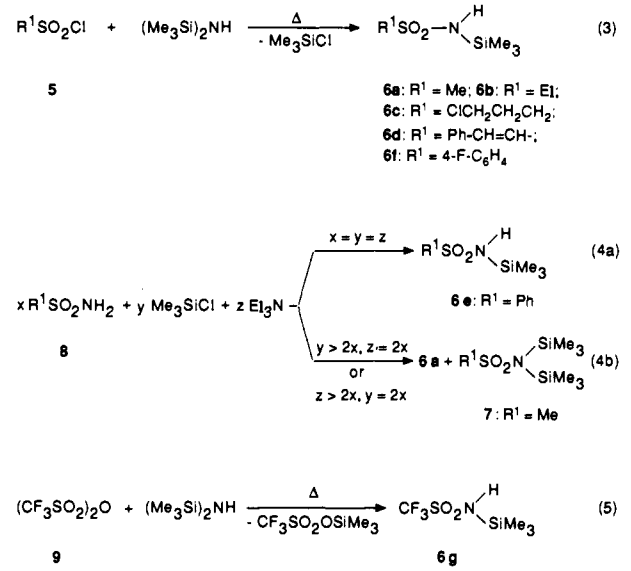
In general, published procedures were followed for the syntheses of **6** and any variation is reported in the Experimental Section. The disilylsulfonamide **7** was obtained as a mixture with **6a** (R^1 = Me) in an approximately 1:1 molar ratio even when a large excess of the chlorosilane or the base was used, and the reaction mixture was refluxed for several hours. Even after two-to-three vacuum distillations, approximately 5 mol% **6a** remained associated with **7**. Compounds **6a–f** are high-boiling liquids or solids with fairly high moisture sensitivity. They were characterized by ^1H and ^{13}C NMR spectroscopy. Satisfactory microanalytical data were obtained for products synthesized directly from **6** as described later.

Reaction of 6 and 7 with Halophosphoranes. In order to convert N-silylated sulfonamides to the desired *N*-silylsulfonimidates, it was first necessary to transform the sulfonamide moiety to a sulfonimidoyl moiety. This meant removal of an oxygen from sulfur and restructuring without altering the oxidation state of sulfur(VI). Consideration of bond energies of oxygen with suitable main-group elements indicated that appropriate phosphorus reagents would be useful for such a transformation. Prior work by Levchenko had shown that under certain conditions reaction of *N*-dichlorophosphorylarenesulfonamides with PCl_5 produced *N*-dichlorophosphorylsulfonimidoyl chlorides.[1a] In a more recent report, a sulfamide derivative containing phosphorus substituents at both nitrogens was shown to yield a sulfonimidoyl-type chloride upon reaction with PCl_5.[9]

We have now found that the course of the reaction of N-silylated sulfonamides **6** and **7** with halophosphoranes of the type Y_3PX_2 (Y = Cl, X = Cl; Y = Ph, X = Cl, Br) is dependent on the steric bulk of the phosphorus reagent, the polarity of the solvent used, and on the electronic effect of the substituent on sulfur (Scheme II). With PCl_5 as the reagent, only the phosphoranylidene product **10a** was obtained from **7** in CCl_4 as solvent. Compound **10a** was

(7) (a) Krebs, K.-W.; Dickopp, H.; Bentz, F.; Nischk, G.-E. German Patent 2,002,065, 1971. (b) Roesky, H. W.; Wiezer, H. *Chem. Ber.* **1971**, *104*, 2258.
(8) (a) Derkach, N. Ya.; Smetankina, N. P. *Zh. Obshch. Khim.* **1964**, *34*, 3613. (b) Golebiowski, L.; Lasocki, Z. *Bulletin De L'Academie Polonaise Des Sciences* **1976**, *24*, 439.
(9) Suzuki, D.; Akagi, H.; Matsumura, K. *Synthesis* **1983**, 369.

Scheme I



(3)

6a: R^1 = Me; **6b**: R^1 = Et; **6c**: R^1 = $ClCH_2CH_2CH_2$; **6d**: R^1 = Ph-CH=CH-; **6f**: R^1 = 4-F-C_6H_4

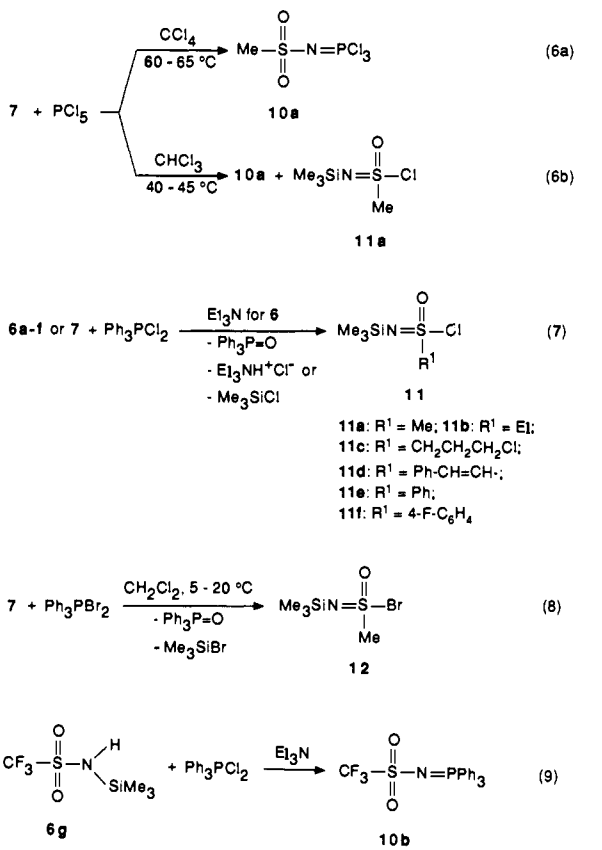
(4a) (4b)

6e: R^1 = Ph

7: R^1 = Me

(5)

Scheme II



(6a) (6b)

11a: R^1 = Me; **11b**: R^1 = Et; **11c**: R^1 = $CH_2CH_2CH_2Cl$; **11d**: R^1 = Ph-CH=CH-; **11e**: R^1 = Ph; **11f**: R^1 = 4-F-C_6H_4

(7)

