REACTION OF *N*-TRIMETHYLSILYLMETHYLIMINODITHIOCARBONATE WITH CARBONYL COMPOUNDS: SYNTHETIC EQUIVALENT OF ALKYLTHIONITRILE YLIDE

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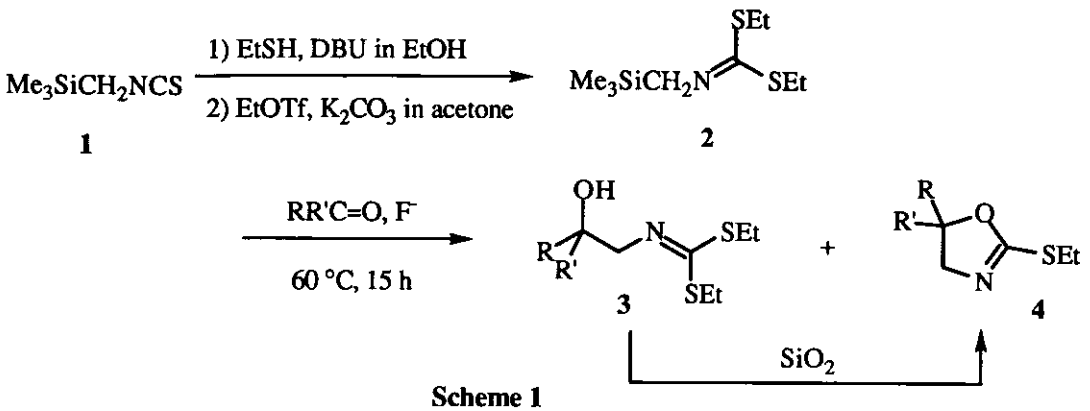
Abstract- Diethyl *N*-trimethylsilylmethyliminodithiocarbonate (**2**) prepared by an addition of ethanethiol toward trimethylsilylmethyl isothiocyanate (**1**) followed by *S*-ethylation was found to react with some carbonyl compounds in the presence of fluoride ion to afford the oxazoline derivatives (**4**) in fair yields after a treatment of the reaction mixture with silica gel, where the dithiocarbonate derivative (**2**) formally served as alkylthionitrile ylide equivalent in the reaction sequence.

For the synthesis of nitrogen-containing five-membered ring, 1,3-dipolar cycloaddition reactions of azomethine ylides and their equivalents have represented one of the most powerful methods.[1] Since the discovery of the mild desilylation methods for generating nonstabilized nitrogen and sulfur ylides,[2] in particular, azomethine ylides continue to be of great interest both synthetically and mechanistically. On the other hand, nitrile ylides are also considered as attractive conjunctive reagents for the heterocyclic synthesis, however, only certain works dealing with the silicon-based generation of the ylides have been appeared so far.[3-6] As one of our recent interest in the utilization of organosilicon compounds having heterocumulene unit for heterocyclic synthesis,[7] we previously reported the reaction of silylated isothiourea derivatives readily available from trimethylsilylmethyl isothiocyanate (**1**) as aminonitrile ylide equivalents.[8] In this paper, we would like to describe the conversion of trimethylsilylmethyl isothiocyanate (**1**) into the silylated iminothio- and iminodithiocarbonate and their reaction with carbonyl compounds in the presence of fluoride ion. Since these compounds carried a good leaving group, methylthio moiety, at the γ-position with respect to the trimethylsilyl group, a formal 1,3-elimination of alkylthiosilane would generate alkoxy- and alkylthionitrile ylides.

RESULTS AND DISCUSSION

The 1,3-dipolar equivalent, diethyl *N*-trimethylsilylmethyliminodithiocarbonate (**2**), was easily prepared in 88% yield by an addition of ethanethiol toward trimethylsilylmethyl isothiocyanate (**1**) followed by *S*-ethylation using ethyl triflate in the presence of potassium carbonate (Scheme 1). Although reactions of dimethyl *N*-trimethylsilylmethyliminodithiocarbonate, prepared *via* an alternative route, with electron

deficient olefins were reported,[3,5] the cyclization with carbonyl compounds has not been investigated.



