New Building Blocks for Heterocyclic Syntheses. Silylated Methyl Isothiocyanates

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Trimethylsilylmethyl isothiocyanate, bis(trimethylsilyl)methyl isothiocyanate, and tris(trimethylsilyl)methyl isothiocyanate were prepared. The fluoride-catalyzed reaction of trimethylsilylmethyl isothiocyanate with aldehydes or ketones afforded oxazolidine-2-thione derivatives, which involves the isothiocyanato carbanion as an intermediate. Imidazolidine-2-thiones were similarly prepared from imines. The reaction of bis(trimethylsilyl)methyl isothiocyanate with benzaldehyde in the presence of a catalytic amount of n-Bu_4NF gave styryl isothiocyanate and 5-phenyl-4-trimethylsilyloxazolidine-2-thione. On the similar treatment of tris(trimethylsilyl)methyl isothiocyanate, 4-benzyl-5-phenyl-4-oxazoline-2-thione, and α-(trimethylsilyl)styryl isothiocyanate were obtained.

The chemistry of functionalized heterocumulene has been recently developed in the field of heterocyclic synthesis.[1] From this point of view, we have previously reported the synthesis of methyl(phenylthio)ketene,[2] methyl(phenylseleno)ketene,[3] α-alkylthio(or arylthio)-vinyl isocyanate,[4] and *N*-[2-(diethoxyphosphoryl)-1-propenylidene]ethylamine,[5] and (2-aryl-2-halovinylidene)arylamine[6] and their cycloaddition reactions.

It is thought to enhance the synthetic utility of isothiocyanates that carbanion center can be generated in the α-position relative to nitrogen. The metalation of activated isothiocyanates was reported by Hoppe,[7] but this method is not applicable to methyl isothiocyanate. We addressed ourselves to this problem by preparing trimethylsilylmethyl isothiocyanate because fluoride ion has been reported to cause bond cleavage between carbon and silicon.[8] In our previous paper, trimethylsilylmethyl isothiocyanate was proved to be an equivalent of isothiocyanatomethanide.[9] Herein, we wish to report further details of the investigation on silylated methyl isothiocyanates as new building blocks for heterocyclic syntheses.

Results and Discussion

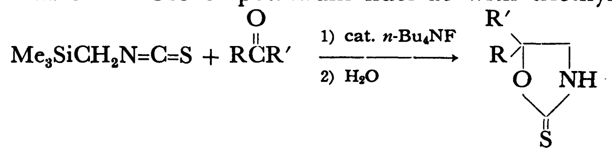
Trimethylsilylmethyl Isothiocyanate. Trimethylsilylmethyl isothiocyanate (**1**) was prepared by the addition of sulfur to trimethylsilylmethyl isocyanide in 76% yield. The isothiocyanate **1** is a stable liquid at room temperature, and can be stored under nitrogen atmosphere.

$$Me_3SiCH_2N{\equiv}C + S_x \xrightarrow[\text{reflux}]{\text{PhH}} Me_3SiCH_2N{=}C{=}S$$

1

The cleavage of a carbon-silicon bond by fluoride ion was confirmed by treatment of the isothiocyanate **1** with D_2O in the presence of a catalytic amount of tetrabutylammonium fluoride to give methyl-d_1 isothiocyanate in 76% yield.

The isothiocyanate **1** was subjected to the n-Bu_4NF-catalyzed reaction with aldehydes or ketones to produce the oxazolidine-2-thiones **2**. The results are summarized in Table 1. Use of potassium fluoride with triethyl-



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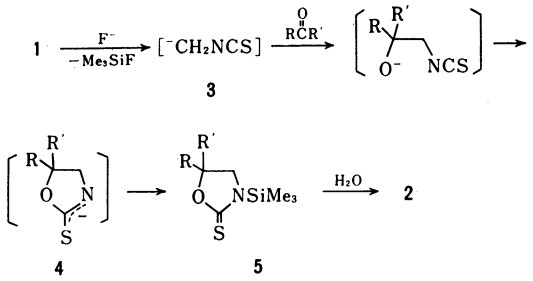
benzylammonium chloride (TEBA·Cl) or 18-crown-6 instead of tetrabutylammonium fluoride also gave the oxazolidine-2-thione **2a** in a good yield.

