prisms (c-hexane); mp 179–191 °C; IR (KBr) 3000, 2900, 1640, 1490, 1100, 970 cm^{-1}; ^{1}H NMR δ 1.76 and 2.46 (total 3 H, s and d with J = 3 Hz), 2.06 and 2.28 (total 3 H, each s), 2.22 and 2.42 (total 6 H, each s), 3.26–4.42 (8 H, m); ^{19}F NMR δ −5.3 and −4.3 (total 1 F, each dt, J = 12, 22 Hz and J = 11, 21 Hz, respectively), 25.4 and 25.7 (total 2 F, each d, each J = 22 Hz), 42.2 and 44.1 (total 1 F, each d, J = 10 Hz and J = 12 Hz, respectively); MS m/z 399 (M$^+$ − 1). Anal. Calcd for $C_{20}H_{20}F_4S_2$: C, 59.98; H, 5.03. Found: C, 60.12; H, 5.10.

Preparation of 6b by the Reaction of 4 with Na_2S. A mixture of 5.00 g (20 mmol) of 4 in 200 mL of ethanol and a mixture of 11.65 g (49 mmol) of Na_2S $9H_2O$ in 100 mL of ethanol and 100 mL of H_2O were added at the same rate from separate addition funnels to 3 L of refluxing ethanol over 24 h. After the addition was completed, the solvent was evaporated. To the residue was added 1 L of H_2O, and the mixture was extracted with 500 mL of CH_2Cl_2. The extracte was dried over $MgSO_4$ and evaporated in vacuo to leave a residue, which was chromatographed on silica gel elutions with a 50:1 mixture of hexane and ethyl acetate, giving 0.93 g (22%) of **6b** and 0.05 g (0.5%) of **5-ethoxy-6,7,9,14,15,16,18-heptafluoro-2,11-dithia[3.3]metacyclophane (6f)**: mp 152–155 °C; IR (KBr) 3000, 1640, 1490, 1480, 1100 cm^{-1}; ^{1}H NMR δ 1.40 (3 H, dt, J = 1, 6 Hz), 3.20–4.52 (10 H, m); ^{19}F NMR δ −3.3 (1 F, dt, J = 11, 21 Hz), 4.0 (1 F, dd, J = 11, 19 Hz), 25.4 (1 F, d, J = 20 Hz), 27.2 (1 F, dd, J = 6, 21 Hz), 37.5 (1 F, dd, J = 11, 71 Hz), 39.2 (1 F, dd, J = 11, 71 Hz); MS m/z 442 (M$^+$). Anal. Calcd for $C_{18}H_{13}F_7OS_2$: C, 48.87; H, 2.96. Found: C, 49.16; H, 3.00.

Preparation of 5,6,7,9-Tetrafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-Tetraoxide (7a). Typical Procedure. A mixture of 1.00 g (2.90 mmol) of **6a** in 20 mL of acetic acid and 8.7 mL of 35% aqueous H_2O_2 was refluxed for 20 h. After the reaction mixture was cooled, it was poured into 30 mL of 20% aqueous KOH. The solid precipitates were collected by filtration and washed with water to afford 1.11 g (93%) of **7a**: colorless prisms; mp >300 °C; IR (KBr) 2950, 1500, 1390, 1330, 1300, 1200, 1160, 1150, 1130, 1120, 990, 910, 840, 810, 740, 700 cm^{-1}; MS m/z 408 (M$^+$). Anal. Calcd for $C_{16}H_{12}F_4O_4S_2$: C, 47.06; H, 2.96. Found: C, 47.27; H, 3.11.

Compounds **7b–d** were synthesized in a similar manner.

5,6,7,9,14,15,16,18-Octafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (7b): yield 91%; colorless prisms; mp >300 °C; IR (KBr) 2940, 1500, 1340, 1310, 1140, 1000, 980 cm^{-1}; MS m/z 352 (M$^+$ − 2SO$_2$).

***syn*-15-*tert*-Butyl-18-methoxy-5,6,7,9-tetrafluoro-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (*syn*-7c)**: yield 86%; colorless prisms; mp >300 °C; IR (KBr) 2960, 1500, 1320, 1300, 1120, 990 cm^{-1}; ^{1}H NMR δ 1.22 (9 H, s), 3.60 (3 H, s), 3.90–5.12 (8 H, m), 7.70 (2 H, s); ^{19}F NMR δ −0.4 (1 F, dt, J = 10, 21 Hz), 34.5 (2 F, d, J = 21 Hz), 49.3 (1 F, d, J = 10 Hz); MS m/z 494 (M$^+$). Anal. Calcd for $C_{21}H_{22}F_4O_5S_2$: C, 51.01; H, 4.48. Found: C, 51.05; H, 4.59.

