Reaction of Trimethylsilyl Isoselenocyanate with Oxiranes and Oxetane

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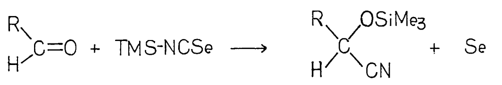
(Received August 24, 1989)

The reaction of trimethylsilyl isoselenocyanate with oxiranes and oxetane gave 2-trimethylsiloxyalkyl selenocyanates and 3-trimethylsiloxypropyl selenocyanate, respectively, in good to excellent yields. Effects of solvents and catalysts on regioselectivity were examined.

Oxiranes and oxetanes have been reported to react with trimethylsilyl cyanide to give trimethylsiloxy nitriles in the presence of aluminum compounds[1] or to give trimethylsiloxy isocyanides in the presence of Lewis acids such as ZnX_2,[2] $Pd(CN)_2$,[1c] $SnCl_2$,[1c] or Me_3Ga.[1c] Trimethylsilyl azide reacts analogously with oxiranes to produce 2-trimethylsiloxyalkyl azides.[3]

On the other hand, I have recently reported the synthesis and reaction of trimethylsilyl isoselenocyanate (TMS-NCSe) in which the reaction of TMS-NCSe with aldehydes gave 1-trimethylsiloxyalkyl cyanides (Eq. 1).[4]



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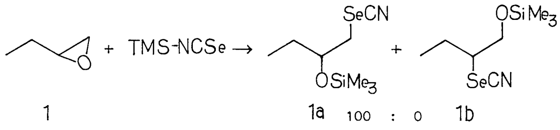
I now wish to report the ring-opening reactions of oxiranes and oxetane with TMS-NCSe to produce trimethylsiloxyalkyl selenocyanates in high yields without the release of selenium.

In a preliminary experiment, the reaction was carried out with 2-ethyloxirane (**1**) and TMS-NCSe (Table 1). In hexane the reaction was considerably slow even in the presence of $ZnCl_2$, whereas the reaction was completed after 3 h in CH_3CN. For different reaction conditions, the product was only 2-trimethylsiloxybutyl selenocyanate (**1a**), and no **1b** and no nitrile were produced (Eq. 2).



(2)

Because TMS-NCSe isolation is very troublesome, TMS-NCSe was not isolated and **1** was added directly

Table 1. Reaction of **1** with TMS-NCSe[a]

Solvent	Catalyst	Time/h	Temp/°C	Conversion of TMS-NCSe/%[b]
Hexane	—	7	60	10
Hexane	$ZnCl_2$[c]	7	60	26
CH_3CN	—	3	40	100 (95)[d]

a) Reactions were carried out with **1** (5.25 mmol), TMS-NCSe (5 mmol), and a solvent (5 ml). b) Determined by GLC. c) 0.3 mmol. d) Isolated yield of **1a** purified by column chromatography.

Table 2. One-Pot Reaction of **1** with TMS-NCSe in the Presence of KSeCN[a]

Solvent	Catalyst	Time/h	Temp/°C	Conversion of TMS-NCSe/%[b]
Hexane	—	7	60	74
Hexane	—	24	60	100 (97)
Hexane	—	7	40	47
Hexane	KSeCN/XAD-4[c]	3	60	100 (96)
Hexane	$ZnCl_2$[d]	7	60	98 (91)
Hexane	$Ti(OPr^i)_4$[d]	0.5	40	100 (80)[e]
CH_2Cl_2	—	7	40	16
CH_2Cl_2	18-Crown-6[d]	7	40	68
CH_3CN	—	1	40	100 (93)

a) After a mixture of TMS-Cl (7.5 mmol) and KSeCN (9 mmol) in a solvent (10 ml) was stirred overnight at room temperature, **1** (7.88 mmol) and a catalyst were added. b) Determined by GLC. Unless otherwise noted, values in parentheses are the isolated yields of **1a**. c) KSeCN (9 mmol)/XAD-4 (2.0 g) was used in place of KSeCN (9 mmol). d) 0.3 mmol. e) GLC yield of **1a**.

