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Mechanisms of Hydrolysis of (Trimethylsilyl)methanesulfonyl Chloride. Sulfene–Enamine Reactions in Water[1]

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Kinetic, product analysis, and deuteration experiments are consistent with the following mechanisms of hydrolysis of (trimethylsilyl)methanesulfonyl chloride (1) (in 0.01 M KCl at 1 °C): (a) pH ≤ 10.0, attack of water at silicon to form sulfene (5) which is trapped by water to give methanesulfonate anion (3), (b) pH ≥ 10.0, attack of hydroxide anion (i) at silicon to yield sulfene (5) and (ii) at an α-hydrogen to form (trimethylsilyl)sulfene (4), in each case followed by trapping of the sulfene to give either methanesulfonate (3) or (trimethylsilyl)methanesulfonate (6) salts. Aqueous potassium fluoride catalyzes the hydrolysis of 1 with formation of the methanesulfonate 3, evidently by way of silicophilic attack of fluoride anion on 1 with formation of sulfene (5). Reaction of 1 with an enamine 7 in water (at pH 8 or 9), with or without fluoride, gives two characteristic sulfene–enamine products, (i) the four-membered cycloadduct 8 and (ii) the methylsulfonyl aldehyde 9. The same or related products are also obtained from methanesulfonyl, 2-propanesulfonyl, and phenylmethanesulfonyl chlorides and enamines in water (at pH 9). Hydrolysis of 1 is also catalyzed by aniline or triethylamine evidently giving 5.

(Trimethylsilyl)methanesulfonyl chloride (1), the simplest α-silylalkanesulfonyl chloride, was first prepared from the reaction of tetramethylsilane with sulfuryl chloride by Cooper,[3] who recorded that it (a) hydrolyzed to give hexamethyldisiloxane (2) and methanesulfonate anion (3) and (b) reacted with dry ammonia in toluene to form (trimethylsilyl)methanesulfonamide. Subsequently, Baukov et al.[4] reported that 1 was also prepared from (trimethylsilyl)methyl chloride by reaction of the Grignard reagent with sulfur dioxide followed by chlorination. They further noted that 1 was readily converted by triethylamine in the presence of alcohols or primary or secondary amines into the (trimethylsilyl)methanesulfonic esters or amides, or, with enamines, into the four-membered ring cycloadduct of the enamine and (trimethylsilyl)sulfene (4). More recently, Block and co-workers[5] provided two additional routes to 1 and showed that it and related compounds undergo a useful fluorodesilylation with cesium fluoride in dry acetonitrile exemplified by the formation of sulfene (5) from 1.

$$\underset{\mathbf{1}}{Me_3SiCH_2SO_2Cl}\qquad \underset{\mathbf{2}}{Me_3SiOSiMe_3}\qquad \underset{\mathbf{3}}{CH_3SO_3^-\ M^+}$$

$$\underset{\mathbf{4}}{Me_3SiCH{=}SO_2}\qquad \underset{\mathbf{5}}{CH_2{=}SO_2}\qquad \underset{\mathbf{6}}{Me_3SiCH_2SO_3^-\ M^+}$$

In the context of our recent study of the mechanisms of hydrolysis of alkanesulfonyl chlorides[2,6] we decided to look at the mechanism of the hydrolysis of 1 to obtain a clearer picture of the influence of the α-trimethylsilyl group on sulfonyl chloride reactivity. This paper describes our results.

Results and Discussion

Materials, Kinetics, and Products of Hydrolysis. (Trimethylsilyl)methanesulfonyl chloride (1) was prepared from (trimethylsilyl)methyl chloride by the sequence $Me_3SiCH_2Cl \rightarrow Me_3SiCH_2MgCl \rightarrow (Me_3SiCH_2SO_2^-)_2Mg \rightarrow$ 1, as outlined by Baukov et al.[4a] The product so obtained showed the same boiling and melting points and refractive index as those reported[3,4a] and ^1H and ^{13}C NMR spectra in full accord with 1; reaction of 1 with ammonia gave $Me_3SiCH_2SO_2NH_2$ with the same melting point as that reported by Cooper.[3]

The rate of hydrolysis of 1, though much too fast at 25 °C for our pH-stat apparatus, could be followed with some difficulty at 1.0 °C (in 0.01 M KCl). The rates so obtained, though approximate, were in accord with pseudo-first-order decomposition of 1 in water over the pH range 4–11; the resulting pH–rate profile is shown in Figure 1 (solid line and circles). Variation of the concentration of potassium chloride from 0.01 to 0.03 M (at pH 8.0) had no effect on k_{obsd} values within experimental uncertainty.

The products isolated at pH 6.0 (at the same concentrations as the rate measurements) were hexamethyldisiloxane (2) and the methanesulfonate salt (3), as previously noted.[3] In dilute sodium hydroxide at pH 10.0 and 11.0 the water-soluble products were found to be the methanesulfonate and (trimethylsilyl)methanesulfonate salts (3 and 6) in the ratios 78:22 and 69:31, respectively. In D_2O at (a) pD 3.5 and (b) 11.4, the products are, respectively, (a) $CH_2DSO_3^-$ and (b) a mixture of $CH_2DSO_3^-$ and $Me_3SiCHDSO_3^-$.

The Mechanisms of Hydrolysis. These observations are consistent with a rate law as in eq 1, with k_w 2.1 × 10^{-2}

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[1] Organic Sulfur Mechanisms. 37. Part 36, see: ref 2. Presented in part at the Third International Conference on Heteroatom Chemistry, Riccione, Italy, June 1992.

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[4] (a) Baukov, Yu. I.; Shipov, A. G.; Gorshkova, L. V.; Savost'yanova, I. A.; Kisin, A. V. *Zh. Obshch. Khim.* **1977**, *47*, 1677–1678 (Engl. trans., 1538–1539). (b) Shipov, A. G.; Kisin, A. V.; Baukov, Yu. I. *Zh. Obshch. Khim.* **1979**, *49*, 1170 (Engl. trans., 1022).

[5] (a) Block, E.; Aslam, M. *Tetrahedron Lett.* **1982**, *23*, 4203–4206. (b) Block, E.; Wall, A. *Tetrahedron Lett.* **1985**, *26* 1425–1428. (c) Block, E.; Wall, A. *J. Org. Chem.* **1987**, *52*, 809–818. (d) Block, E.; Schwan, A.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 3492–3499.

[6] King, J. F.; Lam, J. Y. L.; Skonieczny, S. *J. Am. Chem. Soc.* **1992**, *114*, 1743–1749.