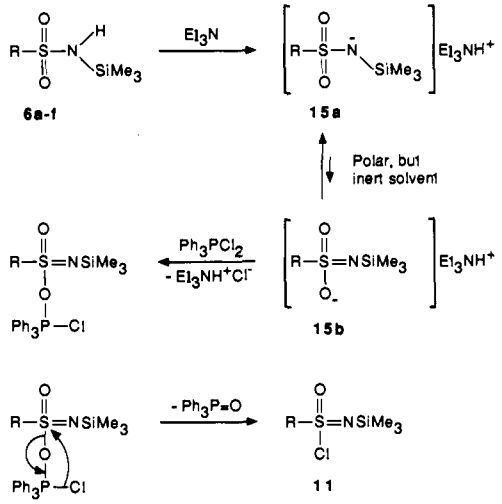
(8)

(9)

identified by a four-bond phosphorus coupling to S–Me protons in the ^1H NMR spectrum (δ = 2.98 in CH_2Cl_2, $^4J_{PH}$ = 3.6 Hz). In relatively polar $CHCl_3$, a 1:1 mixture of **10a** and the sulfonimidoyl chloride **11a** was produced from PCl_5 and **7**. The chemical shift (δ = 3.5) of the S–Me protons in **11a** represents a significant downfield shift from the corresponding resonance in **7** (δ = 2.85) and is in the range of those reported for other N-substituted methanesulfonimidoyl chlorides.[3b] When the bulkier phosphorus reagent Ph_3PCl_2[10] was substituted for PCl_5 in $CHCl_3$, **11a** was the sole product, and the reaction was near-quantitative by ^1H NMR. Further, the reaction of the monosilylsulfonamides **6a–f** with Ph_3PCl_2 in the presence of Et_3N again

(10) Appel, R.; Schöler, H. *Chem. Ber.* **1977**, *110*, 2382.

Scheme III



yielded only the corresponding sulfonimidoyl chlorides **11** at lower temperature than **7**.

The reaction of **7** with Ph_3PBr_2 yielded the first detectible sulfonimidoyl bromide **12** in CH_2Cl_2 solution. Analysis of the ^1H NMR spectrum of the reaction mixture immediately after the disappearance of Ph_3PBr_2 showed a significantly downfield (relative to **7**) S–Me signal at 3.70 ppm (in CH_2Cl_2) attributable to **12**, together with signals for Me_3SiBr and the N–$SiMe_3$ moiety of **12**. No residual **7** was observed. Integration of the Me_3Si signals of Me_3SiBr and **12** indicated partial decomposition of **12**. Indeed, rapid decomposition of **12** to Me_3SiBr and other unidentifiable species was observed over several hours, and only Me_3SiBr could be detected after 18 h. The few hours of stability of **12** allowed the synthesis of the 2,2,2-trifluoroethyl sulfonimidate (albeit in 5–10% yield) from 2,2,2-trifluoroethanol and triethylamine, thereby confirming the identity of **12** as a sulfonimidoyl bromide. Until now, sulfonimidoyl bromides have only been inferred as intermediates in the synthesis of some sulfonimidates and sulfonimideamides from arenesulfinamides via oxidation with bromine or *N*-bromosuccinimide.[11] Ironically, the Me_3Si group, which apparently provides some steric stability to **12**, is also at least partly responsible for its decomposition because of the ease of cleavage of the silicon–nitrogen bond. Based on the synthesis of **12** it is likely that other sulfonimidoyl bromides will be accessible via steric stabilization.

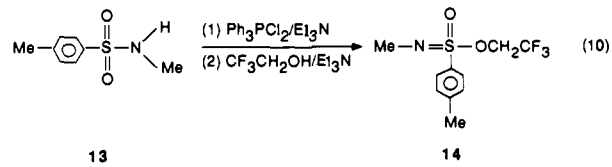
While sulfonimidoyl halides were obtained with electron-donating alkyl groups and mildly electron-withdrawing aryl groups on sulfur, reaction of Ph_3PCl_2 or Ph_3PBr_2 with the *N*-silyltrifluoromethanesulfonamide **6g** produced only the phosphoranylidene product **10b** in 98% yield in a variety of polar solvents (eq 9). Even *N*-(*tert*-butyldimethylsilyl)triflamide reacted with Ph_3PCl_2 (under refluxing conditions in chloroform) to produce only **10b**. This can be interpreted as an indication of higher S=O bond energy (compared with P=O bond energy in Ph_3P=O) in triflamide and other sulfonamides containing strongly electron-withdrawing substituents and confirms Levchenko's results with *N*-dichlorophosphorylarenesulfonamides.[1a] Compound **10b** exhibited a doublet of quartet for the CF_3 signal in the ^{13}C NMR spectrum due to a three-bond phosphorus coupling in addition to the fluorine coupling, and this significantly aided in its characterization.

Based upon the steric, solvent, and electronic effects observed, the following mechanism for the conversion of N-silylated sulfonamides to sulfonimidoyl halides is suggested (Scheme III).

With no steric protection at nitrogen, P–N bond formation would be expected to proceed with ease in unsubstituted sulfonamides **8** because of the high reactivity of N–H in **8**. Once P–N bond formation occurred, the presence of base would lead smoothly to P=N in **10**. With N-silylated sulfonamides, however, the steric energy barrier may be high enough to allow the suggested equilibrium (**15a–15b**, Scheme III) in polar solvents to provide thermodynamic control of the reaction leading to the P=O bond and **11**. For sulfonamides with strongly electron-withdrawing substituents, equilibrium concentration of **15b** is probably too low to allow conversion to **11** and higher temperatures reduce the energy barrier to P–N bond formation. In principle, therefore, it should be possible to convert strongly electronegative sulfonamides to sulfonimidoyl chlorides by placing electronegative substituents on the aromatic nuclei in Ph_3PCl_2. This should have the dual effect of increasing the electrophilicity of phosphorus in the dichlorophosphorane and strengthening the P=O bond in the phosphine oxide. A similar mechanism for the formation of sulfonimidoyl halides from **7** is suggested, with halide ion attack on silicon initiating the reaction. This type of initiation can also be expected with N-phosphorylated sulfonamides in Levchenko's work.[1a]

A number of *N*-trimethylsilylsulfonimidoyl chlorides, representing alkyl, alkenyl, and aryl substitution at sulfur, were made by the above method. All decomposed slowly at room temperature but were stable for several hours in solution at 0 °C. This allowed characterization by ^1H NMR and derivatization to sulfonimidates. Only the alkanesulfonimidoyl chlorides provided the ^1H NMR handle necessary for observing the downfield shift of protons on the α-carbon in going from **6** to **11**. This shift was most prominent with the 3-chloropropyl substituent on sulfur, where alternate upfield and downfield shifts of the S–CH_2 signal starting from 3-chloropropanesulfonyl chloride provided a convincing picture of the sequence of transformations ending with the corresponding *N*-silylsulfonimidate.