5,6,7,9-Tetrafluoro-14,16,18-trimethyl-2,11-dithia[3.3]metacyclophane 2,2,11,11-tetraoxide (7d): yield 89%; colorless prisms; mp >300 °C; IR (KBr) 3000, 1500, 1300, 1130, 1110, 990 cm^{-1}; MS m/z 450 (M$^+$). Anal. Calcd for $C_{19}H_{18}F_4O_4S_2$: C, 50.66; H, 4.03. Found: C, 50.84; H, 3.74.

Pyrolysis of disulfones 7 was carried out in an apparatus of consisting of a horizontal tube (15 mm in diameter) passing through a tube furnace (20-cm long). Disulfone **7a** (1.00 g) was pyrolyzed at 470 °C under reduced pressure (0.5 Torr), and the pyrolysate was dissolved in CH_2Cl_2 and chromatographed on silica gel elutions with hexane to yield the desired [2.2]metacyclophane **8a**. Recrystallization from hexane afforded 0.30 g (44%) of ***anti*-5,6,7,9-tetrafluoro[2.2]metacyclophane (*anti*-8a)**: colorless prisms (hexane); mp 139–142 °C; IR (KBr) 2960, 1490, 1340, 1290, 1270, 1190, 1150, 1090, 1010, 940, 920, 870, 860, 790, 740, 720 cm^{-1}; ^{1}H NMR δ 2.00–2.60 (4 H, m), 2.80–3.40 (4 H, m), 4.56 (1 H, br s), 7.00–7.36 (3 H, m); ^{19}F NMR δ −3.9 (1 F, dt, J = 12, 22 Hz), 19.8 (2 F, d, J = 22 Hz), 44.7 (1 F, d, J = 12 Hz); MS m/z 280 (M$^+$). Anal. Calcd for $C_{16}H_{12}F_4$: C, 68.57; H, 4.36. Found: C, 68.70; H, 4.54.

Compounds **8b–d** were synthesized in the same manner as described above.

***anti*-4,5,6,8,12,13,14,16-Octafluoro[2.2]metacyclophane (*anti*-8b)**: yield 88%; colorless prisms; mp 140–142 °C; IR (KBr) 2970, 1620, 1480, 1450, 1400, 1260, 1180, 1110, 940, 860, 850, 750 cm^{-1}; ^{1}H NMR δ 2.49 (4 H, A_2B_2 pattern, J = 10 Hz), 3.22 (4 H, A_2B_2 pattern, J = 10 Hz); ^{19}F NMR δ −3.0 (2 F, dt, J = 12, 21 Hz), 21.5 (4 F, d, J = 22 Hz), 37.6 (2 F, d, J = 10 Hz); MS m/z 352 (M$^+$). Anal. Calcd for $C_{16}H_8F_8$: C, 54.56; H, 2.29. Found: C, 54.52; H, 2.31.

***syn*-13-*tert*-Butyl-16-methoxy-4,5,6,8-tetrafluoro[2.2]metacyclophane (*syn*-8c)**: yield 6%; colorless prisms (methanol); mp 58–59 °C; IR (KBr) 2950, 1480, 1260, 1240, 1200, 1090, 1010 cm^{-1}; ^{1}H NMR δ 1.16 (9 H, s), 2.48–3.54 (8 H, m), 3.56 (3 H, s), 6.52 (2 H, s); ^{19}F NMR δ −4.5 (1 F, dt, J = 12, 22 Hz), 19.2 (2 F, d, J = 22 Hz), 61.0 (1 F, d, J = 14 Hz); MS m/z 366 (M$^+$). Anal. Calcd for $C_{21}H_{22}F_4O$: C, 68.84; H, 6.05. Found: C, 69.15; H, 6.53.

***anti*-13-*tert*-Butyl-16-methoxy-4,5,6,8-tetrafluoro[2.2]metacyclophane (*anti*-8c)**: yield 39%; colorless prisms (methanol); mp 112–113 °C; IR (KBr) 2950, 1480, 1190, 1160, 1140, 1080, 1020, 1000, 920 cm^{-1}; ^{1}H NMR δ 1.32 (9 H, s), 1.98–3.32 (8 H, m), 3.10 (3 H, s), 7.08 (2 H, s); ^{19}F NMR δ −7.5 (1 F, dt, J = 10, 21 Hz), 18.6 (2 F, d, J = 22 Hz), 39.8 (1 F, d, J = 10 Hz); MS m/z 366 (M$^+$). Anal. Calcd for $C_{21}H_{22}F_4O$: C, 68.84; H, 6.05. Found: C, 68.89; H, 6.15.