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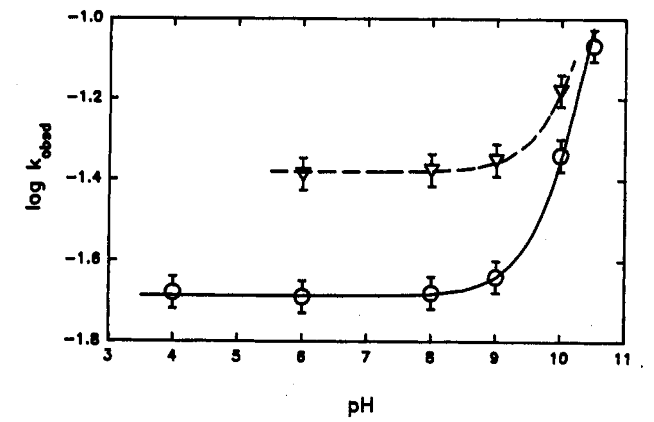


Figure 1. pH–rate profiles (at 1.0 °C, μ = 0.01 M with KCl) for the hydrolysis of (trimethylsilyl)methanesulfonyl chloride (1) (circles) (in 0.01 M KCl) and in the presence of KF (triangles) (total added KF 5 × 10^{-5} M). The points are experimental; the line through the circles is calculated from eq 1 with $k_w = 2.1 \times 10^{-2}$ s^{-1} and $k_{OH} = 1.7 \times 10^3$ M^{-1} s^{-1}. The line through the triangles is given by eq 2 with $k_N = 4.1 \times 10^2$ M^{-1} s^{-1} and [F$^-$] = 5 × 10^{-5} M. The error bars correspond to an estimated error in k_{obsd} values of ±10%.

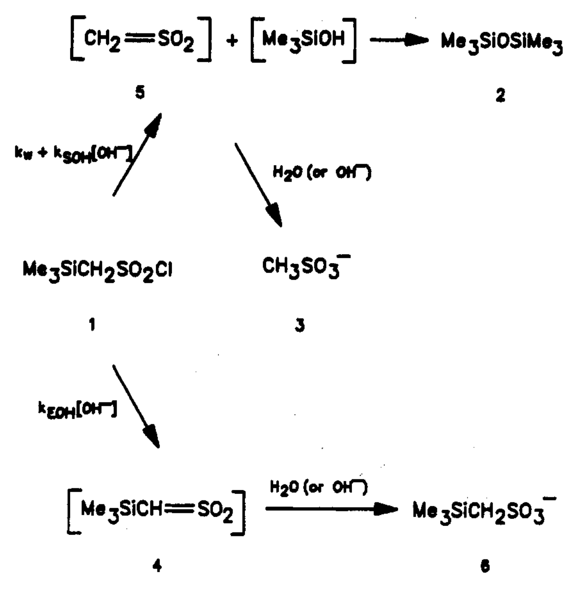
s^{-1}, k_{OH} 1.7 × 10^3 M^{-1} s^{-1}; from these we may deduce that

$$k_{obsd} = k_w + k_{OH}[OH^-] \qquad (1)$$

pH$_i$ is 10.0, where pH$_i$ is defined[7] as the pH at which the water- and hydroxide-promoted reactions have the same rate. For the pH-independent reaction (i.e., pH distinctly below pH$_i$) these results may be simply interpreted on the basis of attack by water on the silicon with formation of sulfene (5), which is then trapped by water to give methanesulfonate anion. At pH's well above pH$_i$ (e.g., ≥11) hydroxide clearly attacks 1 in two ways: (a) chiefly by reaction at silicon to form sulfene (2) much like the reaction of water and (b), the minor process, attack of hydroxide at an α-hydrogen to form (trimethylsilyl)sulfene (4); in each case the sulfene is trapped to form the corresponding sulfonate salt (3 or 6). The measured rate constant k_{OH} is therefore the sum of two specific rates, $k_{SOH} = 1.1 \times 10^3$ M^{-1} s^{-1} for the attack at silicon yielding 5 and $k_{EOH} = 6 \times 10^2$ M^{-1} s^{-1} for the elimination to form 4; these parameters predict the product ratios, 3:6, of 82:18 and 68:32 for the reactions at pH 10.0 and 11.0, respectively, in reasonable accord with the yields quoted above. Scheme I summarizes this picture.[8]

Inspection of the deuterium-labeling results permits the exclusion of two related pathways shown by eqs 2 and 3. Reaction by eq 2 if carried out in D_2O would yield CH_2DSO_2Cl, which with OD$^-$ is known[6] to give a mixture in which $CHD_2SO_3^-$ predominates. Similarly, any reaction

Scheme I



via eq 3 in D_2O would require that the initially formed $Me_3SiCHDSO_3^-$ also lead to $CHD_2SO_3^-$. There is no sign (<2%) of any $CHD_2SO_3^-$ in the reaction product, and hence, these pathways are not significant in the reaction of 1 with hydroxide.

$$HO^- + Me_3SiCH_2SO_2Cl \rightarrow [^-CH_2SO_2Cl] \rightarrow CH_3SO_2Cl \rightarrow CH_3SO_3^- \qquad (2)$$

$$HO^- + Me_3SiCH_2SO_3^- \rightarrow [^-CH_2SO_3^-] \rightarrow CH_3SO_3^- \qquad (3)$$

When we compare these reactions with those of the simple alkanesulfonyl chlorides it is evident that the α-trimethylsilyl group has a profound effect. The reaction of alkanesulfonyl chlorides with water is (a) much slower and is (b) an exclusive attack at the sulfonyl sulfur in a direct S$_N$2–S process; the reaction of hydroxide is an elimination of HCl to form the sulfene. With 1, on the other hand, at low pH the silicophilic attack of water is sufficiently fast that no sign of the S$_N$2–S product ($Me_3SiCH_2SO_3H$) is seen. In the reaction of 1 with hydroxide the silicophilic attack to give 5 is the major reaction, and the elimination to form (trimethylsilyl)sulfene (4) is only a minor process.

Reactions of 1 and Other Sulfonyl Chlorides with Enamines in Water. To confirm the formation of sulfene (5) in the water-promoted reaction, 1 was treated with an enamine (7) in water (containing ~20% DME) at pH 8. As may be seen in Scheme II the major product of the reaction is the sulfene–enamine adduct 8, first obtained by Opitz and Adolph[9] from methanesulfonyl chloride with 7 and triethylamine in ether. Two other sulfonyl-containing products were also observed: (a) 1-(methylsulfonyl)pyrrolidine (10) perhaps from trapping of sulfene (2) with pyrrolidine resulting from hydrolysis of 7 (or 12) and (b) the α-methylsulfonyl aldehyde 9. Formation of 9 is readily accounted for if one assumes that the sulfene–enamine reaction proceeds via the zwitterionic intermediate 11, which either undergoes cyclization to 8 or protonation to 12 which is subsequently hydrolyzed to 9.