In order to examine the scope of the reaction of Ph_3PCl_2 with other types of N-substituted sulfonamides, *N*-methyl-*p*-toluenesulfonamide **13** was allowed to react with the dichlorophosphorane in the presence of Et_3N, in chloroform solution (eq 10). Unlike *N*-silylsulfonamides which react with the phosphorane near 0 °C, **13** reacted at 15–20 °C despite the smaller substituent at nitrogen. However, the 2,2,2-trifluoroethyl ester **14** was obtained from the intermediate sulfonimidoyl chloride[2c] in approximately 10% yield. It is interesting to consider the mechanistic pathway from **13** which has an N–Me substituent, to the corresponding sulfonimidoyl chloride. In this case, an initial P–N bond formation is more probable with subsequent rearrangement in a pseudo-Wittig fashion to the sulfonimidoyl chloride, especially since the reaction occurs at a higher temperature and also produces a lower yield of sulfonimidate. Even though the yield of sulfonimidate was low, the formation of sulfonimidoyl chloride in this reaction indicates potentially wider applicability of Ph_3PCl_2 and other dichlorotriarylphosphoranes for the synthesis of a variety of N-substituted sulfonimidoyl chlorides.



(10)

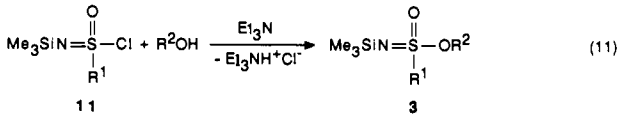
Our results of sulfonimidoyl halide formation from N-silylated sulfonamides and halophosphoranes are in sharp contrast to those of Appel and co-workers who found the reaction of a variety of sulfonamides and sulfonamide-type compounds with the reagent system Ph_3P–CCl_4 led to only the corresponding *N*-phosphoranylidene compounds of the type **10** even in polar solvents.[12] Since

(11) Takei, H.; Watanabe, I.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1989.

(12) (a) Appel, R.; Kleinstück, R.; Ziehn, K.-D. *Chem. Ber.* **1971**, *104*, 2250. (b) Appel, R.; Einig, H. *Z. Naturforsch.* **1975**, *30B*, 134.

at least part of the active reagent in the system Ph_3P–CCl_4 is thought to be Ph_3PCl_2, the above difference in results could arise from kinetic control of the reaction with unsubstituted sulfonamides compared with thermodynamic control in the case of N-silylated sulfonamides.

Synthesis of *N*-Silylsulfonimidates. Since it was not possible to isolate any of the sulfonimidoyl chlorides, derivatization to sulfonimidates was carried out by adding a mixture of alcohol and triethylamine, usually in benzene solution, to the flask already containing the sulfonimidoyl chloride in $CHCl_3$ (eq 11). Based on near quantitative conversion (by ^1H NMR) to **11** for the three alkanesulfonamides, 0.98 equiv each of alcohol and amine were used to derivative the sulfonimidoyl chlorides. For the purpose of polymerization studies that were planned (eq 2), only 2,2,2-trifluoroethyl- and phenyl sulfonimidates (with the exception of one ethyl sulfonimidate) were synthesized from **11**. The yields of the alkanesulfonimidates, particularly the alkyl and fluoroalkyl esters, were moderate to high, while those of the arenesulfonimidates were low suggesting greater instability of the arenesulfonimidoyl chlorides even at 0 °C. The highest yield (78%) was obtained with the ethyl sulfonimidate, in line with the greatest nucleophilicity of ethanol among the three alcohols used.



(11)

11 **3**

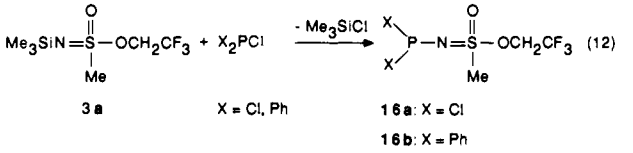
3a: R^1 = Me, OR^2 = OCH_2CF_3;
3b: R^1 = Et, OR^2 = OPh;
3c: R^1 = $CH_2CH_2CH_2Cl$, OR^2 = OPh;
3d: R^1 = Me, OR^2 = OPh;
3e: R^1 = $CH_2CH_2CH_2Cl$, OR^2 = OCH_2CF_3;
3f: R^1 = CH=CH-Ph, OR^2 = OCH_2CF_3;
3g: R^1 = CH=CH-Ph, OR^2 = OPh;
3h: R^1 = Ph, OR^2 = OCH_2CF_3;
3i: R^1 = Ph, OR^2 = OPh;
3j: R^1 = 4-F-C_6H_4, OR^2 = OPh;
3k: R^1 = Me, OR^2 = OEt

All 2,2,2-trifluoroethyl sulfonimidates are distillable liquids while the phenyl sulfonimidates are high boiling liquids which solidify when stored at 5–10 °C. The sulfonimidates **3c** and **3g** could not be distilled. Both underwent condensation to polymer (possibly accelerated by residual $Ph_3P{=}O$ or $Et_3NH^+Cl^-$) during distillation. With the exception of the ethyl ester **3k**, all distillable sulfonimidates showed 1–5% condensation even when stored at 5–10 °C over several months. The phenyl esters, particularly the higher boiling compounds, underwent some condensation (producing the relatively high-boiling Me_3SiOPh) even during distillation. This made obtaining analytically pure samples difficult.

All distillable sulfonimidates were characterized by ^1H and ^{13}C NMR spectroscopy and by elemental microanalysis. Compound **3c** in its crude state was identified by ^1H NMR spectroscopy, while the formation of **3g** was inferred from the $Ph_3P{=}O$ produced in the reaction and also from the successful synthesis of **3f**. Characterization of the 2,2,2-trifluoroethyl sulfonimidates by ^1H NMR was significantly aided by the complex multiplet signal from diastereotopic CH_2CF_3 protons which served to confirm a chiral sulfur atom in these compounds.

Reactions of *N*-Silylsulfonimidates Involving Si–N Cleavage. The primary purpose for the synthesis of 2,2,2-trifluoroethyl- and phenyl *N*-silylsulfonimidates was to study their condensation to polymers. While this aspect of their reactivity is discussed in detail in the following paper in this issue, we report herein preliminary results on the derivatization of **3a** and **3d** utilizing the general, inherent reactivity of the Si–N bond.