Scheme 1

Table 1. Reaction of *N*-Trimethylsilylmethyldithiocarbonate (**2**) with Carbonyl Compounds.

Entry	R	R'		Solvent	Fluoride	**4**, %
1	4-ClC_6H_4	H	(**a**)	DMF	CsF	89
2	4-ClC_6H_4	H	(**a**)	DMF	TBAF	45
3	4-ClC_6H_4	H	(**a**)	DMF	KF [a]	53
4	4-ClC_6H_4	H	(**a**)	HMPA	CsF	86
5	4-ClC_6H_4	H	(**a**)	MeCN	CsF	40
6	4-ClC_6H_4	H	(**a**)	THF	CsF	27
7	4-BrC_6H_4	H	(**b**)	DMF	CsF	61
8	4-$O_2NC_6H_4$	H	(**c**)	DMF	CsF	52
9	Ph	H	(**d**)	DMF	CsF	43
10	4-MeC_6H_4	H	(**e**)	DMF	CsF	11
11	4-$MeOC_6H_4$	H		DMF	CsF	No Reaction
12	2-Pyridyl	H	(**f**)	DMF	CsF	33
13	3-Pyridyl	H	(**g**)	DMF	CsF	75
14	$Me(CH_2)_4$	H		DMF	CsF	No Reaction
15	Ph	Me	(**h**)	DMF	CsF	27
16	4-ClC_6H_4	Me	(**i**)	DMF	CsF	6
17	Ph	Ph	(**j**)	DMF	CsF	33

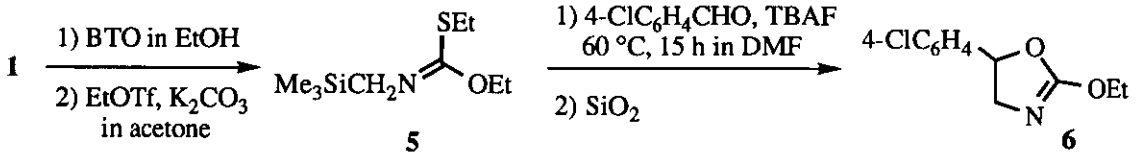
a) 18-Crown-6 (10 mol%) was added.

When a mixture of the dithiocarbonate (**2**) and 4-chlorobenzaldehyde (2 equiv.) in DMF was heated at 60 ℃ for 15 h in the presence of CsF (1.2 equiv.), a direct analysis of the reaction mixture by ^{1}H NMR revealed the formation of the aldol-type adduct (**3a**) as a major product along with a small amount of the expected oxazoline derivative (**4a**).[9] Trying to purify the reaction mixture by a column chromatography on silica gel, however, the aldol-type adduct (**3a**) and 2-ethylthio-5-(4'-chlorophenyl)oxazoline (**4a**) were

isolated in 20 and 47% yields, respectively. Obviously, a cyclization of the compound (**3a**) to the oxazoline (**4a**) occurred during the column chromatography on silica gel. In fact, a treatment of the isolated adduct (**3a**) with silica gel in chloroform for 48 h gave the oxazoline (**4a**) in a quantitative yield. Then, a direct treatment of the reaction mixture with silica gel afforded the oxazoline derivative (**4a**), a formal [3 + 2] cycloadduct, in 89% yield as a sole product (Table 1, Entry 1), where the iminodithiocarbonate (**2**) served as a alkylthionitrile ylide equivalent in the reaction sequence. Similar reaction at room temperature resulted in the formation of the compound (**4a**) in 56% yield. A systematic examination of reaction media and fluoride ion sources was carried out and the results are listed in Table 1. As shown in the Entries 1-6, utilization of CsF in DMF or HMPA resulted in the formation of compound (**4a**) in a satisfactory yield.