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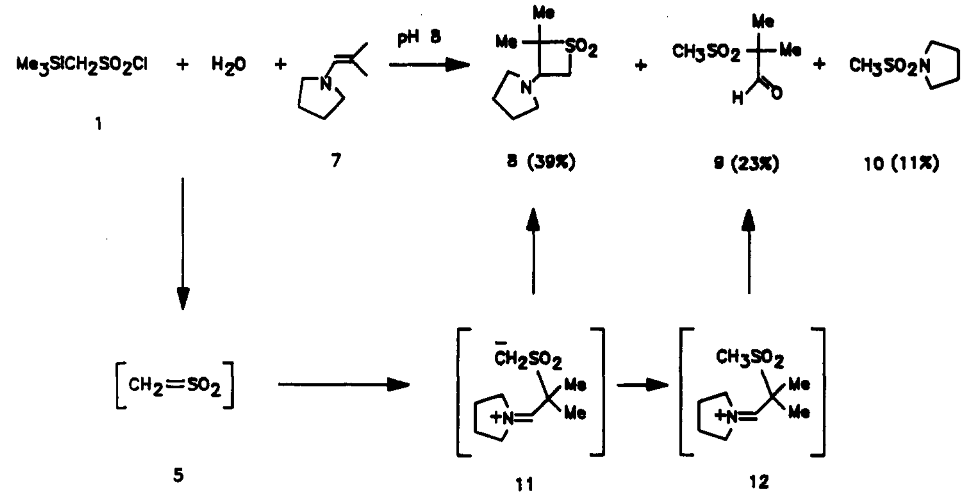
[7] King, J. F.; Rathore, R.; Lam, J. Y. L.; Guo, Z. R.; Klassen, D. F. *J. Am. Chem. Soc.* **1992**, *114*, 3028–3033.

[8] The assumption made in this scheme is that the initially formed trimethylsilanol (Me_3SiOH) proceeds directly to form hexamethyldisiloxane, but it is also conceivable that 5 might arise by the action of Me_3SiOH on 1 (up to 50% of the total reaction 1 → 5). Similarly, it is also possible that the reaction promoted by hydroxide is partially effected by Me_3SiOH or Me_3SiO^-. Though it is not easy with the available evidence to exclude completely the participation of trimethylsilanol and its conjugate base in these reactions, we are inclined to regard their contribution as small on the following grounds: (a) given that the initial concentration of 1 is 5.5 × 10^{-4} M or less, the concentration of Me_3SiOH or Me_3SiO^- must be very small at all times, (b) there is no sign of autocatalysis in the reaction kinetics, and (c) doubling the concentration of 1 at pH 11.0 did not alter the ratio of 3 to 6. More information on the behavior of Me_3SiOH in water, however, is required to settle the point.

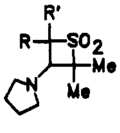
[9] Opitz, G.; Adolph, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 113. Opitz, G.; Schempp, H.; Adolph, H. *Liebigs Ann. Chem.* **1965**, *684*, 92–102.

Scheme II



It has long been regarded[10] as likely that sulfene–enamine additions proceed in nonpolar solvents via a zwitterionic intermediate like **11**; such an intermediate would be even more likely in the highly polar medium used in the present work.

Water has not been the usual solvent for sulfene–enamine cyclizations, and it was of interest to see what extent the previously studied reactions might be altered by being carried out in aqueous medium. It was found that the reactions of methanesulfonyl chloride with **7** in water (containing about 20% DME) at pH 9 gave comparable yields of the same products, specifically, **8**, **9**, and **10**, in, respectively, 40%, 16%, and 32% yields. The generality of the sulfene–enamine reaction in water is shown by the formation of the following products from the reactions of sulfonyl chlorides with enamines: (a) phenylmethanesulfonyl chloride with **7**, **13a** (59%), and **14a** (10%); (b) 2-propanesulfonyl chloride with **7**, **13b** (6%), and **14b** (28%); (c) methanesulfonyl chloride with 1-(*N*-pyrrolidino)cyclohexene, **15** (10%), and **16a** (26%); (d) phenylmethanesulfonyl chloride with 1-(*N*-pyrrolidino)cyclohexene, **16b** (39%).



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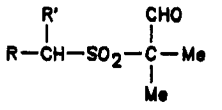

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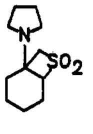
a) R = Ph, R' = H
b) R, R' = Me



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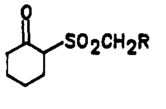

16 a) R = H
b) R = Ph

Reactions with Other Added Nucleophiles. (a) Fluoride Anion. Recalling Block and Aslam's observation of the rapid formation of sulfene (**5**) from **1** with cesium fluoride in dry acetonitrile,[5a] we examined hydrolysis of **1** in the presence of potassium fluoride. As may be seen from Figure 1 (broken line and triangles) even 5×10^{-5} M KF shows a distinct catalytic effect. At pH 8.0 a linear dependence of k_{obsd} on the concentration of fluoride ion was found (see Figure 2); these results point to a rate law as in eq 4 with $k_F = 4.1 \times 10^2\ M^{-1}\ s^{-1}$ (at 1 °C). The products extractable with organic solvents from reaction of **1** and aqueous KF (0.01 M) at 0 °C showed NMR spectra indicating the presence of trimethylsilyl fluoride and hexamethyldisiloxane, along with a trace (<1%) of methanesulfonyl fluoride. In a reaction at pH 11 with 0.01 M KF the water-soluble product was found to consist almost entirely of $CH_3SO_3^-$ (**3**) (>99%) with an estimated 0.3% of $Me_3SiCH_2SO_3^-$ (**6**). Aqueous KF (0.1 M) at pH 9 with **1** in the presence of the enamine **7** gave **8**, **9**, and **10** in, respectively, 46%, 9%, and 28% yields, again in excellent accord with formation of sulfene (**5**).

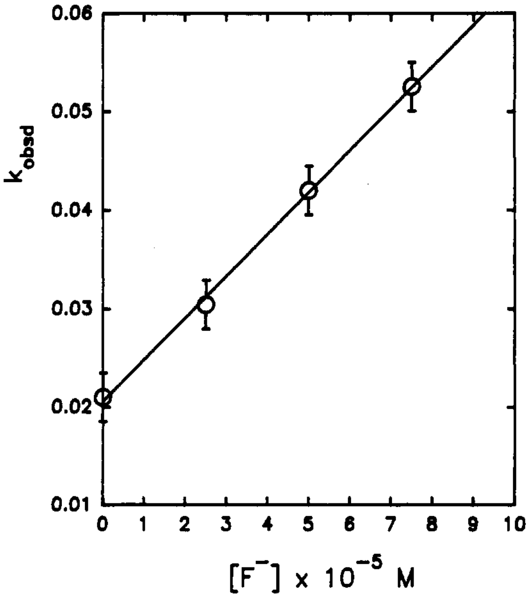

Figure 2. Variation of k_{obsd} for the hydrolysis of (trimethylsilyl)methanesulfonyl chloride (**1**) with the concentration of fluoride anion at pH 8 at 1.0 °C. The points are experimental; the line is that of the least-squares fit: $k_{obsd} = (4.24 \times 10^{-2})\ [F^-] + (2.06 \times 10^{-2})$.