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to the flask in which the TMS-NCSe was prepared. Table 2 shows the results of the one-pot reaction of **1** with TMS-NCSe under various conditions. In CH_3CN, the reaction was completed within 1 h at 40 °C and the rate was in the order of $CH_3CN \gg$ hexane$>CH_2Cl_2$. Excess KSeCN enhanced the rate and the use of KSeCN impregnated on Amberlite XAD-4 resin (KSeCN/XAD-4) in place of KSeCN and the addition of a catalytic amount of 18-crown-6 significantly increased the reaction rate. The addition of a catalytic amount of Lewis acid, $ZnCl_2$ or Ti(OPr^i)$_4$, also promoted the reaction more strongly than only KSeCN. The present findings are quite in contrast to the results of the one-pot reaction of TMS-NCSe with aldehydes,[4] in which results the reaction released selenium, the rate was in the order of hexane>benzene$\approx CH_2Cl_2 \gg CH_3CN$, and addition of a catalytic amount of 18-crown-6 gave a negative effect. The present results suggest a push and pull mechanism by a Lewis acid and base (Eq. 3), which is analogous to that proved in the reaction of trimethylsilyl cyanide with oxiranes catalyzed by ZnI_2.[2] On the other hand, the reaction with aldehydes seems to proceed through a quite different mechanism, which involves a nonionic intermediate. It appears that a small amount of TMS-SeCN,[5] which seems to exist as the isomer of TMS-NCSe, is the true reactant and a driving-force for the release of selenium is the coordination of –CN group to silicon atom (Eq. 4).

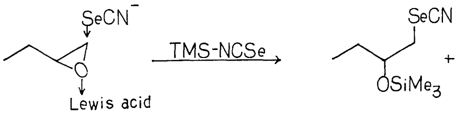

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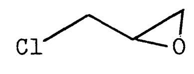
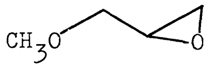
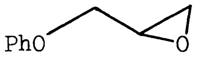
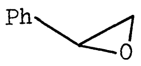
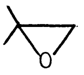
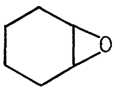
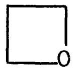
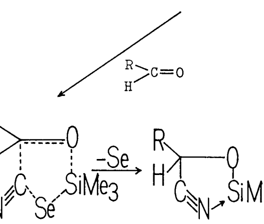
Table 3. One-Pot Reaction of TMS-NCSe with Oxiranes and Oxetane$^{a)}$

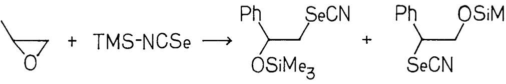
Oxirane	Solvent	Catalyst	Time/h	Temp/°C	Yield/%$^{b)}$	a : b
 **2**	Hexane	—	7	40	(70)	100 : 0
	Hexane	—	24	40	ca. 100 (100)	100 : 0
	Hexane	KSeCN/XAD-4$^{c)}$	3	40	68 (100)	100 : 0
	Hexane	$ZnCl_2^{d)}$	7	40	(75)	100 : 0
	CH_3CN	—	7	40	(58)	100 : 0
 **3**	Hexane	—	7	40	95 (97)	100 : 0
	Hexane	Ti(OPr^i)$_4^{d)}$	0.5	40	77 (100)	100 : 0
	CH_3CN	—	12	40	88 (100)	100 : 0
 **4**	Hexane	—	7	40	$84^{h)}$ (100)	100 : 0
	Hexane	KSeCN/XAD-4$^{c)}$	1	40	$87^{h)}$ (100)	100 : 0
	CH_3CN	—	7	40	$62^{h)}$ (69)	100 : 0
 **5**	Hexane	—	7	60	$93^{h,i)}$ (100)	75 : 25
	Hexane	KSeCN/XAD-4$^{c)}$	3	60	88 (100)	54 : 46
	Hexane	$ZnCl_2^{d)}$	7	60	91 (100)	53 : 47
	Hexane	$ZnCl_2^{e)}$	6	60	$90^{h)}$ (100)	37 : 63
	Hexane	$ZnCl_2^{f)}$	30	60	$86^{h)}$ (100)	13 : 87
	Hexane	$ZnCl_2^{g)}$	30	60	$56^{h)}$ (100)	6 : 94
	Hexane	Ti(OPr^i)$_4^{d)}$	0.5	40	$72^{h,i)}$ (100)	3 : 97
	CH_3CN	—	1	40	j)	
 **6**	Hexane	—	96	60	87 (100)	87 : 13
	Hexane	KSeCN/XAD-4$^{c)}$	7	60	$84^{i)}$ (100)	82 : 18
	Hexane	$ZnCl_2^{d)}$	24	40	$80^{h)}$ (100)	80 : 20
	Hexane	Ti(OPr^i)$_4^{d)}$	3	40	$71^{h)}$ (100)	34 : 66
	CH_3CN	—	2	60	66 (100)	37 : 63
 **7**	Hexane	—	5	60	98 (100)	
	CH_3CN	—	1	40	92 (100)	
 **8**	Hexane	—	24	40	96 (100)	
	Hexane	KSeCN/XAD-4$^{c)}$	7	40	92 (100)	
	CH_3CN	—	1	40	93 (100)	