Other aldehydes were similarly treated with the compounds (**2**) in the presence of CsF in DMF and the representative results are also compiled in Table 1. Although the reaction with 4-bromo- and 4-nitrobenzaldehyde as well as benzaldehyde itself afforded the corresponding oxazoline derivatives (**4b**), (**4c**), and (**4d**) in 61, 52, and 43% yields, respectively (Entries 7-9), similar treatments of the aromatic aldehydes carrying the electron-donating substituents such as methyl or methoxy group gave unsatisfactory results (Entries 10 and 11). These findings indicate the electronic nature of the substituent significantly influences on the reactivity of the carbonyl moiety and the electron-withdrawing group seems to accelerate the reaction in our case. In fact, 2- and 3-pyridinecarboxyaldehydes, the electron-deficient heteroaromatic aldehydes, gave the corresponding oxazoline derivatives (**4f**) and (**4g**) in 33 and 75% yields, respectively (Entries 12 and 13), whereas aliphatic aldehyde such as hexanal was completely unreactive in the present reaction conditions (Entry 14).

A utilization of ketones as dipolarophiles was also investigated and it was found that aromatic ketones such as acetophenone derivatives and benzophenone were also reactive toward dithiocarbonate (**2**) to afford the corresponding cycloadduct (**4h**), (**4i**), and (**4j**) in 27, 6, and 33% yields, respectively (Entries 15-17). However, the cyclization with diethyl ketone or cyclohexanone did not undergo under the reaction conditions employed.



Scheme 2

Furthermore, we investigated a similar reaction of *N*-silylated iminothiocarbonate (**5**), which was also accessible from the isothiocyanate (**1**) in an analogous manner to the preparation of the iminodithiocarbonate (**2**) (Scheme 2).[10] When a reaction of the iminothiocarbonate (**5**) with 4-chlorobenzaldehyde (2 equiv.) in the presence of tetrabutylammonium fluoride (TBAF)[11] was conducted at 60 ℃ in DMF for 15 h, the aldol-type adduct and the expected oxazoline derivative (**6**) were detected in the

reaction mixture in the ratio of 67:33 by ^{1}H NMR spectroscopy. However, the chromatographic separation of the reaction mixture afforded only oxazoline derivative (**6**) in 49% yield. The lower yield of the compound (**6**) in comparison with the corresponding sulfur analogue (**4a**) was probably due to its low stability in silica gel.[12] In this reaction, the methylthio moiety of the compound (**5**) was exclusively eliminated to furnish the 2-ethoxyoxazoline (**6**) where the iminothiocarbonate (**5**) served as alkoxynitrile ylide equivalent.

In summary, diethyl *N*-trimethylsilylmethyliminodithiocarbonate (**2**) readily available from trimethylsilylmethyl isothiocyanate (**1**) and ethanethiol was found to react with some carbonyl compounds to afford the 2-ethylthiooxazoline derivatives (**4**), the formal [3 + 2] cycloadducts, in fair yields, where the iminodithiocarbonate (**2**) served as synthetic equivalents of alkylthionitrile ylide. In addition, the cyclization with the iminothiocarbonate (**5**) also gave the corresponding 2-ethoxyoxazoline (**6**) in a moderate yield.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution on a Varian UNITY-400 spectrometer (399.97 MHz for ^{1}H, 100.58 MHz for ^{13}C). All chemical shifts are reported as δ values (ppm) relative to residual chloroform (7.26 ppm for ^{1}H) and the central peak of deuteriochloroform (77.00 ppm for ^{13}C). IR spectra were recorded on a Perkin Elmer 1600 infrared spectrophotometer. EI and FAB MS spectra were obtained on a JEOL JMS-AX-500 spectrometer with DA7000 data system. GC-MS was measured with the direct combination of GC (Hewlett-Packard GC 5890 Series II with a 25 m × 0.25 mm methylsilicone capillary column) and a JEOL JMS-AX-500 spectrometer. Most of the starting materials and reagents were commercial products and were used as supplied. Trimethylsilylmethyl isothiocyanate (**1**) was prepared according to the literature,[13] bp 89 ℃ / 16 mmHg (lit.,[13] 46 ℃ / 3 mmHg). Solvents were dried by conventional methods and were distilled before use.