The reaction of **3a** with chlorophosphines X_2PCl (X = Ph, Cl) which contain fairly reactive P–Cl bonds was investigated first (eq 12). Both chlorophosphines reacted smoothly with **3a** with near-quantitative formation of the *N*-phosphinyl derivatives **16** and Me_3SiCl which was readily removed from the product mixtures.

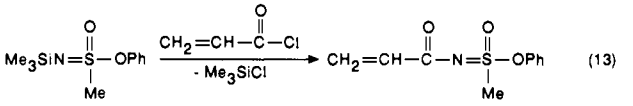


(12)

3a X = Cl, Ph **16a**: X = Cl **16b**: X = Ph

Compounds **16** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. No attempt was made to distill **16a** because of the possibility of OCH_2CF_3/Cl exchange. Compound **16b** was a high-boiling liquid which partially decomposed after standing for 1–2 days. Both **16a** and **16b** were identified on the basis of their ^1H and ^{13}C NMR spectra. The ^1H NMR of **16a** showed a distinct S–Me doublet ($^4J_{PH}$ = 1.7 Hz) and diastereotopic OCH_2CF_3 protons with no phosphorus coupling. The corresponding ^{13}C NMR also showed an S–Me doublet ($^3J_{PC}$ = 2.6 Hz), but no phosphorus coupling to the OCH_2CF_3 carbon nucleii. The ^1H NMR of **16b**, on the other hand, showed diastereotopic OCH_2CF_3 protons but no phosphorus coupling to either the S–Me or the OCH_2CF_3 protons. However, its ^{13}C NMR exhibited a phosphorus coupling ($^4J_{PC}$ = 1.1 Hz) to the CH_2 carbon in OCH_2CF_3 even though no three-bond coupling to the S–Me carbon was observed. Further, the phenyl resonances were nonequivalent in **16b** even for both para-carbon nucleii, a feature not observed with Ph_2PCl itself.

Since P–Cl bonds are usually quite reactive and might be expected to readily cleave the Si–N bond in **3**, it was necessary to test the suitability of a less reactive halide for derivatization of **3** through Si–N bond cleavage. It was found that acryloyl chloride reacts quite cleanly with **3d** at 65–70 °C to produce the *N*-acryloylsulfonimidate **17** in greater than 90% NMR yield (eq 13). The distilled yield was only 56% possibly due to partial vinyl polymerization at the high distillation temperature. Compound **17** was characterized by ^1H and ^{13}C NMR spectroscopy. Levchenko has reported the reaction of a free sulfonimidate with acetyl chloride to yield the corresponding *N*-acetyl sulfonimidate,[13] but the method suffers from the drawback that half the free sulfonimidate used must act as acid acceptor because other bases cannot be included due to the base-instability of free phenyl sulfonimidates.



(13)

3d **17**

The above reactions of the *N*-silylsulfonimidates **3** serve to demonstrate the potential for the synthesis of an extremely wide variety of N-substituted sulfonimidates and other S–N compounds by utilizing the susceptibility of the Si–N bond to cleavage by appropriate reagents. In this respect, the method is potentially as diverse in scope as the ones based on the synthesis of sulfonimidates from sulfur(IV) compounds. It is also complementary to the latter methods since N-derivatization can be readily achieved at the sulfonimidate stage and does not involve the usually difficult nitrogen–carbon bond cleavage.

Conclusion

The reaction of N-silylated sulfonamides with appropriate halophosphoranes is a convenient, new method for the synthesis of sulfonimidoyl halides, based on readily available (or accessible) and relatively inexpensive starting materials. The reaction is

(13) Levchenko, E. S.; Kozlov, E. S.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1962**, *32*, 2585.

generally applicable to substituted or unsubstituted alkane-, arene-, and alkenesulfonamides, provided any substituent on these groups does not exert a strongly electronegative influence on sulfur or does not react with the phosphorane. The sulfonimidoyl halides react in situ with alcohols to yield *N*-silylsulfonimidates. While alkanesulfonimidates are obtained in moderate to high yields, lower yields of sulfonimidates are obtained from arenesulfonamides. The transformation of an $-SO_2N-$ moiety to an $-S(O)(=N-)-$ moiety using appropriate halophosphoranes is also applicable to other types of N-substituted sulfonamides. The $-SO_2-$ group has been considered a bastion of chemical stability in organic sulfur(VI) compounds, and its alteration (without reduction at sulfur) using appropriate phosphorus reagents may provide a window into newer areas of sulfur chemistry.

Experimental Section

Materials and General Procedures. The following chemicals were obtained from Aldrich Chemical Co. or Lancaster Synthesis Ltd. and used without further purification: sulfonyl chlorides, sulfonamides, triflic anhydride, hexamethyldisilazane, chlorotrimethylsilane, Et_3N, Ph_3P, PCl_5, Br_2, C_2Cl_6, PhOH (loose crystals), CF_3CH_2OH, anhydrous EtOH, PCl_3, Ph_2PCl, and acryloyl chloride. Chloroform (pentene stabilized) and CH_2Cl_2 were distilled from P_2O_5, while benzene and Et_2O were distilled from CaH_2. Isomeric hexanes (Fisher, pesticide grade) were used as received. All syntheses and extended manipulations dealing with air sensitive species were carried out under an atmosphere of dry nitrogen. The reagent Ph_3PCl_2 was prepared according Appel's simple procedure[11] except that $CHCl_3$ was substituted for CH_3CN as solvent, and the mixture of Ph_3P (0.5 mol % excess) and C_2Cl_6 (0.5–1.5 molar in $CHCl_3$) was refluxed for 4–4.5 h in order to ensure completion of reaction (incomplete reaction caused unreacted C_2Cl_6 to sublime later during distillation of sulfonimidates). The solution–suspension of Ph_3PCl_2 in $CHCl_3$ was then used as the reagent. Proton and ^{13}C NMR spectra were recorded on Varian EM-360L, EM-390, VXR-200, or Bruker-360 instruments. Phosphorus-31 NMR spectra were recorded on the VXR-200 instrument. All NMR spectra were obtained in $CDCl_3$ unless otherwise noted. Chemical shifts are relative to tetramethylsilane for ^1H and ^{13}C NMR and to 85% H_3PO_4 for ^{31}P NMR. Elemental analyses were performed by Galbraith Labs. Inc., Knoxville, TN.