a) Unless otherwise noted, after a mixture of TMS-Cl (7.5 mmol) and KSeCN (9 mmol) in a solvent (10 ml) was stirred overnight at room temperature, oxirane (7.88 mmol) and a catalyst were added. b) Isolated yields. Values in parentheses are TMS-NCSe conversions. c) KSeCN (9 mmol)/XAD-4 (2.0 g) was used in place of KSeCN (9 mmol). d) 0.3 mmol. e) 1.0 mmol. f) $ZnCl_2$ (0.3 mmol) was used without KSeCN. g) $ZnCl_2$ (4.5 mmol) was used without KSeCN. h) Determined by GLC. i) KSeCN (27 mmol), TMS-Cl (22.5 mmol), oxirane (23.6 mmol), and hexane (20 or 30 ml) were used. j) Substantial quantities of unidentified products were observed.



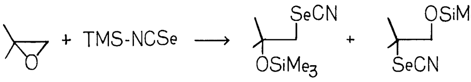
(4)

In order to reveal the regioselectivity, reactions were carried out with other oxiranes under various conditions (Table 3). In general, the best yields of trimethylsiloxyalkyl selenocyanates were obtained in hexane. The use of KSeCN/XAD-4, KSeCN in CH_3CN, or Lewis acids such as $ZnCl_2$ and $Ti(OPr^i)_4$ gave lower yields probably because of the polymerization of the oxiranes. Interestingly, in the case of the 1,2-epoxyalkanes having an electron-withdrawing group at the C-3 position such as 1-chloro-2,3-epoxypropane (**2**), 1,2-epoxy-3-methoxypropane (**3**), and 1,2-epoxy-3-phenoxypropane (**4**), the reaction in CH_3CN was slower than in hexane. The reaction of **2**, **3**, or **4** gave only the normal addition product, type **a**, identical to **1**. On the other hand, the reaction of 2-phenyloxirane (**5**) or 2,2-dimethyloxirane (**6**) gave a mixture of type **a** and the abnormal addition product, type **b**, the ratio of which depended on the catalysts and the solvents. The reaction using excess KSeCN catalyst in hexane gave predominantly type **a** product, whereas the reaction with a Lewis acid catalyst or the reaction in CH_3CN produced mainly type **b** product. In particular, the reaction of **5** gave regioselectively **5b** (**5a**:**5b**=3:97) in the presence of $Ti(OPr^i)_4$.



(5)

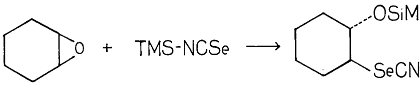
5 5a 5b



(6)

6 6a 6b

2-Trimethylsiloxycyclohexyl selenocyanate (**8**) obtained from cyclohexene oxide (**7**) was estimated to be *trans* by ^1H NMR.