Diethyl *N*-Trimethylsilylmethyliminodithiocarbonate (2).

A solution of trimethylsilylmethyl isothiocyanate (**1**, 2.72 g, 20.0 mmol), ethanethiol (1.36 g, 22.0 mmol), and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in ethanol (20 mL) was stirred at rt for 1 h. After a usual workup of the reaction mixture, the crude dithiocarbamate was dissolved in acetone (20 mL) and the chilled solution was treated with ethyl triflate (6.05 g, 34.0 mmol) in the presence of K_2CO_3 (2.82 g, 20.4 mmol) for 2 h. Then, the concentrated reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and evaporated *in vacuo*. The crude product was purified by chromatography on silica gel (hexane : AcOEt = 95 : 5) to give diethyl *N*-trimethylsilylmethyliminodithiocarbonate (**2**, 4.10 g, 88%) as a pale yellow oil. ^{1}H NMR δ 0.05 (s, 9 H), 1.26 (t, 3 H, *J* = 7 Hz), 1.33 (t, 3 H, *J* = 7 Hz), 2.94 (q, 2 H, *J* = 7 Hz), 3.05 (q, 2 H, *J* = 7 Hz), 3.36 (s, 2 H). ^{13}C NMR δ -2.22, 14.41, 15.56, 25.60, 26.54, 47.51, 151.30. HRMS (EI) *m/z* 235.0840 (M^+ calcd for $C_9H_{21}NSSi$ 235.0885).

Reaction of Dithiocarbonate (2) with Carbonyl Compounds.

A mixture of dithiocarbonate (**2**, 0.705 g, 3.00 mmol), 4-chlorobenzaldehyde (0.843 g, 6.00 mmol), and CsF (0.547 g, 3.60 mmol) in DMF (3 mL) was heated at 60 ℃ for 15 h. Then, the reaction mixture was diluted with ethyl acetate. The organic layer was washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and evaporated *in vacuo*. The crude products were chromatographed on silica gel and elution with a mixture of hexane and AcOEt (93 : 7) furnished the aldol-type adduct (**3**, 0.180 g, 20%) as a pale yellow oil. ^{1}H NMR δ 1.29 (t, 3 H, *J* = 7 Hz), 1.34 (s, 3 H, *J* = 7 Hz), 3.00 (q, 2 H, *J* = 7 Hz), 3.08 (q, 2 H, *J* = 7 Hz), 3.37 (br s, 1 H), 3.37 (dd, 1 H, *J* = 9, 14 Hz), 3.62 (dd, 1 H, *J* = 4, 14 Hz), 4.89 (dd, 1 H, *J* = 4, 9 Hz), 7.32 and 7.35 (AA'BB'q, 4 H, *J* = 9 Hz). ^{13}C NMR δ 13.93, 15.11, 25.80, 26.50, 60.24, 72.28, 127.53, 128.44, 133.24, 140.71, 160.88. MS (FAB) *m/z* 304 [(M + H)$^+$]. HRMS (EI) *m/z* 242.0406 [(M - SEt)$^+$ calcd for $C_{11}H_{13}NO^{35}ClS$ 242.0412]. IR (neat) ν_{MAX} 3450 (OH) and 1575 (C=N) cm^{-1}.