General Procedure for the Synthesis of 6a–d and 6f from Sulfonyl Chlorides. Typically, 0.1–1.0 mol each of hexamethyldisilazane (0.5–5 mol % excess) and sulfonyl chloride (together with any catalyst used) were cautiously mixed together at 0–25 °C in a nitrogen-flushed flask equipped with a mechanical stirrer, gas inlet, and reflux condenser. The stirred mixture was heated for 1–3 h at 100–150 °C with initial caution in heating because of the possibility of exothermic formation of Me_3SiCl. In reactions where a significant quantity of ammonium chloride formed, the salt was filtered out. Chlorotrimethylsilane was removed under vacuum, and the monosilylsulfonamide was either used in the crude form when of high purity or was vacuum distilled one to two times. Reaction conditions for individual compounds were as follow: **6a**, 120 °C/2 h (*caution*, exothermic formation of Me_3SiCl at 95–105 °C); **6b**, 125 °C/2 h; **6c**, 120 °C/1.5 h, 145 °C/0.25 h; **6d**, 120 °C/1.3 h; **6f**, 115 °C/2 h, 2.0 mol % pyridine catalyst.

For **6a**: yield 94%; bp 101–105 °C/0.6 mm; ^1H NMR (in $CHCl_3$) ∂ 0.1 (s, Me_3Si), 2.80 (s, Me–S), 5.3 (br, NH); ^{13}C NMR (in $CDCl_3$) ∂ 0.14 (Me_3Si), 44.4 (Me–S).

For **6b**: yield 41%; bp 94–96 °C/0.65 mm; ^1H NMR ∂ 0.24 (s, Me_3Si), 1.32 (t, CH_3CH_2-S, J_{HH} = 7.4 Hz), 2.95 (q, CH_3CH_2-S), 5.1 (br, NH); ^{13}C NMR ∂ 0.25 (Me_3Si), 8.7 (CH_3CH_2-S), 50.2 (CH_3CH_2-S).

For **6c**: yield 72%; bp 138–139 °C/0.07 mm; ^1H NMR ∂ 0.30 (s, Me_3Si), 3.65 (t, $ClCH_2CH_2CH_2$-S, J_{HH} = 6.2 Hz), 2.2–2.3 (m, $ClCH_2CH_2CH_2$-S), 3.1–3.2 (m, $ClCH_2CH_2CH_2$-S), 5.1 (br, NH); ^{13}C NMR ∂ 0.20 (Me_3Si), 53.2 ($ClCH_2CH_2CH_2$-S), 27.2 ($ClCH_2CH_2CH_2$-S), 42.9 ($ClCH_2CH_2CH_2$-S).

For **6d**: yield 65–70% (the product contained 5 mol % of an inseparable impurity, as indicated by ^1H NMR); bp 155–160 °C/0.05 mm; ^1H NMR ∂ 0.32 (s, Me_3Si), 6.89 (d, Ph-CH=CH-S, J_{HH} = 15.5 Hz), 7.3–7.5 (*m*, *Ph*-CH=CH-S, overlapping with Ph-CH=CH-S signal), 5.2 (br, NH); ^{13}C NMR ∂ 0.25 (Me_3Si), 129.2 (Ph-CH=CH-S, tentative assignment), 138.2 (Ph-CH=CH-S, tentative assignment) [Ph; 132.8-ipso, 128.1-ortho, 129.0-meta, 130.4-para].

For **6f**: yield 98%; bp 140–143 °C/0.25 mm; ^1H NMR ∂ 0.22 (s, Me_3Si), 7.1–7.2 and 7.8–7.9 (m, 4-F-C_6H_4-S), 5.5 (br, NH); ^{13}C NMR ∂ 0.11 (Me_3Si) [4-F-C_6H_4-S, ring position of carbon atom with respect to sulfur; 140-i (d, $^4J_{FC}$ = 3.3 Hz), 128.8-*o* (d, $^3J_{FC}$ = 9.2 Hz), 116.0-m (d, $^2J_{FC}$ = 22.3 Hz), 164.6-p (d, $^1J_{FC}$ = 253.4 Hz)].

General Procedure for the Synthesis of 6e and 7 from the Corresponding Sulfonamides, Me_3SiCl, and Et_3N. To a mixture of the sulfonamide (0.1–0.7 mol) and Et_3N in dry benzene, Me_3SiCl was slowly added at 0–25 °C. For **6e**, an equimolar amount of chlorosilane, but a 5 mol % excess of Et_3N was used. For **7**, up to 200 mol % excess (based on monosilylsulfonamide) of either chlorosilane or base was used. The reaction mixture was refluxed for 3–18 h and filtered to remove salts using benzene for washing. Excess amine or chlorosilane and solvent were removed under vacuum, and the silylated sulfonamide was vacuum distilled (once for **6e** and up to three times for **7** to remove 95% of **6a** that remained unconverted to **7**).

For **6e**: yield 91%; bp 147–148 °C/0.05 mm; ^1H NMR ∂ 0.22 (s, Me_3Si), 5.5 (br, NH), 7.4–7.5 and 7.8–7.9 (m, C_6H_5-S); ^{13}C NMR ∂ 0.14 (Me_3Si) [C_6H_5-S; 143.8-i, 126.0-o, 128.9-m, 132.0-p].

For **7**: yield 50% (including approximately 5 mol % inseparable **6a** that did not affect reaction of **7** with halophosphoranes); bp 100–106 °C/5.2 mm; ^1H NMR (in $CHCl_3$) ∂ 0.28 (s, Me_3Si), 2.85 (s, Me-S); ^{13}C NMR ∂ 3.4 (Me_3Si), 45.2 (Me-S).

Preparation of 6g from Triflic Anhydride and $(Me_3Si)_2NH$. A mixture of triflic anhydride (0.35 mol) and the disilazane (0.5 mol % excess) was refluxed for 90 min at 120 °C and then for 30 min at 100 °C. Compound **6g** was separated from the silyl triflate byproduct by careful distillation at 10–12 mmHg: yield 90–95%. Previous preparation of **6g** at room temperature from the same reactants was reported to provide a 41% yield.[7b]

For **6g**: yield 93%; bp 82–84 °C/11.5 mm; ^1H NMR ∂ 0.34 (s, Me_3Si), 6.5 (br, NH); ^{13}C NMR ∂ –0.14 (Me_3Si), 119.6 (q, CF_3-S, $^1J_{FC}$ = 320.1 Hz).