A possible reaction path is shown in Scheme 1. The isothiocyanato carbanion **3**, which is generated from the fluoride-catalyzed reaction of **1**, may be involved as a key intermediate. The carbanion **3** reacts with carbonyl compound to give the 1 : 1 adduct, which undergoes intramolecular cyclization resulting in **4**. The following mechanism may be operative to achieve a reaction cycle. The fluoride ion appears to be regenerated by the reaction of trimethylsilyl fluoride with **4**. It is also

Table 1. Preparation of oxazolidine-2-thiones (**2**)

RC(O)R′: R	R′	F^- (equiv.)	Reaction time/h	Oxazolidine-2-thione, **2** (%)
Ph	H	n-Bu_4NF (0.1)	8	**2a** 74
Ph	H	KF (1.0), TEBA·Cl (0.1)	2	**2a** 74
Ph	H	KF (1.0), 18-Crown-6 (0.1)	5	**2a** 65
Et	H	n-Bu_4NF (0.1)	5	**2b** 63
i-Pr	H	n-Bu_4NF (0.1)	10	**2c** 67
Ph	Ph	n-Bu_4NF (0.1)	40	**2d** 25
Ph	Me	n-Bu_4NF (0.1)	23	**2e** 35[a]

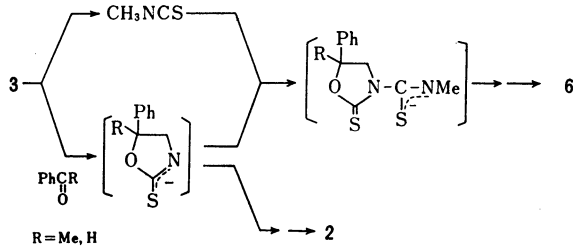
a) 5-Methyl-3-[methyl(thiocarbamoyl)]-5-phenyloxazolidine-2-thione (**6a**) was obtained in 17% yield.



Scheme 1.

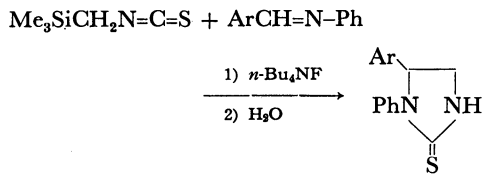
conceivable that the attack of **4** to **1** gives the isothiocyanato carbanion **3** and the 3-trimethylsilyloxazolidine-2-thione **5**. It has not been clarified which path is preferred. Thus formed **5** is easily hydrolyzed to **2**.

When the phase-transfer reaction of the isothiocyanate **1** with benzaldehyde was carried out in the presence of potassium fluoride and TEBA·Cl in benzene–water, 3-[methyl(thiocarbamoyl)]-5-phenyloxazolidine-2-thione (**6b**, 30%) was produced together with 5-phenyloxazolidine-2-thione (**2a**, 31%). The formation of the 3-[methyl(thiocarbamoyl)] derivative **6a** (17%) was also observed in the *n*-Bu_4NF-catalyzed reaction of **1** with acetophenone in dry THF, but only a trace amount of the corresponding 3-[methyl(thiocarbamoyl)]oxazolidine-2-thione was given from aldehyde. These 3-[methyl(thiocarbamoyl)] derivatives are considered to be produced by the reaction of **4** with methyl isothiocyanate, which is derived from proton abstraction of **3** from H_2O (phase-transfer reaction) or acetophenone[8a] (Scheme 2). The possibility of desilylation of 3-(*N*-trimethylsilylmethylthiocarbamoyl)oxazolidine-2-thiones, however, could not necessarily be excluded.



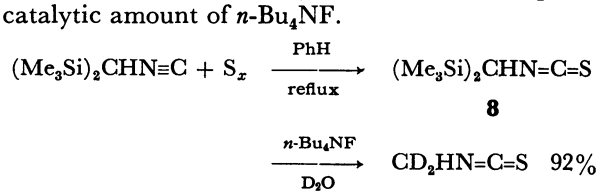
Scheme 2.

Imines were also allowed to react with **1** in the presence of a catalytic amount of *n*-Bu_4NF to produce the imidazolidine-2-thione derivatives **7**.