Further elution with a mixture of hexane and AcOEt (89 : 11) afforded the oxazoline (**4a**, 0.340 g, 47%) as a pale yellow oil. ^{1}H NMR δ 1.40 (t, 3 H, *J* = 7 Hz), 3.05 (dq, 2 H, *J* = 1, 7 Hz), 3.77 (dd, 1 H, *J* = 8, 14 Hz), 4.29 (dd, 1 H, *J* = 10, 14 Hz), 5.54 (dd, 1 H, *J* = 8, 10 Hz), 7.24 and 7.35 (AA'BB'q, 4 H, *J* = 8 Hz). ^{13}C NMR δ 14.73, 26.21, 62.79, 81.74, 127.11, 129.03, 134.33, 137.93, 165.46. HRMS (EI) *m/z* 241.0328 (M$^+$ calcd for $C_{11}H_{12}NO^{35}ClS$ 241.0283). Anal. Calcd for $C_{11}H_{12}NOClS$: C, 54.65; H, 5.00; N, 5.79. Found: C, 54.94; H, 4.95; N, 5.90.

Alternatively, a similar reaction was carried out and the reaction mixture was directly treated with silica gel (*ca.* 10 g) in $CHCl_3$ (*ca.* 100 mL) at rt for 48 h. After removal of the silica gel and solvents, the crude product was chromatographed on silica gel (hexane : AcOEt = 9 : 1) to give oxazoline (**4a**, 0.640 g, 89%) as a sole product.

The reaction of other carbonyl compounds with dithiocarbonate (**2**) was similarly performed and the results are listed in Table 1. The spectral data are as follows.

4b: oil. ^{1}H NMR δ 1.40 (t, 3 H, *J* = 8 Hz), 3.048 (q, 1 H, *J* = 8 Hz), 3.05 (q, 1 H, *J* = 8 Hz), 3.77 (dd, 1 H, *J* = 14, 8 Hz), 4.27 (dd, 1 H, *J* = 14, 10 Hz), 5.52 (dd, 1 H, *J* = 10, 8 Hz), 7.17 and 7.50 (AA'BB'q, 4 H, *J* = 8 Hz). ^{13}C NMR δ 14.69, 26.18, 81.73, 122.37, 127.36, 131.98, 139.46, 165.43. HRMS (EI) *m/z* 286.9788 (M$^+$ calcd for $C_{11}H_{12}NO^{81}BrS$ 286.9802).

4c: oil. ^{1}H NMR δ 1.41 (t, 3 H, *J* = 7 Hz), 3.06 (q, 1 H, *J* = 7 Hz), 3.07 (q, 1 H, *J* = 7 Hz), 3.77 (dd, 1 H, *J* = 14, 7 Hz), 4.37 (dd, 1 H, *J* = 14, 10 Hz), 5.66 (dd, 1 H, *J* = 10, 7 Hz), 7.46 and 8.23 (AA'BB'q, 4 H, *J* = 9 Hz). ^{13}C NMR δ 14.67, 26.37, 62.98, 81.06, 124.14, 126.32, 128.39, 147.63, 165.64. HRMS (EI) *m/z* 252.0594 (M$^+$ calcd for $C_{11}H_{12}N_2O_3S$ 252.0569).

4d: oil. ^{1}H NMR δ 1.40 (t, 3 H, *J* = 7 Hz), 3.057 (q, 1 H, *J* = 7 Hz), 3.059 (q, 1 H, *J* = 7 Hz), 3.82 (dd, 1 H, *J* = 14, 8 Hz), 4.30 (dd, 1 H, *J* = 14, 10 Hz), 5.57 (dd, 1 H, *J* = 10, 8 Hz), 7.35 (m, 5 H). ^{13}C NMR δ 14.77, 26.25, 62.84, 82.57, 125.75, 128.40, 140.34, 165.46. HRMS (EI) *m/z* 207.0765 (M$^+$ calcd for $C_{11}H_{13}NOS$ 207.0718).

4e: oil. ^{1}H NMR δ 1.40 (t, 3 H, *J* = 8 Hz), 2.35 (s, 3 H), 3.049 (q, 1 H, *J* = 8 Hz), 3.050 (q, 1 H, *J* = 8 Hz), 3.82 (dd, 1 H, *J* = 13, 8 Hz), 4.27 (dd, 1 H, *J* = 13, 10 Hz), 5.54 (dd, 1 H, *J* = 10, 8 Hz), 7.18

and 7.20 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 14.78, 21.06, 26.14, 62.75, 125.87, 129.48, 137.38, 165.44. HRMS (EI) m/z 221.0895 (M^+ calcd for $C_{12}H_{15}NOS$ 221.0874).