Reaction of 7 with PCl_5. A 1–1.5 molar solution of **7** (0.03–0.04 mol) was added at 0 °C to a solution–suspension of PCl_5 (1 mol-equiv) in CCl_4 or $CHCl_3$ in a flask equipped with a magnetic stirring bar and a gas inlet. Reaction in CCl_4 required heating at 60–65 °C for 1.5–2.5 h. An oily, second phase separated in this solvent. Reaction in $CHCl_3$ required heating at 40–45 °C for 1–2 h (a slower rate of reaction was observed at 25 °C). Chlorotrimethylsilane and solvent were removed under reduced pressure at 40–50 °C, but in both cases ^1H NMR spectra were run before and after volatiles removal. With the CCl_4 reaction, virtually pure **10a** was obtained, but no attempt was made to distill it since signs of condensation/decomposition were evident even at 100 °C. Proton NMR of **10a** was run in three different solvents of varying polarity to confirm that the S–Me doublet was due to phosphorus coupling and not because of separate resonances. With the $CHCl_3$ reaction, the sulfonimidoyl chloride **11a** which was obtained in a 1:1 ratio with **10a** decomposed completely (with elimination of Me_3SiCl) on removal of volatiles at 40–50 °C under reduced pressure.

Reaction of 7 with Ph_3PCl_2 and with Ph_3PBr_2. The dibromophosphorane was made by titrating Ph_3P (0.03–0.075 mol) in CH_2Cl_2 solution with bromine (1 mol-equiv) in CH_2Cl_2, to a yellow end-point at 0 °C, and then stirring for 30 min at room temperature. A 1–2 molar solution of **7** (1 mol-equiv based on Ph_3PBr_2) in CH_2Cl_2 was added from a dropping funnel to this at –78 °C. The mixture was then allowed to warm to room temperature. A clear yellow-orange solution was usually obtained between 5 and 20 °C, and this indicated consumption of the dibromophosphorane and formation of the sulfonimidoyl bromide **12**. The same procedure was followed (in $CHCl_3$) for the reaction of Ph_3PCl_2 (0.03–0.1 mol) with **7** (1 mol-equiv), except that the phosphorane was prepared as described earlier, and the solution of **7** was added at 0 °C before allowing the reaction mixture to warm to room temperature. As with Ph_3PBr_2, a clear, colorless-to-light-yellow solution at 10–15 °C indicated completion of the reaction. Attempts to remove volatiles from the reaction mixture always resulted in rapid decomposition of the sulfonimidoyl halide.

For **12**: ^1H NMR (in CH_2Cl_2) ∂ 0.22 (s, Me_3Si), 3.70 (s, Me-S).

Reaction of 6 with Ph_3PCl_2. To Ph_3PCl_2 (0.05–0.65 mol) prepared in $CHCl_3$ in a three-necked flask equipped with a stirrer and gas inlet, Et_3N (1 mol-equiv) was added over 5 min at 0 °C with stirring. The mixture was cooled to –78 °C, and a 4–7 molar solution of **6** (1 mol-equiv) in $CHCl_3$ was added over 10–20 min. The mixture was warmed to 0 °C using an ice bath. At or slightly below 0 °C, the mixture turned virtually clear. Proton NMR run at this point of solution clarity showed complete disappearance of **6**, and formation of **11** along with 10–20% Me_3SiCl from the partial decomposition of **11**. No attempt was made to isolate sulfonimidoyl chlorides **11**. Instead, they were held at 0 °C and immediately converted to sulfonimidates as described next.

For **11a**: ^{1}H NMR (in $CHCl_3$) ∂ 0.13 (s, Me_3Si), 3.45 (s, Me-S).

For **11b**: ^{1}H NMR (in $CHCl_3$) ∂ 0.00 (s, Me_3Si), 1.27 (t, CH_3CH_2-S, J_{HH} = 7.2 Hz), 3.23 (q, CH_3CH_2-S).

For **11c**: ^{1}H NMR (in $CHCl_3$) ∂-0.05 (s, Me_3Si), 1.95–2.32 (m, $ClCH_2CH_2CH_2$-S), 3.38 (t, -CH_2-S, overlapping with $ClCH_2$), 3.45 (t, $ClCH_2$-, overlapping with -CH_2-S).

For the reaction of **6g** with Ph_3PCl_2, once it was determined that only **10b** (and no sulfonimidoyl chloride) is formed, the following procedure was followed. To Ph_3PCl_2–Et_3N (0.083 mol, each), prepared as above, was added a solution of **6g** (0.083 mol, in 45 mL of $CHCl_3$) at 0 °C. After the mixture became clear at that temperature, it was refluxed for 45 min. Solvent and volatiles were then removed at 50–55 °C under reduced pressure. The residue was stirred in distilled water for 18 h and filtered through a 0.8 μm nylon membrane filter, and the solid on the filter was washed 5–10 times with distilled water. Crude **10b** was then washed once with HPLC grade 2-propanol and thrice with hexanes and dried under vacuum at 68 °C. The compound was recrystallized from hot benzene.

For **10b**: yield 97%; mp 168–169 °C; ^{13}C NMR ∂ 119.8 (dq, CF_3-S, $^1J_{FC}$ = 320.8 Hz, $^3J_{PC}$ = 6.6 Hz), [P-C_6H_5; 125.5-i (d, $^1J_{PC}$ = 101.5 Hz), 128.9-o (d, $^2J_{PC}$ = 13.2 Hz), 132.7-m (d, $^3J_{PC}$ = 11.0 Hz), 133.5-p (d, $^4J_{PC}$ = 3.0 Hz); ^{31}P NMR ∂ 20.8. Anal. Calcd: C, 56.53; H, 3.69; N, 3.42. Found: C, 56.19; H, 3.64; N, 3.41.

Conversion of 11 to Sulfonimidates. A 3–5 molar solution of the alcohol (2,2,2-trifluoroethanol, phenol, or ethanol) and triethylamine (each 0.98 mol-equiv based on **6**) in dry benzene was added from a dropping funnel over 15–25 min to **11** held at 0 °C in solution. The mixture was stirred for 1–2 h at 0 °C, hexanes (20–40% by volume of $CHCl_3$ present) were added, and the mixture was stirred for a further 16–18 h at room temperature. Approximately 70–80% of the solvents and other volatiles were then removed under reduced pressure at 40–45 °C. Enough hexanes to make a 0.5–1.0 molar solution of **3** (based on theoretical yield) were added, the mixture was stirred for 30–60 min and filtered, and solids were washed several times with hexanes. Solvents were removed from the combined filtrate and washings under reduced pressure, at 45–55 °C. This precipitated more solids, mostly Ph_3P=O. More hexane was added, and the filtration, washing, and solvent removal procedures were repeated. The crude sulfonimidate was purified by one to three distillations under reduced pressure.