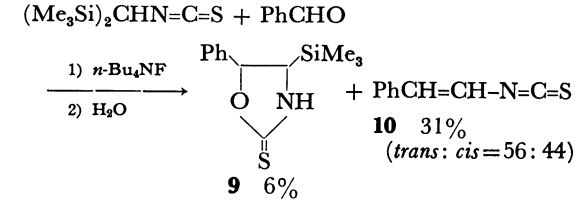


7a: Ar=Ph 40%
7b: Ar=*p*-ClC_6H_4 60%

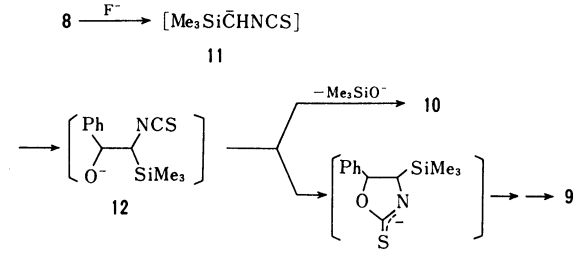
Bis(trimethylsilyl)methyl Isothiocyanate. Bis(trimethylsilyl)methyl isothiocyanate (**8**) was analogously prepared from the corresponding isocyanide and sulfur in 80% yield. The isothiocyanate **8** was desilylated to methyl-d_2 isothiocyanate by treatment with D_2O and a catalytic amount of *n*-Bu_4NF.



The methodology mentioned above was able to be applied to the reaction of **8** with benzaldehyde, but 5-phenyl-4-trimethylsilyloxazolidine-2-thione (**9**) was produced in only 6% yield. It is of interest that styryl isothiocyanate (**10**) was obtained as a main product in this case.

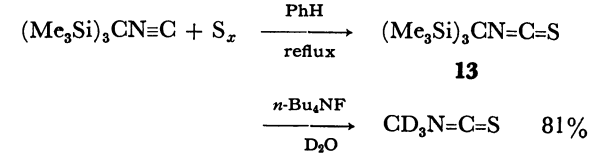


The formation path for styryl isothiocyanate is outlined in Scheme 3. The β-trimethylsilylalkoxide intermediate **12** undergoes elimination of Me_3SiO^- to give styryl isothiocyanate. Both silyl groups of **8** participate in the synthesis of **10**, generation of carbanion by fluoride ion and Peterson-olefination.[14] Ring closure of a rotamer of **12** leads to **9**.

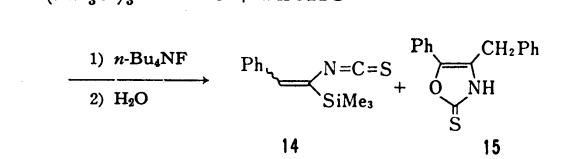


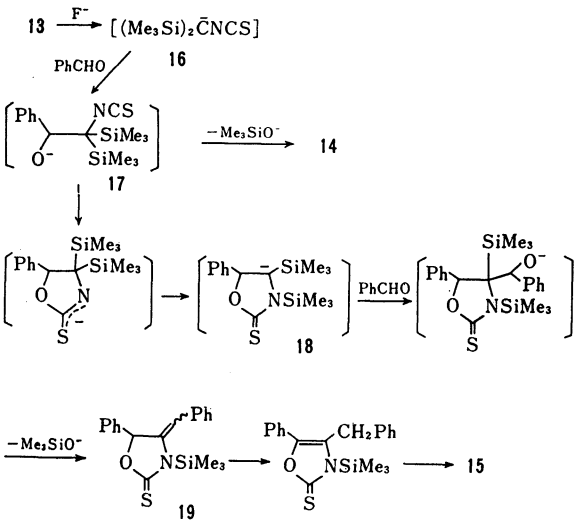
Scheme 3.

Tris(trimethylsilyl)methyl Isothiocyanate. Tris(trimethylsilyl)methyl isothiocyanate (**13**) was prepared by the addition of sulfur to tris(trimethylsilyl)methyl isocyanide in 76% yield. The isothiocyanate **13** was converted to methyl-d_3 isothiocyanate on treatment with D_2O in the presence of a catalytic amount of *n*-Bu_4NF.