4f: oil. ^{1}H NMR δ 1.38 (t, 3 H, J = 7 Hz), 3.02 (dq, 1 H, J = 12, 7 Hz), 3.07 (dq, 1 H, J = 12, 7 Hz), 3.98 (dd, 1 H, J = 14, 7 Hz), 4.35 (dd, 1 H, J = 14, 10 Hz), 5.65 (dd, 1 H, J = 10, 7 Hz), 7.21 (ddd, 1 H, J = 8, 5, 1 Hz), 7.36 (d, 1 H, J = 8 Hz), 7.69 (ddd, 1 H, J = 8, 8, 2 Hz), 8.56 (ddd, 1 H , J = 5, 2, 1 Hz). ^{13}C NMR δ 14.68, 26.27, 61.01, 82.21, 119.87, 122.87,136.85, 149.56, 159.85, 165.09. HRMS (EI) m/z 209.0794 [(M + H)$^+$ calcd for $C_{10}H_{13}N_2OS$ 209.0749].

4g: oil. ^{1}H NMR δ 1.41 (t, 3 H, J = 7 Hz), 3.061 (q, 1 H, J = 7 Hz), 3.063 (q, 1 H, J = 7 Hz), 3.83 (dd, 1 H, J = 14, 8 Hz), 4.35 (dd, 1 H, J = 14, 10 Hz), 5.61 (dd, 1 H, J = 10, 8 Hz), 7.33 (m, 1 H), 7.64 (m,1 H), 8.56 (d, 1 H, J = 2 Hz), 8.59 (dd, 1 H, J = 5, 2 Hz). ^{13}C NMR δ 14.63, 26.18, 62.54, 80.06, 123.57, 133.13, 135.84, 147.55, 149.83, 165.44. HRMS (EI) m/z 208.0681 (M^+ calcd for $C_{10}H_{12}N_2OS$ 208.0670).

4h: oil. ^{1}H NMR δ 1.40 (t, 3 H, J = 8 Hz), 1.73 (s, 3 H), 3.046 (q, 1 H, J = 8 Hz), 3.049 (q, 1 H, J = 8 Hz), 3.97 (ABq, 2 H, J = 1 Hz), 7.33 (m, 5 H). ^{13}C NMR δ 14.79, 22.61, 27.87, 68.69, 88.71, 124.33, 127.50, 128.59, 145.05, 164.45. HRMS (EI) m/z 221.0876 (M^+ calcd for $C_{12}H_{15}NOS$ 221.0874).

4i: oil. ^{1}H NMR δ 1.39 (t, 3 H, J = 7 Hz), 1.70 (s, 3 H), 3.037 (q, 1 H, J = 7 Hz), 3.308 (q, 1 H, J = 7 Hz), 3.92 and 3.96 (ABq, 2 H, J = 14 Hz), 7.26 and 7.33 (AA'BB'q, 4 H, J = 9 Hz). ^{13}C NMR δ 14.73, 26.10, 27.76, 68.62, 88.20, 125.83, 128.77, 133.55, 143.57, 164.50. HRMS (EI) m/z 255.0485 (M^+ calcd for $C_{12}H_{14}NO^{35}ClS$ 255.0485).

4j: oil. ^{1}H NMR δ 1.39 (t, 3 H, J = 7 Hz), 3.07 (q, 2 H, J = 7 Hz), 4.49 (s, 2 H), 7.29 (m, 10 H). ^{13}C NMR δ 14.74, 26.18, 68.63, 92.06, 125.96, 128.47, 143.85, 164.50. MS (FAB) m/z 283 (M^+). HRMS (EI) m/z 221.0809 [(M - SEt - H)$^+$ calcd for $C_{15}H_{11}NO$ 221.0841].