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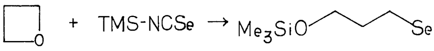
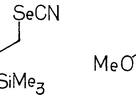
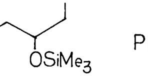
Oxetane (**9**) reacted analogously to give 3-trimethylsiloxypropyl selenocyanate (**10**) in excellent yield.

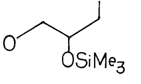


(8)

9 10


2a


3a


4a

Experimental

Materials. All the solvents were dried with Molecular Sieves 4A. Trimethylsilyl chloride (TMS-Cl), oxiranes, oxetane, $ZnCl_2$, and $Ti(OPr^i)_4$ were used as obtained. TMS-NCSe was prepared by the method previously reported.[4] Potassium selenocyanate was dried under vacuum (0.05—0.01 mmHg, 1 mmHg=133.322 Pa) at 90 °C for 4 h. KSeCN/XAD-4 was prepared as follows: XAD-4 (2.0 g) was added to a solution of KSeCN (1.3 g, 9 mmol) in 50% aqueous methanol (3 g) and the whole mixture was then allowed to stand for 0.5 h. The solvent was removed under reduced pressure (ca. 20 mmHg) at ambient temperature to 90 °C. The half-dried KSeCN/XAD-4 reagent was further dried at 90 °C for 4 h under vacuum (0.05—0.01 mmHg).

All of the reactions were carried out in a nitrogen atmosphere.

Reaction of 1 with TMS-NCSe. After a mixture of **1** (5.25 mmol) and TMS-NCSe (5.0 mmol) was stirred in a solvent (5 ml) under the indicated conditions (Table 1), the resulting mixture was directly analyzed by GLC (Silicone SE-30, 10%, 1 m×3 mm, 60 °C, 140 °C).

One-Pot Ring-Opening Reaction of Oxiranes and Oxetane with TMS-NCSe. 2-Trimethylsiloxybutyl Selenocyanate (1a): After a mixture of TMS-Cl (0.81 g, 7.5 mmol) and KSeCN (1.3 g, 9 mmol) in hexane (10 ml) had been stirred at room temperature overnight, **1** (0.57 g, 7.88 mmol) was added and the whole mixture was stirred for 24 h at 60 °C. GLC showed the complete conversion of TMS-NCSe and only one product. After the solid material was filtered, the filtrate was passed through a 50 mm SiO_2 column and eluted with CH_2Cl_2 (30 ml). Removing the solvent gave 1.82 g (98% purity, 97% yield) of **1a**, distillation of which gave 1.54 g (82% yield) of pure **1a**, bp 92.0—93.0 °C/2 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^1H NMR ($CDCl_3$): δ=0.156 (9H, s), 0.928 (3H, t, J=7 Hz), 1.630 (2H, qui, J=7 Hz), 3.075 (1H, dd, J=11.5, 6.5 Hz), 3.555 (1H, dd, J=11.5, 4.4 Hz), 3.7—4.1 (1H, m). MS (m/z): 236,234 (M^+-CH_3), 222, 220 (M^+-CH_3-N). Found: C, 38.10; H, 7.00; N, 5.38%. Calcd for $C_8H_{17}NOSeSi$: C, 38.39; H, 6.85; N, 5.60%.

2-Trimethylsiloxy-3-methoxypropyl Selenocyanate (3a): After a mixture of TMS-Cl (0.81 g, 7.5 mmol) and KSeCN (1.3 g, 9 mmol) in CH_3CN (10 ml) had been stirred for 0.5 h at room temperature, 1,2-epoxy-3-methoxypropane (**3**) (0.70 g, 7.88 mmol) was added and the whole mixture was stirred at 40 °C for 12 h. The solid material was filtered and the solvent was removed. The residue was dissolved in hexane (20 ml) and the solid material was filtered. The filtrate was passed through a 50 mm SiO_2 column and eluted with CH_2Cl_2. Removing the solvent gave 1.83 g (97% purity, 88% yield) of **3a**, distillation of which gave 1.40 g (70% yield) of pure **3a**, bp 100.0—100.5 °C/1.5 mmHg. IR (neat): 2150 cm^{-1} (—SeCN). ^1H NMR ($CDCl_3$): δ=1.64 (9H, s), 3.1—3.6 (7H, m), 3.9—4.2 (1H, m). MS (m/z): 252, 250 (M^+-CH_3).