The isothiocyanate **13** reacted with benzaldehyde in the presence of a catalytic amount of *n*-Bu_4NF to afford α-(trimethylsilyl)styryl isothiocyanate (**14**) and 4-benzyl-5-phenyl-4-oxazoline-2-thione (**15**) in 26% and 7% yields, respectively.





Scheme 4.

The probable reaction path for these products is outlined in Scheme 4. The isothiocyanate **14** was formed by the elimination of Me_3SiO^- from **17**. A rotamer of **17** is subjected to ring closure, followed by transposition of trimethylsilyl group to generate the carbanion **18**. The carbanion **18** reacts with another benzaldehyde to give the benzylideneoxazolidine-2-thione **19**, which may be rearranged and hydrolyzed to **15**.

The fluoride-catalyzed reactions of silylated methyl isothiocyanates provide a facile and mild generation of isothiocyanato carbanions (**3**, **11**, and **16**).

Experimental

Melting points were measured by a Yanagimoto micro melting point apparatus and uncorrected. ^1H NMR spectra were obtained on a JEOL JNN-PMX-60 with tetramethylsilane as an internal standard. IR spectra were recorded with a JASCO IRA-1 spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer.

Materials. Trimethylsilylmethyl isocyanide, bis(trimethylsilyl)methyl isocyanide, and tris(trimethylsilyl)methyl isocyanide were prepared by the reported method.[10] Tetrabutylammonium fluoride was prepared by the literature method[8a] and dried before use. Imines were obtained by the reaction of aldehydes with aniline,[11] and recrystallized prior to use. Carbonyl compounds were purified by distillation or recrystallization.

*Preparation of Trimethylsilylmethyl Isothiocyanate (**1**).* Trimethylsilylmethyl isothiocyanate was prepared by the addition of sulfur to the isocyanide in the same manner as mentioned in the reported method.[12] A mixture of trimethylsilylmethyl isocyanide (12.3 g, 109 mmol) and sulfur (4.2 g, 130 mmol) in benzene (20 ml) was refluxed for 26 h. Hexane (20 ml) was added to the cooled solution. After excess of sulfur was removed by filtration, the solution was distilled *in vacuo* to give **1** (12.0 g, 76%): bp 46 °C/3 mmHg;† IR (neat) 2180 and 2080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 3.00 (s, 2H); MS *m/e* 145 (M^+); Found: C, 41.16; H, 7.98; N, 9.72; S, 22.32%. Calcd for $C_5H_{11}NSSi$: C, 41.33; H, 7.63; N, 9.64; S, 22.07%.

† 1 mmHg≈133.322 Pa.

*Treatment of **1** with D_2O in the Presence of* n-Bu_4NF. To a solution of *n*-Bu_4NF (78 mg, 0.3 mmol) and D_2O (66 mg, 3.3 mmol) in THF (3 ml), the isothiocyanate **1** (0.44 g, 3.0 mmol) in THF (2 ml) was added dropwise at room temperature. The mixture was stirred for 4 h under nitrogen atmosphere. Water (60 ml) was added to the resultant mixture, which was extracted with chloroform (3×30 ml). The combined organic layer was washed with water (10 ml) and dried on anhydrous sodium sulfate. After evaporation, methyl-d_1 isothiocyanate was isolated in 76% yield by preparative GLC (conditions: PS-410 column, 100 °C). IR (neat) 2230 and 2120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.27 (t, 2H, J=2.0 Hz); MS *m/e* 74 (M^+).

*n-Bu_4NF-Catalyzed Reaction of **1** with Benzaldehyde.* To a solution of benzaldehyde (0.64 g, 6.0 mmol) and *n*-Bu_4NF (78 mg, 0.3 mmol) in THF (3 ml), the isothiocyanate **1** (0.44 g, 3.0 mmol) in THF (2 ml) was added dropwise at room temperature. The resultant solution was stirred for 8 h under nitrogen atmosphere. Water (60 ml) was added to the resultant mixture, which was extracted with chloroform (3×30 ml). The combined organic layer was washed with water (10 ml) and dried on anhydrous sodium sulfate. After evaporation, the residue was chromatographed on a silica gel column eluting with chloroform to give 0.40 g (74%) of 5-phenyloxazolidine-2-thione (**2a**): mp 130—131 °C; IR (Nujol) 3160 and 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (dd, 1H, J=8.4 and 10.0 Hz), 4.13 (dd, 1H, J=9.2 and 10.0 Hz), 5.87 (dd, 1H, J=8.4 and 9.2 Hz), 7.35 (s, 5H), 8.20 (br, 1H); MS *m/e* 179 (M^+). Found: C, 60.35; H, 4.89; N, 7.66; S, 17.67%. Calcd for C_9H_9ONS: C, 60.31; H, 5.06; N, 7.81; S, 17.89%.