$$k_{obsd} = k_w + k_{OH}[OH^-] + k_F[F^-] \tag{4}$$

(b) Aniline. With aniline (at pH 8.0 and 1.0 °C) a weak catalytic effect corresponding to $k_N = 2.2 \pm 0.2\ M^{-1}$

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[10] Paquette, L.; Rosen, M. *J. Am. Chem. Soc.* 1967, *89*, 4102–4112; *Tetrahedron Lett.* 1967, 703–707. Opitz, G. *Angew. Chem., Int. Ed. Engl.* 1967, *6*, 107–123.

s^{-1} was found. The products obtained under the conditions of the rate measurements were methanesulfonanilide ($MeSO_2NHPh$, 6.3%) and the methanesulfonate salt (**3**) with no sign of any (trimethylsilyl)methanesulfonanilide ($Me_3SiCH_2SO_2NHPh$) or the (trimethylsilyl)methanesulfonate salt (**6**). The absence of the (trimethylsilyl)methanesulfonate derivatives in the product clearly excludes any (a) direct nucleophilic attack of aniline on the sulfonyl sulfur atom[11] or (b) formation of (trimethylsilyl)sulfene (**4**). This in turn points to attack of either aniline itself or of water with the assistance of aniline at the silicon to give sulfene (**5**) which is then trapped by aniline or water. The trapping ratio, k_{TN}/k_{TW}, for aniline vs water estimated from the above yield of $MeSO_2NHPh$ is roughly 3.4 (±0.3), in agreement with the value of 3.2 determined from more extensive experiments with aniline and methanesulfonyl chloride in water.[12]

(c) Triethylamine. We have also briefly looked at the hydrolysis of **1** in the presence of triethylamine and observed a catalytic effect in rate measurements at pH 8 corresponding to a k_N value for Et_3N of 1.2×10^2 M^{-1} s^{-1}. Upon examination of the products at pH 8 with the concentration of the free amine estimated to be 2.0×10^{-5} M, the water-soluble product showed the presence of only $CH_3SO_3^-$ (**3**) with no sign of any $Me_3SiCH_2SO_3^-$ (**6**). Since at this concentration of Et_3N $\geq$50% of the product would be expected to arise from the reaction of **1** with the amine, it would appear that the amine does not react with **1** to form trimethylsilylsulfene (**4**) but rather (like aniline) either (a) attacks the silicon directly with formation of **5** or (b) acts as a general base aiding the attack of water on **1** at silicon to form **5**. It has been reported by Shipov et al.[4b] that **1** reacts with Et_3N in *ether* to give **4**. In our view it is less likely that change in solvent would lead to a complete switch in site of attack of the base from hydrogen to silicon and more probable that triethylamine is acting as a general base assisting attack of water on **1**.

Experimental Section

General. ^1H NMR spectra were obtained with a Varian XL-200 or Gemini-200 spectrometer and ^{13}C NMR spectra with either a Varian XL-300 or the Gemini instrument. Mass spectra were run on a Finnigan MAT 8230 instrument using electron impact except where otherwise noted and infrared spectra on a Bruker IFS 32 FTIR spectrometer using NaCl plates for neat liquids or KBr pellets for solid samples. Melting points are uncorrected. 1,2-Dimethoxyethane (DME) was dried by distillation from CaH_2. Standard sodium hydroxide solution (0.1 M, Fisher) was used as supplied or diluted appropriately. Unless otherwise stated, other solvents and reagents were reagent-grade commercial materials used as supplied. Solvent evaporation after extraction was carried out under reduced pressure using a Büchi Rotovap apparatus. The following parameters at 1.0 °C were estimated by extrapolation from values given in the sources cited: K_w 1.34×10^{-15} (ref 13), pK_a's of $PhNH_2$ 5.04, and Et_3N 11.29.[14] Further experimental details are given elsewhere.[12]

(Trimethylsilyl)methanesulfonyl Chloride (cf. ref 4a). A 20-mL portion of a solution of Me_3SiCH_2Cl (5.0 g, 0.04 mol) and anhydrous ether (50 mL) was added to magnesium (Fisher "coarse", 1.1 g, 0.045 mol) with stirring in a 1-L three-necked flask under a stream of dry N_2. The reaction started within 15 min. More ether (100 mL) was added to the flask through the condenser and the rest of the Me_3SiCH_2Cl–ether solution then added dropwise to give a dark gray solution of Me_3SiCH_2MgCl. More ether (150 mL) was added to the mixture which was then cooled in an ice bath and SO_2 bubbled into the mixture vigorously for 20 min. The solvent was removed, initially on the Rotovap and then on the vacuum pump for 3 h. The residue was dissolved in CH_2Cl_2 (150 mL) and a solution of Cl_2 in CH_2Cl_2 then added dropwise until a yellow color just appeared. The mixture was filtered and the solvent evaporated; the residue was distilled under reduced pressure to give $Me_3SiCH_2SO_2Cl$ (6.4 g, 84% yield) as a colorless oil: bp 100 °C (0.01 Torr); mp 18 °C (lit.[4a] mp 18–19 °C); n^{20}_D 1.4700 (lit.[3,4a] n^{20}_D 1.4680); IR ν_{max} 760, 783, 857, 1175, 1258, 1366 cm^{-1}; ^1H NMR δ 0.29 (s, 9H), 3.60 (s, 2H); ^{13}C NMR δ −1.2, 59.9; ^{29}Si NMR δ 3.99.

Derivatives. (a) (Trimethylsilyl)methanesulfonanilide. A solution of aniline (0.4 g, 4 mmol) and Et_3N (0.5 g, 5 mmol) in CH_2Cl_2 (20 mL) was added to a stirred solution of $Me_3SiCH_2SO_2Cl$ (0.5 g, 2.7 mmol) in CH_2Cl_2 (25 mL) and stirring continued for 30 min. The reaction mixture was then washed (aqueous HCl) and dried ($MgSO_4$) and the solvent evaporated to give the sulfonanilide (0.55 g, 84.6% yield) as a yellow viscous oil. A sample was distilled in the cold finger apparatus to give a pale yellow oil: bp 160 °C (0.05 Torr); IR ν_{max} 1150, 1254 cm^{-1}; ^1H NMR δ 0.22 (s, 9H), 2.73 (s, 2H), 7.08 (broad, H, NH), 7.25 (m, 5H); ^{13}C NMR δ −0.9, 42.9, 120.7, 125.3, 130.2, 138.2; exact mass calcd for $C_{10}H_{17}NO_2SSi$ 243.0749, found 243.0755. **(b) (Trimethylsilyl)methanesulfonamide** was prepared as described[3] from NH_3 gas and $Me_3SiCH_2SO_2Cl$ (0.5 g, 2.7 mmol) in CH_2Cl_2, in 67% yield: mp 120–122 °C (ethanol–pentane) (lit.[3] mp 122–123 °C; IR ν_{max} 1148, 1310 cm^{-1}; ^1H NMR δ 0.23 (s, 9H), 2.89 (s, 2H), 4.83 (broad, 2H, NH); ^{13}C NMR δ −1.0, 48.1; exact mass calcd for $C_4H_{13}SO_2SiN$ 167.0436, found 167.0440.