For **3a**: yield 73%; bp 77–78 °C/7.7 mm; ^{1}H NMR (in C_6H_6) ∂ 0.28 (s, Me_3Si), 2.35 (s, Me-S, 2.98 in $CDCl_3$), 3.92 (m, diastereotopic OCH_2CF_3); ^{13}C NMR ∂ 1.8 (Me_3Si), 43.2 (Me-S), 63.7 (q, OCH_2CF_3, $^2J_{FC}$ = 36.9 Hz), 122.9 (q, OCH_2CF_3, $^1J_{FC}$ = 278.1 Hz). Anal. Calcd: C, 29.14; H, 5.66; N, 5.62. Found: C, 29.01; H, 5.47; N, 5.65.

For **3b**: yield 31%; bp 85–86 °C/0.4 mm; ^{1}H NMR ∂ 0.06 (s, Me_3Si), 1.47 (t, CH_3CH_2-S, J_{HH} = 7.4 Hz), 3.22 (q, CH_3CH_2-S), 7.2–7.4 (m, OC_6H_5); ^{13}C NMR ∂ 1.8 (Me_3Si), 8.8 (CH_3CH_2-S), 49.2 (CH_3CH_2-S) [OC_6H_5; 150.0-i, 123.1-o, 129.5-m, 126.3-p]. Anal. Calcd: C, 51.32; H, 7.44; N, 5.44. Found: C, 50.81; H, 7.47; N, 5.42.

For **3c**: yield of crude product 60–65% (by ^{1}H NMR), complete condensation to polymer occurred during attempted distillation; ^{1}H NMR (in CH_2Cl_2) ∂ 0.03 (s, Me_3Si), 2.1–2.6 (m, $ClCH_2CH_2CH_2$-S), 3.35 (t, $ClCH_2CH_2CH_2$-S), 3.68 (t, $ClCH_2$), 7.1–7.5 (m, OC_6H_5).

For **3d**: yield 53%; bp 73–78 °C/0.03 mm; ^{1}H NMR (in CH_2Cl_2) ∂ 0.03 (s, Me_3Si), 3.05 (s, Me-S), 7.1–7.6 (m, OC_6H_5); ^{13}C NMR ∂ 1.7 (Me_3Si), 42.6 (Me-S) [OC_6H_5; 150.2-i, 122.9-o, 129.6-m, 126.4-p]. Anal. Calcd: C, 49.35; H, 7.04; N, 5.75. Found: C, 49.52; H, 7.06; N, 5.80.

For **3e**: yield 67%; bp 85–87 °C/1.0 mm; ^{1}H NMR ∂ 0.16 (s, Me_3Si), 2.2–2.3 (m, $ClCH_2CH_2CH_2$-S), 3.24 (t, $ClCH_2CH_2CH_2$-S, J_{HH} = 7.7 Hz), 3.65 (t, $ClCH_2$, J_{HH} = 6.2 Hz), 4.3–4.4 (m, OCH_2CF_3); ^{13}C NMR ∂ 1.4 (Me_3Si), 27.4 ($ClCH_2CH_2CH_2$-S), 42.4 ($ClCH_2CH_2CH_2$-S) 52.1 ($ClCH_2$), 62.6 (q, OCH_2CF_3, $^2J_{FC}$ = 37.0 Hz), 122.7 (q, OCH_2CF_3, $^1J_{FC}$ = 277.2 Hz). Anal. Calcd: C, 30.81; H, 5.50; N, 4.49. Found: C, 30.82; H, 5.51; N, 4.57.

For **3f**: yield 45%; bp 105–108 °C/0.04 mm; ^{1}H NMR ∂ 0.31 (s, Me_3Si), 6.83 (d, Ph-CH=CH-S, J_{HH} = 15.3 Hz), 4.2–4.4 (m, OCH_2CF_3), 7.4–7.6 (m, C_6H_5-, overlapping with C_6H_5-CH=CH- signal); ^{13}C NMR ∂ 1.7 (Me_3Si), 125.4 (Ph-CH=CH-S, tentative assignment), 142.4 (Ph-CH=CH-S, tentative assingment), 64.1 (q, OCH_2CF_3, $^2J_{FC}$ = 36.6 Hz), 122.8 (q, OCH_2CF_3, $^1J_{FC}$ = 277.6 Hz) [C_6H_5; 132.2-i, 128.4-o, 129.0-m, 131.0-p]. Anal. Calcd: C, 46.27; H, 5.38; N, 4.15. Found: C, 46.63; H, 5.09; N, 4.09.

For **3g**: the product decomposed on attempted distillation, but formation was inferred based on the successful isolation and purification of **3f** and on the detection of Ph_3P=O in the crude.

For **3h**: yield 27%; bp 84–86 °C/0.7 mm; ^{1}H NMR (in C_6H_6, CH_2Cl_2) ∂ 0.37 (s, Me_3Si, in C_6H_6), 3.6–4.2 (m, diastereotopic OCH_2CF_3, in C_6H_6), 7.4–8.0 (m, C_6H_5-S, in CH_2Cl_2); ^{13}C NMR ∂ 1.8 (Me_3Si), 64.2 (q, OCH_2CF_3, $^2J_{FC}$ = 36.9 Hz), 122.5 (q, OCH_2CF_3, $^1J_{FC}$ = 277.9 Hz) [C_6H_5; 139.5-i, 127.6-o, 129.1-m, 133.1-p]. Anal. Calcd: C, 42.43; H, 5.18; N, 4.50. Found: C, 41.90; H, 5.16; N, 4.59.

For **3i**: yield 21%; bp 91–98 °C/0.025 mm; ^{1}H NMR ∂ 0.29 (s, Me_3Si), 6.9–7.9 (m, overlapping C_6H_5-S and OC_6H_5); ^{13}C NMR ∂ 2.0 (Me_3Si) [C_6H_5-S; 140.1-i, 127.8-o, 128.5-m, 132.6-p] [OC_6H_5; 150.7-i, 122.9-o, 129.1-m, 126.1-p]. Anal. Calcd: C, 58.98; H, 6.38; N, 4.59. Found: C, 59.49, H, 6.32; N, 4.39.