In a similar manner, 5-ethyloxazolidine-2-thione (**2b**), 5-isopropyloxazolidine-2-thione (**2c**), 5,5-diphenyloxazolidine-2-thione (**2d**), and 5-methyl-5-phenyloxazolidine-2-thione (**2e**) were prepared in 63%, 67%, 25%, and 35% yields, respectively. Reaction time was shown in Table 1. In the preparation of **2e**, 5-methyl-3-[methyl(thiocarbamoyl)]-5-phenyloxazolidine-2-thione (**6a**) was obtained in 17% yield as a by-product.

2b: mp 87—89 °C; IR (Nujol) 3200 and 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (t, 3H, J=7.0 Hz), 1.87 (dq, 2H, J=6.4 and 7.0 Hz), 3.47 (dd, 1H, J=8.4 and 9.6 Hz), 3.93 (dd, 1H, J=8.8 and 9.6 Hz), 4.97 (ddt, 1H, J=6.4, 8.4, and 8.8 Hz), 8.55 (br, 1H); MS *m/e* 131 (M^+); Found: C, 45.60; H, 6.89; N, 10.70; S, 24.29%. Calcd for C_5H_9ONS: C, 45.78; H, 6.91; N, 10.68; S, 24.44%.

2c: mp 101—101.5 °C; IR (Nujol) 3220 and 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (d, 3H, J=6.4 Hz), 1.03 (d, 3H, J=6.4 Hz), 2.00 (m, 1H), 3.53 (dd, 1H, J=8.4 and 8.8 Hz), 3.87 (dd, 1H, J=8.8 and 8.8 Hz), 4.76 (ddd, 1H, J=6.4, 8.8, and 8.8 Hz), 8.53 (br, 1H); MS *m/e* 145 (M^+); Found: C, 49.45; H, 7.61; N, 9.68; S, 22.06%. Calcd for $C_6H_{11}ONS$: C, 49.63; H, 7.63; N, 9.65; S, 22.08%.

2d: mp 186—188 °C; IR (Nujol) 3180 and 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30 (s, 2H), 7.30 (s, 10H), 8.30 (br, 1H); MS *m/e* 255 (M^+); Found: C, 70.66; H, 5.05; N, 5.47; S, 12.71%. Calcd for $C_{15}H_{13}ONS$: C, 70.56; H, 5.13; N, 5.49; S, 12.56%. **2e**: mp 201—203 °C; IR (Nujol) 3210 and 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (s, 3H), 3.83 (s, 2H), 7.33 (s, 5H), 8.20 (br, 1H); MS *m/e* 193 (M^+); Found: C, 62.09; H, 5.72; N, 7.29; S, 16.31%. Calcd for $C_{10}H_{11}ONS$: C, 62.15; H, 5.74; N, 7.25; S, 16.59%.

6a: IR (Nujol) 3150 and 1560 cm^{-1}; ^1H NMR (CCl_4) δ 1.85 (s, 3H), 3.15 (d, 3H, J=5.0 Hz), 4.77 (s, 2H), 7.20—7.60 (m, 5H), 11.80 (br, 1H); MS *m/e* 266 (M^+).

*KF-Catalyzed Reaction of **1** with Benzaldehyde in the Presence of TEBA·Cl or 18-Crown-6 in Acetonitrile.* To a mixture of

benzaldehyde (0.64 g, 6.0 mmol), anhydrous KF (0.17 g, 3.0 mmol), and TEBA·Cl (68 mg, 0.3 mmol) or 18-crown-6 (72 mg, 0.3 mmol) in acetonitrile (3 ml), the isothiocyanate **1** (0.44 g, 3.0 mmol) in acetonitrile (2 ml) was added dropwise at room temperature. The resultant mixture was stirred under nitrogen atmosphere for 2 or 5 h, respectively. Work up was carried out in the same procedure as mentioned above. The yields of 5-phenyloxazolidine-2-thione (**2a**) were shown in Table 1.