Authentic Specimens. (a) Fluorotrimethylsilane. A solution of Me_3SiCl (5.0 g, 0.05 mol) and aqueous HF (49%, 2.0 g) in a 100-mL round-bottomed flask connected to a cold trap (0 °C) was stirred for 15 min. The colorless liquid (1.0 g) collected in the trap contained a mixture of Me_3SiF and Me_3SiCl (^1H NMR showed the ratio 13:7). Me_3SiF (14.4% yield): ^1H NMR δ 0.21 (d, 9H, J = 7.4 Hz); ^{13}C NMR δ 0.05 (d, J = 15 Hz). Me_3SiCl (7.8% yield): ^1H NMR δ 0.41 (s, 9H); ^{13}C NMR δ 3.2. **(b) 1-(Methylsulfonyl)pyrrolidine (10).** A solution of pyrrolidine (0.5 g, 7.0 mmol) and NEt_3 (0.6 g, 6 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of methanesulfonyl chloride (0.5 g, 4 mmol) in CH_2Cl_2 (40 mL) and stirring continued for 10 min. The reaction mixture was washed (aqueous HCl) and dried ($MgSO_4$) and the solvent evaporated; the residue was recrystallized (ethanol) to give **10** (0.5 g, 77% yield) as colorless crystals: mp 68–69 °C (lit.[15] mp 69–70 °C); IR ν_{max} 1148, 1323 cm^{-1}; ^1H NMR δ 1.95 (t, 4H), 2.83 (s, 3H), 3.33 (t, 4H); ^{13}C NMR δ 25.6, 34.4 47.8. **(c) 1-(2-Propylsulfonyl)pyrrolidine.** The same procedure with 2-propanesulfonyl chloride gave (2-propanesulfonyl)pyrrolidide as a colorless oil (97% yield): IR ν_{max} 1138, 1323 cm^{-1}; ^1H NMR δ 1.36 (d, 6H), 1.94 (t, 4H), 3.25 (septet, 1H), 3.40 (t, 4H); ^{13}C NMR δ 16.4, 25.8, 48.0, 52.7. Similarly prepared was **(d) 1-(Phenylmethylsulfonyl)pyrrolidine** (61% yield) as a white solid: mp 76–77 °C (ethanol) (lit.[16] mp 75–76 °C and 93–94 °C); IR ν_{max} 1150, 1329 cm^{-1}; ^1H NMR δ 1.80 (t, 4H), 3.15 (t, 4H), 4.25 (s, 2H), 7.37 (m, 5H); ^{13}C NMR δ 25.7, 48.0, 56.2, 128.5, 128.6, 129.4, 130.5. **(e) 2,2-Dimethyl-3-pyrrolidinothietane 1,1-dioxide (8)** was prepared as described[9] from methanesulfonyl chloride (0.5 g, 4.4 mmol), **7** (0.6 g, 4.8 mmol), and NEt_3 (0.9 g, 9 mmol) in ether (50 mL) in 79% yield: mp 66 °C (lit.[9] mp 67–68 °C); IR ν_{max} 1107, 1302 cm^{-1}; ^1H NMR δ 1.51 (s, 3H), 1.56 (s, 3H), 1.79 (m, 4H), 2.45 (m, 4H), 2.79 (t, 1H), 3.91 (d, 2H); ^{13}C NMR δ 17.0, 21.6, 23.1, 53.2, 59.0, 64.4, 80.1. **(f) 2,2,4,4-Tetramethyl-3-pyrrolidinothietane 1,1-dioxide (13b)** was prepared as described[17] from 2-propanesulfonyl chloride (0.5 g, 3.5 mmol), **7** (0.53 g, 4.2 mmol), and NEt_3 (0.75 g, 6.9 mmol) in acetonitrile (100 mL) at −40 °C in 80% yield: mp 113–115 °C (lit.[17] mp 111 °C); IR ν_{max} 1096, 1293 cm^{-1}; ^1H NMR δ 1.45 (s, 6H),

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[11] Direct nucleophilic attack of aniline on the sulfonyl sulfur has been observed in the reaction of aniline with methanesulfonyl chloride in water.[12]

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1.59 (s, 6H), 1.75 (m, 4H), 2.37 (s, 1H), 2.41 (m, 4H); ^{13}C NMR δ 18.3, 23.1, 23.8, 54.2, 72.4, 77.3. **(g) 1-Pyrrolidino-7-thiabicyclo[4.2.0]octane 7,7-dioxide (15)** was prepared as described[18] from methanesulfonyl chloride (2.0 g, 17.5 mmol), 1-(*N*-pyrrolidino)cyclohexene (2.64 g, 17.5 mmol), and NEt_3 (2.65 g, 26.2 mmol) in benzene (300 mL) at 0 °C in 75% yield: mp 43–44 °C (lit.[18] mp 42–43 °C); IR ν_{max} 1312, 1134 cm^{-1}; ^{1}H NMR δ 1.4–2.0 (m, 10H), 2.13–2.27 (m, 2H), 2.54–2.64 (m, 2H), 2.72–2.83 (m, 2H), 3.57 (d, 1H), 4.15 (d, 1H), 4.47 (t, 1H); ^{13}C NMR δ 18.4, 19.6, 20.0, 23.9, 30.0, 47.3, 49.3, 68.6, 76.4. **(h) 4,4-Dimethyl-2-phenyl-3-pyrrolidinothietane 1,1-dioxide (13a)** was prepared as described[9] from phenylmethanesulfonyl chloride (1.0 g, 5.2 mmol), 7 (0.7 g, 5.6 mmol), and NEt_3 (0.8 g, 7.9 mmol) in benzene (100 mL) at 0 °C, in 68% yield: mp 160 °C (lit.[9] mp 161 °C); IR ν_{max} 1103, 1294, cm^{-1}; ^{1}H NMR δ 1.62 (s, 3H), 1.69 (s, 3H), 1.7 (t, 4H), 2.31 (t, 4H), 3.03 (d, 1H), 5.15 (d, 1H), 7.36–7.45 (m, 5H); ^{13}C NMR δ 17.7, 21.9, 23.2, 53.9, 66.3, 76.7, 81.0, 128.7, 129.0, 129.2, 129.7.