Diethyl *N*-Trimethylsilylmethyliminothiocarbonate (5).

A solution of trimethylsilylmethyl isothiocyanate (**1**, 1.45 g, 10.0 mmol) and bis(tributyltin) oxide (BTO, 5.96 g, 10.0 mmol) in ethanol (20 mL) was stirred at 60 ℃ for 24 h. After removal of the solvent, the crude product was extracted with chloroform. The organic layer was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel (hexane) to give 1.41g (74%) of ethyl *N*-trimethylsilylmethylthioxocarbamate. ^{1}H NMR δ 0.06 and 0.09 (2s, 9 H), 1.29 and 1.35 (2t, 3 H, J = 7 Hz), 2.80 and 3.07 (2d, 2 H, J = 6 Hz), 4.46 and 4.53 (2q, 2 H, J = 7 Hz), 6.10 and 6.74 (2br s, 1 H). MS m/z 191 (M^+). The obtained thioxocarbamate was dissolved in acetone (10 mL) and the chilled solution was treated with ethyl triflate (3.56 g, 20.0 mmol) in the presence of K_2CO_3 (1.66 g, 12.0 mmol) overnight. Then, the concentrated reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and evaporated *in vacuo*. The crude product was purified by chromatography on silica gel (hexane : AcOEt = 99 : 1) to give diethyl *N*-trimethylsilylmethyliminothiocarbonate (**5**, 951 mg, 60%) as a colorless oil. ^{1}H NMR δ 0.03 (s, 9 H), 1.27 (t, 3 H, J = 7 Hz), 1.28 (t, 3 H, J = 7 Hz), 2.88 (s, 2 H), 2.90 (q, 2 H, J = 7 Hz), 4.15 (q, 2 H, J =

7 Hz). ^{13}C NMR δ -2.37, 14.26, 15.82, 24.85, 41.40, 62.99, 152.96. HRMS (EI) *m/z* 219.1093 (M^+ calcd for $C_9H_{21}NOSSi$ 219.1113).

Reaction of Thiocarbonate (5) with 4-Chlorobenzaldehyde.

A mixture of dithiocarbonate (**5**, 219 mg, 1.00 mmol), 4-chlorobenzaldehyde (280 mg, 2.00 mmol), and TBAF (1 *M* solution in THF, 1.2 mL, 1.20 mmol) in DMF (1 mL) was heated at 60 ℃ for 15 h. Then, the reaction mixture was diluted with ethyl acetate. The organic layer was washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and evaporated *in vacuo*. The crude product was chromatographed on silica gel and elution with a mixture of hexane and AcOEt (8 : 2) afforded the oxazoline (**6**, 115 mg, 49%) as a pale yellow oil. ^{1}H NMR δ 1.37 (t, 3 H, *J* = 7 Hz), 3.67 (dd, 1 H, *J* = 13, 8 Hz), 4.20 (dd, 1 H, *J* = 13, 10 Hz), 4.32 (q, 2 H, *J* = 7 Hz), 5.56 (dd, 1 H, *J* = 10, 8 Hz), 7.26 and 7.35 (AA'BB'q, 4 H, *J* = 8 Hz). ^{13}C NMR δ 14.25, 59.90, 66.84, 81.01, 126.93, 128.98, 134.31, 138.91, 162.57. HRMS (EI) *m/z* 225.0553 (M^+ calcd for $C_{11}H_{12}NO_2{}^{35}Cl$ 225.0557).

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9. A prolonged reaction time resulted in the formation of complex reaction mixture.
10. In the addition reaction of ethanol toward the isothiocyanate (**1**), bis(tributyltin) oxide (BTO) was found to be the most effective promoter among the bases tested.
11. In this case, CsF was not effective.
12. Long standing of the reaction mixture in silica gel resulted in the decomposition of the product.
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