*KF-Catalyzed Reaction of **1** with Benzaldehyde in the Presence of TEBA·Cl in Benzene–Water.* To 1.5 ml of aqueous solution of TEBA·Cl (68 mg, 0.3 mmol) and KF (1.00 g, 17.2 mmol), benzaldehyde (0.64 g, 6.0 mmol) and the isothiocyanate **1** (0.44 g, 3.0 mmol) in benzene (1 ml) were added at room temperature. The mixture was stirred for 4 h, and then chloroform (10 ml) was added. The organic layer was dried on anhydrous sodium sulfate. After evaporation, the residue was chromatographed on a silica-gel column to give 5-phenyloxazolidine-2-thione (**2a**, 0.17 g, 31%) and 3-[methyl-(thiocarbamoyl)]-5-phenyloxazolidine-2-thione (**6b**, 0.22 g, 30%). **6b**: mp 85—86 °C; IR (Nujol) 3130 and 1545 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.22 (d, 3H, J=5.0 Hz), 4.62 (dd, 1H, J=8.4 and 11.6 Hz), 5.12 (dd, 1H, J=8.4 and 11.6 Hz), 5.72 (dd, 1H, J=8.4 and 8.4 Hz), 7.40 (br, 5H), 11.80 (br, 1H); MS *m/e* 252 (M^+); Found: C, 52.47; H, 4.79; N, 11.12; S, 25.26%. Calcd for $C_{11}H_{12}ON_2S_2$: C, 52.36; H, 4.79; N, 11.10; S, 25.41%.

*Preparation of 1,5-Diphenylimidazolidine-2-thione (**7a**).* To a solution of *N*-benzylideneaniline (1.09 g, 6.0 mmol) and *n*-Bu_4NF (0.16 g, 0.6 mmol) in THF (3 ml), the isothiocyanate **1** (0.44 g, 3.00 mmol) in THF (2 ml) was added dropwise at room temperature. The resultant solution was stirred for 13 h under nitrogen atmosphere, and worked up in the same procedure as given for **2a**. The imidazolidine-2-thione **7a** was isolated by column chromatography on silica gel eluting with chloroform in 40% yield (0.31 g). **7a**: mp 188—190 °C; IR (KBr) 3200, 1620, 1590, and 1575 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (dd, 1H, J=7.6 and 9.8 Hz), 4.13 (dd, 1H, J=8.8 and 9.8 Hz), 5.40 (dd, 1H, J=7.6 and 8.8 Hz), 7.00—7.50 (m, 10H); MS *m/e* 254 (M^+); Found: C, 70.56; H, 5.53; N, 11.02; S, 12.38%. Calcd for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01; S, 12.61%.

Similarly, 5-(*p*-chlorophenyl)-1-phenylimidazolidine-2-thione (**7b**) was prepared in 60% yield. **7b**: mp 212 °C; IR (KBr) 3200, 1620, 1580, and 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (dd, 1H, J=7.6 and 10.4 Hz), 4.12 (dd, 1H, J=9.2 and 10.4 Hz), 5.35 (dd, 1H, J=7.6 and 9.2 Hz), 7.05—7.50 (m, 10H); MS *m/e* 288 (M^+); Found: C, 61.96; H, 4.42; Cl, 12.46; N, 9.56; S, 11.13%. Calcd for $C_{15}H_{13}ClN_2S$: C, 62.38; H, 4.54; Cl, 12.28; N, 9.70; S, 11.10%.

*Preparation of Bis(trimethylsilyl)methyl Isothiocyanate (**8**).* The isothiocyanate **8** was prepared in 80% yield by the reaction of bis(trimethylsilyl)methyl isocyanide and sulfur in benzene at 80 °C for 26 h in the same manner as given for **1**. **8**: bp 48—50 °C/0.5 mmHg, mp 45—47 °C; IR (neat) 2140 and 2060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 18H), 2.56 (s, 1H); MS *m/e* 217 (M^+); Found: C, 44.35; H, 9.09; N, 6.53; S, 14.37%. Calcd for $C_8H_{19}NSSi_2$: C, 44.18; H, 8.76; N, 6.44; S, 14.74%.