Kinetics. The pH-stat apparatus and general procedure have been described.[19] **(a) Hydrolysis.** The initial concentrations of the (trimethylsilyl)methanesulfonyl chloride varied from 4.4×10^{-4} to 5.5×10^{-4} M (added in DME) in 50 mL of 0.01 M aqueous KCl at 1.0 °C, with the reaction followed by titration with NaOH (0.1 M). The temperature was maintained by an external circulating cooler, Gebrüder Haake K.G. KT_{62}, filled with ethanol/water (1:1 in vol). The k_w (2.1×10^{-2} s^{-1}) was obtained from the mean of k_{obsd} values at pH 4–8 and k_{OH} (1.7×10^3 M^{-1} s^{-1}) from $k_{OH} = (k_{obsd} - k_w)[H^+]/K_w$ using k_{obsd} values at pH 10 and 10.5 with K_w 1.34×10^{-15}. The rate constants k_{SOH} and k_{EOH} are calculated from the equations $k_{OH} = k_{SOH} + k_{EOH}$ and $[3]/[6] = (k_w + k_{SOH}[OH^-])/k_{EOH}[OH^-]$, where the product ratio was determined as described below. **(b) With Added Nucleophiles. (i) Amines.** The conjugate base concentration was calculated from $[NR_3] = [NR_3]_T/(1 + [H^+]/K_a)$, where $K_a = [H^+][NR_3]/[HNR_3^+]$ and $[NR_3]_T = [NR_3] + [HNR_3^+]$; the rate constant k_N is calculated from $k_N = (k_{obsd(N)} - k_{obsd(w)})/[NR_3]$, where $k_{obsd(N)} = k_w + k_{OH}[OH^-] + k_N[NR_3]$ and $k_{obsd(w)} = k_w + k_{OH}[OH^-]$. **(ii) Potassium Fluoride.** The rate constant was calculated from $k_N = (k_{obsd(N)} - k_{obsd(w)})/[F^-]$. The reactions were followed by titration with NaOH (0.1 M) and the end point determined from the infinity titre.

Deuterium Substitution Experiments. Hydrolysis. (a) $Me_3SiCH_2SO_2Cl$ (70 μL) was injected into DCl in D_2O (8 mL, pD 3.5). The mixture was stirred for 30 min and extracted with $CDCl_3$ (1 mL). The $CDCl_3$ extract was pipetted and eluted through a small column of $MgSO_4$ into an NMR tube. NMR spectra showed the presence of 2: ^{1}H NMR δ 0.04 (s); ^{13}C NMR δ 2.0. The aqueous portion was washed (CH_2Cl_2) and evaporated to give 3: ^{1}H NMR δ 2.83 (1:1:1 t, J = 2 Hz); ^{13}C NMR δ 40.9 (1:1:1 t, J = 21 Hz) (est. >99% mono α-D). (b) $Me_3SiCH_2SO_2Cl$ (70 μL) was injected into NaOD in D_2O (8 mL, pD 11.4). The mixture was stirred for 30 min and after the usual workup gave the following: (i) organic extract 2 [^{1}H NMR δ 0.05; ^{13}C NMR δ 2.1] and (ii) aqueous layer, a mixture of $CH_2DSO_3^-$ and $Me_3SiCHDSO_3^-$ (^{1}H NMR showed the ratio to be 15:9). $CH_2DSO_3^-$: ^{1}H NMR δ 2.79 (1:1:1 t, J = 2 Hz); ^{13}C NMR δ 40.9 (1:1:1 t, J = 21 Hz) (est. >99% mono α-D). $Me_3SiCHDSO_3^-$: ^{1}H NMR δ 0.15 (s, 9H), 2.65 (1:1:1 t, J = 2 Hz); ^{13}C NMR δ 0.5, 45.2 (1:1:1 t, J = 19 Hz) (est. >99% mono α-D).

Product Analyses. (a) (Trimethylsilyl)methanesulfonyl Chloride (1) with Water. A solution of 1 (0.1 g, 1.1×10^{-3} M) in DME (0.5 mL) was injected into H_2O (500 mL, adjusted to pH 11 with NaOH) maintained by pH-stat (0.01 M NaOH) with stirring at 1 °C and stirring continued for 30 min. The mixture was washed with CH_2Cl_2 and the water evaporated to give a mixture of $CH_3SO_3^-$ and $Me_3SiCH_2SO_3^-$ (ratio 69:31 by ^{1}H NMR). $CH_3SO_3^-$ (3): ^{1}H NMR δ 2.81 (s); ^{13}C NMR δ 41.1. $Me_3SiCH_2SO_3^-$ (6): ^{1}H NMR δ 0.15 (s, 9H), 2.67 (s, 2H); ^{13}C NMR δ 0.5, 45.5. Similarly reacted were (i) 1 (0.2 g, 2.2×10^{-3} M) at pH 11, as above, giving a 70:30 mixture of $CH_3SO_3^-$ and $Me_3SiCH_2SO_3^-$; (ii) 1 (0.15 g, 1.65×10^{-3} M) at pH 10 giving a 78:22 mixture of $CH_3SO_3^-$ and $Me_3SiCH_2SO_3^-$; and (iii) 1 (0.1 g, 5×10^{-4} M) at pH 6 to give only $CH_3SO_3^-$ with no sign of any $Me_3SiCH_2SO_3^-$.

(b) (Trimethylsilyl)methanesulfonyl Chloride (1) with Water and Aniline. A solution of 1 (0.2 g, 5.4×10^{-4} M) in DME (0.5 mL) was injected into a stirred solution of $PhNH_2$ (4 mL, 0.02 M) and H_2O (2000 mL, pH 8, maintained by pH-stat) and stirring continued for 30 min. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed (aqueous HCl), dried ($MgSO_4$), and evaporated to give methanesulfonanilide (CH_3SO_2NHPh) (11.5 mg, 6.3% yield) as a brown oil: ^{1}H NMR δ 3.0 (s, 3H), 6.8 (broad, H, NH), 7.2–7.4 (m, 5H); ^{13}C NMR δ 39.3, 120.8, 125.5, 129.7, 136.7 (identical to those of an authentic speciment prepared from $MeSO_2Cl$, Et_3N, and $PhNH_2$ in CH_2Cl_2); the spectra showed no sign (<1%) of any $Me_3SiCH_2SO_2NHPh$. The aqueous portion was evaporated to give $CH_3SO_3^-$: ^{1}H NMR δ 2.82; ^{13}C NMR δ 41.1, with no sign (<1%) of any $Me_3SiCH_2SO_3^-$. The sulfene trapping ratio for aniline vs water is given by $k_{TN}/k_{TW} = 6.3/(93.7 \times 0.02) = 3.4$ M^{-1}.

(c) (Trimethylsilyl)methanesulfonyl Chloride (1) with Water and Triethylamine. A solution of 1 (0.1 g, 5.4×10^{-4} mol) in DME (0.5 mL) was injected into a stirred solution of triethylamine (5.6 mL, $[Et_3N]_T = 0.04$ M, $[Et_3N] = 2.05 \times 10^{-5}$ M) and H_2O (1000 mL, set at pH 8 with HCl) maintained by pH-stat (0.1 M NaOH) and stirring continued for 30 min. NaOH pellets (1.6 g) were added to neutralize the reaction mixture, and the water was evaporated. The residue was extracted with ethanol and the solvent evaporated to give $CH_3SO_3^-$: ^{1}H NMR δ 2.81; ^{13}C NMR δ 41.1 with no sign (<1%) of any $Me_3SiCH_2SO_3^-$.