Found: C, 35.73; H, 6.66; N, 5.15%. Calcd for $C_8H_{17}NO_2SeSi$: C, 36.08; H, 6.44; N, 5.26%.

3-Chloro-2-trimethylsiloxypropyl Selenocyanate (2a): Bp 97.0—99.0 °C/0.5 mmHg (slightly decomposed during distillation). IR (neat): 2155 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.200 (9H, s), 3.0—3.7 (4H, m), 4.0—4.4 (1H, m). MS (m/z): 258, 256, 254 (M^+-CH_3). Found: C, 30.85; H, 5.07; N, 5.10%. Calcd for $C_7H_{14}ClNOSeSi$: C, 31.06; H, 5.26; N, 5.17%.

2-Trimethylsiloxy-3-phenoxypropyl Selenocyanate (4a): This compound was purified by column chromatography (SiO_2, Wako gel Q-12; eluted with hexane, hexane+CH_2Cl_2, and CH_2Cl_2), because of its vigorous decomposition during distillation. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.203 (9H, s), 3.235 (1H, dd, J=11.5, 6.0 Hz), 3.516 (1H, dd, J=11.5, 4.2 Hz), 3.951 (2H, d, J=5 Hz), 4.1—4.4 (1H, m), 6.79—7.43 (5H, m). MS (m/z): 329, 327 (M^+), 314, 312 (M^+-CH_3). Found: C, 46.58; H, 5.40; N, 3.74%. Calcd for $C_{13}H_{19}NO_2SeSi$: C, 47.40; H, 5.81; N, 4.25%.

2-Trimethylsiloxy-2-phenylethyl Selenocyanate (5a): After a mixture of TMS-Cl (2.43 g, 22.5 mmol) and KSeCN (3.9 g, 27 mmol) in hexane (20 ml) had been stirred overnight at room temperature, 2-phenyloxirane (**5**)(2.84 g, 23.6 mmol) was added and the whole mixture was stirred for 24 h at 60 °C. GLC showed the ratio of **5a**:**5b**=75:25 (Silicone SE-30, 10%, 1 m×3 mm, 60 °C, 180 °C). A similar work-up as **1a** gave 6.90 g (91% purity, 93% yield) of an isomeric mixture (**5a**:**5b**=75:25), which was twice distilled using a 150 mm column (with 5 mm×5 mm raschig ring) to give an analytical sample of **5a** (97% purity), bp 108.5—109.5 °C/0.3 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.073 (9H, s), 3.310 (2H, d, J=6.3 Hz), 4.970 (1H, t, J=6.3 Hz), 7.319 (5H, s). MS (m/z): 284, 282 (M^+-CH_3). Found: C, 48.39; H, 5.82; N, 4.62%. Calcd for $C_{12}H_{17}NOSeSi$: C, 48.31; H, 5.75; N, 4.70%.

2-Trimethylsiloxy-1-phenylethyl Selenocyanate (5b): After a mixture of TMS-Cl (2.43 g, 22.5 mmol) and KSeCN (3.9 g, 27 mmol) in hexane (20 ml) had been stirred overnight at room temperature, **5** (2.84 g, 23.6 mmol) and $Ti(OPr^i)_4$ (0.24 g, 0.9 mmol) were added and the whole mixture was stirred for 0.5 h at 40 °C. GLC showed the ratio of **5a**:**5b**=3:97. A similar work-up as **1a** gave 5.10 g (94% purity, 72% yield) of an isomeric mixture, which was twice distilled using a 100 mm coulmn (with 5 mm×5 mm rasching ring) to give an analytical sample of **5b** (>98% purity), bp 117.5—118.0 °C/0.3 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.139 (9H, s), 4.143 (2H, d, J=6.5 Hz), 4.831 (1H, dd, J=7.17, 5.86 Hz), 7.351 (5H, s). MS (m/z): 284, 282 (M^+-CH_3). Found: C, 48.71; H, 5.73; N, 4.77%. Calcd for $C_{12}H_{17}NOSeSi$: C, 48.31; H, 5.75; N, 4.70%.