*Treatment of **8** with D_2O in the Presence of* n-*Bu_4NF.* The reaction of **8** (3.0 mmol) with D_2O (6.6 mmol) in the presence of *n*-Bu_4NF (0.3 mmol) was carried out in the same manner as given for **1** to produce methyl-d_2 isothiocyanate in 92% yield. IR (neat) 2220, 2180, and 2100 cm^{-1}; ^1H NMR (CCl_4) δ 3.30 (quintet, 1H, J=2.0 Hz); MS *m/e* 75 (M^+).

*n-Bu_4NF-Catalyzed Reaction of **8** with Benzaldehyde.* In the same manner as described in the preparation of **2a**, *n*-Bu_4NF-catalyzed reaction of **8** with benzaldehyde gave styryl isothiocyanate (**10**)[13] and 5-phenyl-4-trimethylsilyloxazolidine-2-thione (**9**) in 31% and 6% yields, respectively. The *trans-cis* ratio (56 : 44) of **10** was determined by the ^1H NMR spectrum.

9: mp 178 °C (dec); IR (Nujol) 3180 and 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.18 (s, 9H), 3.89 (d, 1H, J=9.4 Hz), 6.06 (d, 1H, J=9.4 Hz), 7.26—7.47 (m, 5H), 8.20 (br, 1H); MS *m/e* 251 (M^+); Found: C, 57.21; H, 6.88; N, 5.55; S, 13.13%. Calcd for $C_{12}H_{17}ONSSi$: C, 57.33; H, 6.81; N, 5.57; S, 12.75%.

10: IR (neat) 2100, 2040, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.10 (2d, 0.88H, J=8.6 Hz, cis CH=CH), 6.60 (2d, 1.12H, J=12.2 Hz, *trans* CH=CH), 7.20—7.90 (m, 5H); MS *m/e* 161 (M^+).

*Preparation of Tris(trimethylsilyl)methyl Isothiocyanate (**13**).* Tris(trimethylsilyl)methyl isothiocyanate was prepared in 76% yield by the reaction of tris(trimethylsilyl)methyl isocyanide and sulfur in benzene at 80 °C for 29 h in the same manner as given for **1**. The isothiocyanate **13** was purified by column chromatography on silica gel eluting with hexane. **13**: mp>300 °C; IR (KBr) 2140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 27H); MS *m/e* 289 (M^+); Found: C, 45.93; H, 9.62; N, 4.60; S, 11.08%. Calcd for $C_{11}H_{27}NSSi_3$: C, 45.61; H, 9.40; N, 4.34; S, 11.07%.

*Treatment of **13** with D_2O in the Presence of* n-*Bu_4NF.* The reaction of **13** (3.0 mmol) with D_2O (9.9 mmol) in the presence of *n*-Bu_4NF (0.3 mmol) was carried out in the same manner as given for **1** to produce methyl-d_3 isothiocyanate in 81% yield. IR (neat) 2260, 2200, and 2120 cm^{-1}; MS *m/e* 76 (M^+).

*n-Bu_4NF-Catalyzed Reaction of **13** with Benzaldehyde.* The *n*-Bu_4NF-catalyzed reaction of **13** with benzaldehyde was carried out at room temperature for 24 h in the same manner as mentioned in the preparation of **2a**. After evaporation of the solvent, the residue was chromatographed on a silica-gel column to give α-(trimethylsilyl)styryl isothiocyanate (**14**) and 4-benzyl-5-phenyl-4-oxazoline-2-thione (**15**) in 26% and 7% yields, respectively, with a small amount of styryl isothiocyanate (6%). **14**: IR (neat) 2040 and 1620 cm^{-1}; ^1H NMR (CCl_4) δ 0.28 (s, 9H), 6.23 (s, 1H), 7.00—7.73 (m, 5H); MS *m/e* 233 (M^+). **15**: mp 182—185 °C; IR (KBr) 1480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.06 (s, 2H), 7.00—7.77 (m, 10H); MS *m/e* 267 (M^+).

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