(d) (Trimethylsilyl)methanesulfonyl Chloride (1) with Water and Fluoride Anion. (i) Nonpolar Products. A solution of 1 (0.2 g, 2.4×10^{-3} M) and aqueous KF (0.01 M, 450 mL) in a 500-mL round-bottomed flask connected to a 5-mL round-bottomed flask containing $CDCl_3$ (2 mL) was stirred at 0 °C for 25 min whereupon the two liquids were shaken together. The organic layer was pipetted out and eluted through a small column of $MgSO_4$ into an NMR tube. The ^{1}H NMR spectrum showed the sample to contain a mixture of $Me_3SiOSiMe_3$, Me_3SiF (ratio 1:3), and CH_3SO_2F (<1%). $Me_3SiOSiMe_3$: ^{1}H NMR δ 0.04; ^{13}C NMR δ 1.9. Me_3SiF: ^{1}H NMR δ 0.21 (d, J = 7.5 Hz); ^{13}C NMR δ 0.1 (d, J = 15 Hz). CH_3SO_2F: ^{1}H NMR δ 3.26 (d, J = 5 Hz) (est. <1%). **(ii) Ionic Products.** A solution of 1 (0.2 g, 2.1×10^{-3} M) in DME (1 mL) was injected into a stirred solution of KF (0.01 M, 500 mL, set at pH 11 with NaOH) maintained by pH-stat (0.1 M NaOH) at 1 °C and stirring continued for 30 min; the usual workup gave a mixture of $CH_3SO_3^-$ and $Me_3SiCH_2SO_3^-$ (ratio 99.7: 0.3 from ^{1}H NMR). $CH_3SO_3^-$: ^{1}H NMR δ 2.82; ^{13}C NMR δ 41.1. $Me_3SiCH_2SO_3^-$: ^{1}H NMR δ 0.15 (s, 9H), 2.72 (s, 2H).

Reaction of Alkanesulfonyl Chlorides with 1-(2-Methylpropenyl)pyrrolidine (7) in Aqueous Solution. (a) Methanesulfonyl Chloride. Solutions of 7 (0.65 g, 5.2 mmol) in DME (5 mL) and aqueous NaOH (40 mL, pH 9) were added simultaneously to a stirred solution of CH_3SO_2Cl (0.24 g, 2.1 mmol) in DME (5 mL) and stirring continued for 10 min. The reaction mixture was acidified (aqueous H_2SO_4) and extracted (CH_2Cl_2, 50 mL). The organic extract was dried ($MgSO_4$) and evaporated to give a mixture (0.15 g) of 10 and 9 (^{1}H NMR showed the ratio 2:1) as a yellow oil. (i) 10 (0.10 g, 32% yield): ^{1}H NMR δ 1.95 (t, 4H), 2.8 (s, 3H), 3.33 (t, 4H); ^{13}C NMR δ 25.6, 34.4, 47.8. (ii) 9 (0.05 g, 16% yield): ^{1}H NMR δ 1.60 (s, 6H), 2.8 (s, 3H), 9.72 (s, 1H); ^{13}C NMR δ 16.2, 36.8, 69.3, 197.3. The aqueous portion was basified (aqueous NaOH) and extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and evaporated to give 8 (0.17 g, 40% yield), with ^{1}h NMR and ^{13}C NMR spectra identical to those of the authentic specimen. The mixture of 10 and 9 in methanol (1 mL) was added to a solution of 2,4-dinitrophenylhydrazine (0.1 g, 0.5 mmol) and concd HCl (seven drops) in methanol (10 mL) and the mixture set on the steam bath for 2 min, allowed to stand at room temperature for 15 min, and cooled in an ice bath. The precipitate was filtered, washed (cold methanol), and dried (air) to give the 2,4-dinitrophenylhydrazone as orange-red crystals: mp 187–188 °C; IR ν_{max} 1080, 1289, 1333, 1518, 1619, 3272 cm^{-1}; ^{1}H NMR δ 1.72 (s, 6H), 2.89 (s, 3H), 7.63 (s, HC=N), 7.90 (d, 1H), 8.36 (d, 1H), 9.14 (s, 1H), 11.27 (broad, NH); ^{13}C NMR δ 19.1, 35.5, 64.6, 116.4, 123.3, 129.8, 130.1, 138.8, 144.5, 147.7; exact mass (M + 1) calcd 331.0712, found 331.0711

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(CI, isobutane). Reactions with other sulfonyl chlorides were carried out similarly. **(b) 2-Propanesulfonyl chloride** (0.52 g, 4.2 mmol), 7 (0.65 g, 5.2 mmol) in DME (5 mL), and aqueous NaOH (40 mL, pH 10.5) gave **13b** (0.03 g, 6%) and (2-propanesulfonyl)pyrrolidide (0.11 g, 31% yield) (each with ^{1}H and ^{13}C NMR spectra identical to those of the authentic specimens) and **14b** (0.11 g, 28% yield): ^{1}H NMR δ 1.33 (d, 6H), 1.55 (s, 6H), 3.40 (septet, 1H), 9.77 (s, 1H); ^{13}C NMR δ 15.8, 16.6, 51.7, 69.5, 197.5; exact mass (M + 1) calcd for $C_7H_{14}SO_3$ 179.0742, found 179.0750 (CI, isobutane). The aldehyde (**14b**) was converted to the 2,4-dinitrophenylhydrazone: mp 178 °C; IR ν_{max} 1080, 1298, 1335, 1516, 1619, 3276 cm^{-1}; ^{1}H NMR δ 1.38 (d, 6H), 1.72 (s, 6H), 3.43 (septet, 1H), 7.66 (s, HC=N), 7.91 (d, 1H), 8.37 (d, 1H), 9.15 (s, 1H), 11.22 (broad, 1H); ^{13}C NMR δ 16.8, 19.8, 50.9, 65.6, 116.3, 123.3, 129.8, 130.1, 138.7, 144.6, 149.0; exact mass (M + 1) calcd for $C_{13}H_{18}N_4O_6S$ 359.1025, found 359.1020 (CI, isobutane). **(c) Phenylmethanesulfonyl chloride** (0.3 g, 1.6 mmol), 7 (0.4 g, 3.2 mmol) in DME (5 mL), and aqueous NaOH (40 mL, pH 8) gave **13a** (0.26 g, 59% yield) and (phenylmethanesulfonyl)pyrrolidide (0.01 g, 3% yield), both with ^{1}H and ^{13}C NMR spectra identical to those of the authentic specimens, and **14a** (plus a roughly equal amount of an unidentified material) (0.08 g, total 20% yield): ^{1}H NMR δ 1.57 (s, 6H), 4.22 (s, 2H), 7.38 (m, 5H), 9.50 (s, 1H); ^{13}C NMR δ 16.4, 55.9, 70.1, 128.9, 129.3, 131.3, 196.0. **14a** was converted to the 2,4-dinitrophenylhydrazone: mp 115–116 °C; IR ν_{max} 1113, 1306, 1333, 1516, 1619, 3297 cm^{-1}; ^{1}H NMR δ 1.72 (s, 6H), 4.32 (s, 2H), 7.21–7.32 (m, 3H), 7.35–7.41 (m, 2H), 7.43 (s, HC=N), 7.85 (d, 1H), 8.33 (d, 1H), 9.07 (s, 1H), 10.93 (broad, 1H); ^{13}C NMR δ 19.2, 55.0, 65.7, 116.4, 123.1, 126.7, 128.6, 129.5, 129.9, 131.0, 138.5, 144.4, 147.6, 147.8; exact mass (M + 1) calcd for $C_{17}H_{18}N_4O_6S$ 407.1025, found 407.1020 (CI, isobutane).