2-Methyl-2-trimethylsiloxypropyl Selenocyanate (6a): After a mixture of TMS-Cl (2.43 g, 22.5 mmol) and KSeCN (3.9 g, 27 mmol)/XAD-4 (6.0 g) in hexane (30 ml) had been stirred for 1 h at room temperature, 2,2-dimethyloxirane (**6**) (1.71 g, 23.6 mmol) was added and the whole mixture was stirred for 7 h at 60 °C. GLC showed the ratio of **6a**:**6b**=82:18 (silicone SE-30, 10%, 1 m×3 mm, 60 °C, 140 °C). A similar work-up as **1a** gave 4.74 g (97% purity, 84% yield) of an isomeric mixture, which was twice distilled using a 80 mm column (with 5 mm×5 mm raschig ring) to give an analytical sample of **6a** (>98% purity), bp 94.5—95.0 °C/3 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.132 (9H, s), 1.420 (6H, s), 3.279 (2H, s). MS (m/z): 236, 234 (M^+-CH_3). Found: C, 38.63; H, 7.07; N, 5.67%. Calcd for $C_8H_{17}NOSeSi$: C, 38.39; H, 6.85; N, 5.6%.

1,1-Dimethyl-2-trimethylsiloxyethyl Selenocyanate (6b): Since this compound could not be isolated in the pure state, a mixture of **6a**:**6b**=40:60 (GLC), bp 83 °C/2.5 mmHg, was analyzed. IR (neat): 2150 cm^{-1} (—SeCN). ^{1}H NMR ($CDCl_3$): δ=0.14 (9H, s), 1.425 (**6a**) and 1.638 (**6b**) (6H, s), 3.282 (**6a**) and 3.630 (**6b**) (2H, s). GC-MS (m/z): 236, 234 (M^+-CH_3). Found: C, 38.14; H, 6.92; N, 5.63%. Calcd for $C_8H_{17}NOSeSi$: C, 38.39; H, 6.85; N. 5.60%.

2-Trimethylsiloxycyclohexyl Selenocyanate (8): Bp 117.5—118.5 °C/2 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.161 (9H, s), 1.1—2.2 (8H, m), 3.1—3.7 (2H, m). MS (m/z): 277, 275 (M^+), 262, 260 (M^+-CH_3). Found: C, 43.56; H, 7.34; H, 4.86%. Calcd for $C_{10}H_{19}NOSeSi$: 43.47; H, 6.93; N, 5.07%.

3-Trimethylsiloxypropyl Selenocyanate (10): Bp 87.0—87.5 °C/2 mmHg. IR (neat): 2150 cm^{-1} (-SeCN). ^{1}H NMR ($CDCl_3$): δ=0.127 (9H, s), 2.094 (2H, qui, J=6 Hz), 3.230 (2H, t, J=6.5 Hz), 3.708 (2H, t, J=5.5 Hz). MS (m/z): 236, 234 (M^+-1), 222, 220 (M^+-15). Found: C, 35.02; H, 6.60; N, 5.66%. Calcd for C_7H_{15} NOSeSi: C, 35.59; H, 6.40; N, 5.93%.

I thank Nihon Tokushu Kagaku Kogyo Co., Ltd., for permission to publish this article. I am also grateful to Professor H. Hikichi and Dr. K. Aoyagi (Fukushima National College of Technology) for measuring the NMR and to Mr. T. Nakura (Nippon Kasei Chemical Co., Ltd.) for carrying out elemental analyses.

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5) Although no IR absorption band corresponding to Si-SeCN was observed[4], a small amount of TMS-SeCN seems to exist as the isomer of TMS-NCSe.