For **3j**: yield 21%; bp 113–119 °C/0.05 mm; ^{1}H NMR ∂ 0.26 (s, Me_3Si), 6.9–7.9 (m, overlapping 4-F-C_6H_4-S and OC_6H_5); ^{13}C NMR ∂ 2.0 (Me_3Si) [4-F-C_6H_4-S, ring position of carbon atom with respect to sulfur; 136.3-i ($^4J_{FC}$ = 3.3 Hz), 130.7-o ($^3J_{FC}$ = 9.5 Hz), 115.8-m ($^2J_{FC}$ = 22.7 Hz), 165.2-p ($^1J_{FC}$ = 254.5 Hz)] [OC_6H_5; 150.7-i, 123.0-o, 129.3-m, 126.3-p]. Anal. Calcd: C, 55.70; H, 5.61; N, 4.33. Found: C, 55.30; H, 5.62; N, 4.75.

For **3k**: yield 78%; bp 76–79 °C/4.8 mm; ^{1}H NMR ∂ 0.18 (s, Me_3Si), 2.93 (s, Me-S), 1.31 (apparent triplet, OCH_2CH_3, J_{HH} = 7.2 Hz), 4.0–4.1 (m, diastereotopic (OCH_2CH_3); ^{13}C NMR ∂ 1.7 (Me_3Si), 41.9 (Me-S), 14.9 (OCH_2CH_3), 63.9 (OCH_2CH_3). Anal. Calcd: C, 36.89; H, 8.77; N, 7.17. Found: C, 36.80; H, 8.56; N, 7.63.

For **14**: yield 10%; bp 92–94 °C/0.75 mm; ^{1}H NMR ∂ 2.42 (s, CH_3-C_6H_4-S), 2.96 (s, N-Me), 4.12 (apparent quartet, OCH_2CF_3), 7.29–7.33 and 7.82–7.86 (m, Me-C_6H_4-S); ^{13}C NMR ∂ 21.6 (CH_3-C_6H_4-S), 28.5 (N-Me), 64.7 (q, OCH_2CF_3, $^2J_{FC}$ = 36.6 Hz), 122.8 (q, OCH_2CF_3, $^1J_{FC}$ = 278.0 Hz) [CH_3-C_6H_4-S, ring position of carbon atom with respect to sulfur; 144.7-i, 127.8-o, 129.9-m, 133.8-p]. Anal. Calcd: C, 44.94; H, 4.53; N, 5.24. Found: C, 44.70; H, 4.50; N, 5.24.

Reaction of *N*-Silylsulfonimidates with Chlorophosphines. To 0.005–0.04 mol of **3a** in a two-necked flask equipped with a magnetic stirring bar, rubber septum, and gas inlet, was slowly added chlorophosphine (1 mol-equiv) via syringe (at −78 °C for PCl_3, at 0 °C for Ph_2PCl). The mixture was allowed to warm to room temperature and stirred for 1 h for PCl_3 and for 3–4 h for Ph_2PCl. Chlorotrimethylsilane was then removed under reduced pressure at 25–30 °C. Compound **16a** was relatively quite pure in the crude state and was characterized by NMR as mentioned earlier. Compound **16b** distilled at high vacuum as a very high boiling liquid and was characterized by NMR soon after distillation.

For **16a**: ^{1}H NMR ∂ 3.4 (d, Me-S, $^4J_{PH}$ = 1.7 Hz), 4.5–4.7 (m, diastereotopic OCH_2CF_3 protons); ^{13}C NMR ∂ 43.5 (d, Me-S $^3J_{PC}$ = 2.6 Hz), 63.8 (q, OCH_2CF_3, $^2J_{FC}$ = 38.5 Hz), 122.0 (q, OCH_2CF_3, $^1J_{FC}$ = 278.0 Hz); ^{31}P NMR ∂ 150.8.

For **16b**: bp 152–154 °C/0.05 mm; ^{1}H NMR ∂ 3.27 (s, Me-S), 4.1–4.4 (m, diastereotopic OCH_2CF_3 protons), 7.3–7.7 (m, C_6H_5); ^{13}C NMR ∂ 41.8 (s, Me-S), 63.3 (dq, OCH_2CF_3, $^2J_{FC}$ = 37.4 Hz, $^4J_{PC}$ = 1.1 Hz), 122.5 (q, OCH_2CF_3, $^1J_{FC}$ = 277.6 Hz), [nonequivalent $(C_6H_5)_a(C_6H_5)_bP$ signals; 141.6-i ($^1J_{PC}$ = 13.9 Hz), 141.5-i ($^1J_{PC}$ = 13.9 Hz), 128.48-o ($^2J_{PC}$ = 7.3 Hz), 128.55-o ($^2J_{PC}$ = 7.7 Hz), 130.7-m ($^3J_{PC}$ = 13.2 Hz), 131.2-m ($^3J_{PC}$ = 13.6 Hz), 129.2-p, 129.4-p]; ^{31}P NMR ∂ 41.8.

Reaction of 3d with Acryloyl Chloride. Acryloyl chloride (98%, 0.02 mol, 1.7 mL) was added via syringe at room temperature to **3d** (0.02 mol, 4.86 g) in a flask equipped with a rubber septum, magnetic stirring bar, gas inlet, and reflux condenser. The mixture was heated for 7–8 h at 65–70 °C. Volatiles were then removed at 40–50 °C (0.2 mm). Proton NMR at this point showed >90% conversion of **3d** to the acryloyl sulfonimidate **17**. Compound **17** distilled under reduced pressure and provided clean ^{1}H and ^{13}C NMR spectra but repeated distillation for microanalysis caused a marked increase in viscosity indicative of partial polymerization of the vinyl functionality.

For **17**: bp 100–105 °C/0.05 mm; ^{1}H NMR ∂ 3.51 (s, Me-S), 6.34 (dd, CH_x=CH_aH_b, J_{ab} = 1.9 Hz, $^{trans}J_{ax}$ = 17.2 Hz), 5.73 (dd, CH_x=CH_aH_b, $^{cis}J_{bx}$ = 9.8 Hz), 6.12 (dd, CH_x=CH_aH_b), 7.3–7.4 (OC_6H_5); ^{13}C NMR ∂ 39.2 (Me-S), 129.4 (CH_x=CH_aH_b), 134.1 (CH_x=CH_aH_b) [OC_6H_5; 148.0-i, 122.4-o, 129.9-m, 127.7-p], 171.8 (C=O).

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