Reaction of Alkanesulfonyl Chlorides with 1-(*N*-Pyrrolidino)cyclohexene in Aqueous Solution. (a) Methanesulfonyl Chloride. Solutions of 1-(*N*-pyrrolidino)cyclohexene (2.6 g, 17.2 mmol) in DME (5 mL) and of aqueous NaOH (40 mL, pH 9) were added simultaneously to a stirred solution of CH_3SO_2Cl (1.0 g, 8.7 mmol) in DME (5 mL) and stirring continued for 10 min. The reaction mixture was acidified (aqueous H_2SO_4) and extracted with CH_2Cl_2 (50 mL). The two layers were treated as follows: (i) The aqueous portion was basified (aqueous NaOH) and extracted with CH_2Cl_2; the organic extract was dried ($MgSO_4$) and evaporated to give **15** (0.2 g, 10% yield). (ii) The organic layer was extracted with aqueous NaOH (5%) and then dried ($MgSO_4$) and evaporated to give **10** (0.3 g, 23% yield); the basic aqueous extract was then acidified with dilute HCl and extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and evaporated to give **16a** (0.4 g, 26% yield): mp 56–57 °C (95% ethanol) (lit.[20] mp 57–58 °C); IR ν_{max} 1125, 1304, 1716 cm^{-1}; ^{1}H NMR δ 1.6–2.1 (m, 4H), 2.3–2.5 (m, 3H), 2.6–2.7 (m, 1H), 2.97 (s, 3H), 3.73 (dd, 1H); ^{13}C NMR δ 22.4, 25.79, 25.82, 40.6, 41.5, 70.4, 203.2; exact mass calcd for $C_7H_{12}O_3S$ 176.0507, found 176.0500. Both **15** and **10** showed ^{1}H NMR and ^{13}C NMR identical to those of the authentic specimens. **(b) Phenylmethanesulfonyl chloride** (0.7 g, 3.7 mmol), 1-(*N*-pyrrolidino)cyclohexene (1.1 g, 7.3 mmol) and aqueous NaOH (pH 8, 40 mL) were treated similarly to give **16b** (0.36 g, 39% yield) as the only extractable product: mp 101–102 °C (methanol) (lit.[16] mp 98–100 °C); IR ν_{max} 1121, 1312, 1713 cm^{-1}; ^{1}H NMR δ 1.60–2.46 (m, 7H), 2.7 (m, 1H), 3.61 (t, 1H), 4.29, 4.43 (AB quartet, 2H, J = 13.8 Hz), 7.39 (m, 5H); ^{13}C NMR δ 22.0, 24.8, 25.5, 41.3, 59.0, 66.1, 127.5, 128.7, 128.8, 130.8, 203.5; exact mass calcd for $C_{13}H_{16}SO_3$ 252.0820; found 252.0828. **16b** was converted to the 2,4-dinitrophenylhydrazone: mp 221–222 °C (methanol) (lit.[16] mp 219–220 °C); IR ν_{max} 1121, 1341, 1516, 1619, 3322 cm^{-1}; ^{1}H NMR δ 1.49–2.16 (m, 5H), 2.65–2.90 (m, 3H), 4.04 (m, 1H), 4.24, 4.47 (AB quartet, 2H, J = 14 Hz), 7.43 (s, 5H), 7.98 (d, 1H), 8.42 (d, 1H), 9.18 (s, 1H), 11.41 (s, NH); ^{13}C NMR δ 21.3, 24.6, 25.2, 25.4, 57.7, 63.0, 115.9, 123.6, 127.7, 129.0, 129.2, 130.0, 130.3, 131.0, 138.7, 144.7, 153.5.

(Trimethylsilyl)methanesulfonyl Chloride with 1-(2-Methylpropenyl)pyrrolidine (7). (a) Aqueous Solution at pH 8. Solutions of 7 (0.65 g, 5.2 mmol) in DME (5 mL) and aqueous NaOH (40 mL, pH 8) were added simultaneously to a stirred solution of 1 (0.4 g, 2.1 mmol) in DME (5 mL) and stirring continued for 10 min. The reaction mixture was acidified (aqueous H_2SO_4) and extracted (CH_2Cl_2, 50 mL). The organic extract was dried ($MgSO_4$) and evaporated to give a mixture (0.07 g) of **10** and **9** as a yellow oil. **10** (11% yield): ^{1}H NMR δ 1.95 (t, 4H), 2.8 (s, 3H), 3.33 (t, 4H); ^{13}C NMR δ 25.7, 34.4, 47.8. **9** (23% yield): ^{1}H NMR δ 1.60 (s, 6H), 2.8 (s, 3H), 9.72 (s, 1H); ^{13}C NMR δ 16.2, 36.8, 69.3, 197.3. The aqueous portion was basified with aqueous NaOH and extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and evaporated to give **8** (0.16 g, 39% yield): ^{1}H NMR δ 1.52 (s, 3H), 1.57 (s, 3H), 1.80 (t, 4H), 2.44 (m, 4H), 2.79 (t, 1H), 3.90 (d, 2H); ^{13}C NMR δ 17.2, 21.8, 23.3, 53.4, 59.2, 64.6, 80.4. **(b) Aqueous KF, pH 9.** Solutions of 7 (0.65 g, 5.2 mmol) in DME (5 mL) and aqueous KF (30 mL, 0.1 M, pH 9) were added simultaneously to a stirred solution of 1 (0.4 g, 2 mmol) in DME (5 mL) and stirring continued for 10 min; the usual workup gave **10** (28% yield), **9** (9% yield), and **8** (46% yield), with ^{1}H NMR identical to those described above.

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Supplementary Material Available: NMR spectra (^{1}H and/or ^{13}C) for new compounds (29 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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