***anti*-4,5,6,8-Tetrafluoro-12,14,16-trimethyl[2.2]metacyclophane (8d)**: yield 44%; colorless prisms (hexane); mp 184–186 °C; IR (KBr) 2960, 1480, 1090, 950 cm^{-1}; ^{1}H NMR δ 0.89 (3 H, d, J = 2 Hz), 2.28 (6 H, s), 2.20–3.32 (8 H, m), 6.76 (1 H, br s); ^{19}F NMR δ −5.3 (1 F, dt, J = 11, 21 Hz), 19.0 (2 F, d, J = 22 Hz), 44.3 (1 F, d, J = 12 Hz); MS m/z 322 (M$^+$). Anal. Calcd for $C_{19}H_{18}F_4$: C, 70.80; H, 5.63. Found: C, 71.03; H, 5.61.

Reaction of 5b and 5d with CH_3ONa. Typical Procedure. To a solution of CH_3ONa (2.84 mmol) in methanol (prepared from 70 mg of sodium and 2 mL of anhydrous methanol) was added 50 mg (0.14 mmol) of **8b** and 10 mL of DMF. After the mixture was stirred at 60–70 °C under nitrogen for 24 h and cooled to room temperature, it was poured into water and extracted with ether. The extract was washed with water, dried over $MgSO_4$, and evaporated in vacuo to leave a residue, which, on chromatography on silica gel elutions with chloroform, afforded 22 mg (39%) of ***anti*-5,8,13,16-tetrafluoro-4,6,12,14-tetramethoxy[2.2]metacyclophane (*anti*-9)**: colorless prisms (hexane); mp 137–140 °C; IR (KBr) 2960, 1610, 1470, 1430, 1420, 1350, 1200, 1170, 1110, 1000, 990, 920, 900, 840 cm^{-1}; ^{1}H NMR δ 2.30 (4 H, d, J = 8 Hz), 3.15 (4 H, d, J = 8 Hz), 3.94 (12 H, d, J = 2 Hz); ^{19}F NMR δ 8.8 (2 F, d, J = 13 Hz), 37.3 (2 F, d, J = 13 Hz); MS m/z 400 (M$^+$). Anal. Calcd for $C_{20}H_{20}F_4O_4$: C, 60.00; H, 5.04. Found: C, 60.20; H, 5.15.

***anti*-4,5,8-Trifluoro-6-methoxy-12,14,16-trimethyl[2.2]metacyclophane (*anti*-10)** was obtained in a similar manner as described above as colorless prisms (hexane): yield 87%; mp 142–143 °C; ^{1}H NMR δ 0.80 (3 H, s), 2.24 (6 H, s), 1.94–3.24 (8 H, m), 3.92 (3 H, d, J = 2 Hz), 6.68 (1 H, br s); ^{19}F NMR δ 0.7 (1 F, dd, J = 12, 21 Hz), 17.4 (1 F, d, J = 20 Hz), 43.4 (1 F, d, J = 10 Hz); MS m/e 334 (M$^+$). Anal. Calcd for $C_{20}H_{21}F_3O$: C, 71.84; H, 6.33. Found: C, 71.81; H, 6.56.

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Alkylsilyl Isoselenocyanate: A New Silicon Pseudohalide. Synthesis, Characterization, and Reaction with Carbonyl Compounds

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Silicon pseudohalides,[1] typically trimethylsilyl cyanide (Me_3SiCN),[2] trimethylsilyl azide,[3] and trimethylsilyl iso-

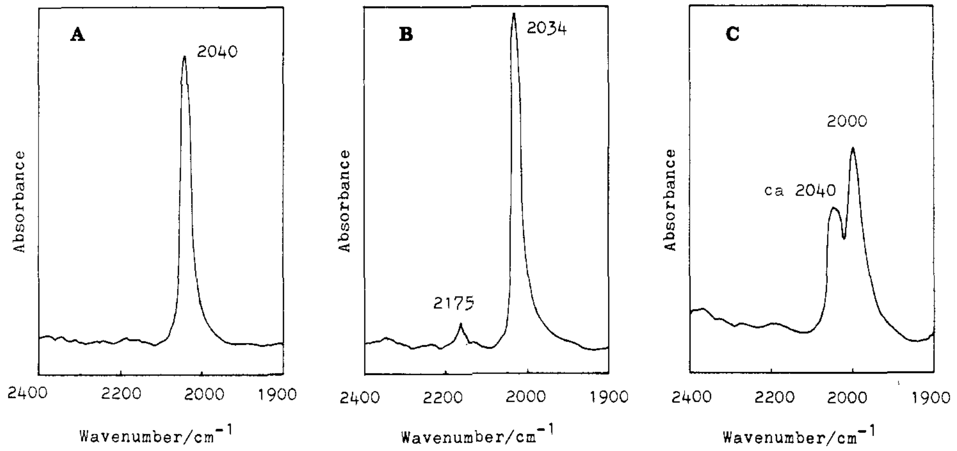


Figure 1. IR spectra of (A) $Me_3SiNCSe$, (B) $Ph_2HSiNCSe$, and (C) $Me_2Si(NCSe)_2$ (in hexane).

Table I. Reaction of Me_3SiCl with KSeCN in Various Solvents[a]

solvent	catalyst	time, h	yield,[b] %
CH_3CN	-	<0.25	~90
DME	-	<0.25	~80[c]
CH_2Cl_2	-	5	>95
	-	2	~85
	KSeCN/XAD-4[d]	<0.5	>95
benzene	-	5	>95
hexane	-	5	>95
	KSeCN/XAD-4[d]	<0.5	>95
	18-crown-6[e]	2	~90

[a] All reactions were carried out with KSeCN (9 mmol), Me_3SiCl (5 mmol), and a solvent (10 mL) at room temperature. [b] Determined by GLC with toluene as an internal standard. [c] A small amount of unidentified product was detected. [d] KSeCN (9 mmol)/XAD-4 (2.0 g) was used in place of KSeCN (9 mmol). [e] 0.25 mmol.

Table II. Preparation of Silyl Isoselenocyanates[a]

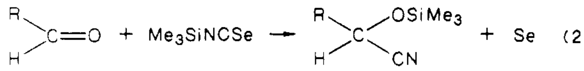
silyl chloride	solvent	time, h	temp,[b] °C	product	yield,[c] %
Me_3SiCl	hexane	5	RT	$Me_3SiNCSe$ (**1**)	82 (>95)
$Me_2PhSiCl$	hexane	7	RT	$Me_2PhSiNCSe$ (**2**)	76 (>95)
t-$BuMe_2SiCl$	CH_2Cl_2	48	40	*t*-$BuMe_2SiNCSe$ (**3**)	77 (>95)
	hexane	48	40		(75)
	CH_3CN	<0.5	RT		(~93)
Et_3SiCl	hexane	40	40	$Et_3SiNCSe$ (**4**)	85 (~99)
	CH_2CN	<0.5	RT		(~90)
$MePh_2SiCl$	hexane	7	RT	$MePh_2SiNCSe$ (**5**)	69 (91)
Ph_2HSiCl	hexane	5	RT	$Ph_2HSiNCSe$ (**6**)	38 (~100)[d]
Me_2SiCl_2	CH_2Cl_2	5	RT	$Me_2Si(NCSe)_2$ (**7**)	80 (>95)
	hexane	5	RT		(>95)

[a] Reactions were carried out with KSeCN (9 mmol), R_3SiCl (7.5 mmol) or R_2SiCl_2 (4.3 mmol), and a solvent (10 mL). [b] RT: room temperature. [c] Isolated yields. Values in parentheses are the yields determined by GLC. [d] Ph_2HSiCl conversion.

thiocyanate (Me_3SiNCS),[4] are useful reagents in organic synthesis. I wish to report on the synthesis of silyl isoselenocyanate, which may be used as a new silicon reagent, by the reaction of the corresponding silyl chloride and KSeCN (eq 1), and the unique reactivity of trimethylsilyl

$$R_{4-n}SiCl_n + nKSeCN \rightarrow R_{4-n}Si(NCSe)_n + nKCl \quad (1)$$

isoselenocyanate ($Me_3SiNCSe$) with carbonyl compounds, in which $Me_3SiNCSe$ adds chemoselectively to aldehydes, producing the corresponding O-trimethylsilylated cyanohydrins (eq 2).



$$RHC{=}O + Me_3SiNCSe \rightarrow RHC(OSiMe_3)(CN) + Se \quad (2)$$

Synthesis and Characterization of Alkylsilyl Isoselenocyanate. In a preliminary experiment, the reaction was carried out with trimethylsilyl chloride (Me_3SiCl) and KSeCN in various solvents. Table I shows the results. Since acetonitrile and 1,2-dimethoxyethane (DME) dissolved substantial quantities of KSeCN, the reaction was completed within 15 min at room temperature in these solvents. On the other hand, substantially complete conversion was observed after 5 h at room temperature without any catalyst even in CH_2Cl_2, benzene, or hexane. The impregnation of KSeCN on Amberlite XAD-4 resin and the addition of a catalytic amount of 18-crown-6 strongly increased the reaction rate.

Table II shows the results of the preparation of other silyl isoselenocyanates. In general, their yields were very high. In the cases of *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$) and triethylsilyl chloride (Et_3SiCl), in comparison with the other silyl chlorides, the reaction was very slow in a nonpolar solvent because of steric hindrance. The isolated yield of diphenylsilyl isoselenocyanate ($Ph_2HSiNCSe$) was very poor, because of its decomposition during distillation.

Figure 1 shows the IR spectra of (A) $Me_3SiNCSe$, (B) $Ph_2HSiNCSe$, and (C) $Me_2Si(NCSe)_2$. Although, in a hexane solution of $Me_3SiNCSe$, the absorption band in the ν (CN) region was observed only at 2040 cm^{-1}, $Ph_2HSiNCSe$ had a weak absorption band at 2175 cm^{-1} in addition to the strong absorption band at 2034 cm^{-1}. Wharf et al.[5] have recently reported that in a CH_2Cl_2 solution of triphenyltin isoselenocyanate, the absorption bands at 2042 and 2175 cm^{-1} correspond to $Ph_3Sn{-}NCSe$

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and $Ph_3Sn{-}SeCN$, respectively. Similarly, the two absorption bands at 2030–2040 and 2175 cm^{-1} can be assigned to a Si–NCSe and a Si–SeCN bond, respectively. Thus, the present findings suggest that, for trialkylsilyl isoselenocyanate ($R_3SiNCSe$) in hexane, no selenocyanate ($R_3Si{-}SeCN$) exists, whereas $Ph_2HSiNCSe$ exists partly as the isomer, $Ph_2HSi{-}SeCN$. For $Me_2Si(NCSe)_2$, two absorption bands were observed at ca. 2040 and 2000 cm^{-1}. This finding is similar to that for silyl diazide[6] and suggests that the two isoselenocyanate groups are not equal to each other.

In mass spectra, for $R_3SiNCSe$, two parent-ion peaks based on ^{80}Se and ^{78}Se and a fragment-ion peak corresponding to $M^+ - Se$ were observed with small intensities and with large intensity, respectively. In the case of $Me_2Si(NCSe)_2$, three parent-ion peaks based on ^{80}Se and ^{78}Se and two fragment-ion peaks corresponding to $M^+ - Se$ (^{80}Se and ^{78}Se) were observed with small intensities and large intensities, respectively. These findings also suggest the structure of Si–NCSe.

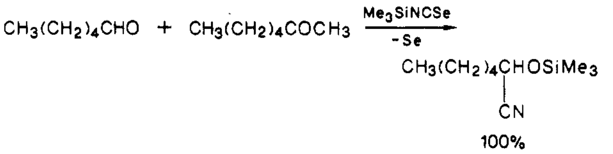
Table III (supplementary material) summarizes the physical and spectral properties of the silyl isoselenocyanates. It should be noted that all the compounds were not only strongly moisture sensitive but also extremely air sensitive.

Reaction of $Me_3SiNCSe$ with Carbonyl Compounds. Table IV shows the results of the reaction of $Me_3SiNCSe$ with hexanal in acetonitrile or hexane. Substantially no reaction took place in the absence of any catalyst. In the presence of $ZnCl_2$, the reaction in hexane produced the corresponding O-silylated cyanohydrin in high yield, whereas in acetonitrile the reaction was very slow.

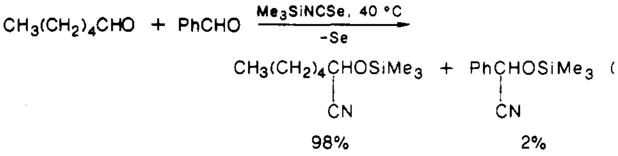
Since $Me_3SiNCSe$ is strongly sensitive to moisture and to air, its isolation is very troublesome. Therefore, $Me_3SiNCSe$ was not isolated and hexanal was added directly to the flask where the $Me_3SiNCSe$ was prepared. Table V shows the results of the one-pot reaction. Potassium selenocyanate, used in excess, catalyzed the reaction as well as $ZnCl_2$. The impregnation of KSeCN on Amberlite XAD-4 resin considerably increased the reaction rate, whereas the addition of a catalytic amount of 18-crown-6 had a slightly negative effect. Interestingly, the reaction rate was in the order hexane > benzene ≈ CH_2Cl_2 ≫ acetonitrile. This finding is in sharp contrast to that in the one-pot reaction of trimethylsilyl cyanide (Me_3SiCN) with carbonyl compounds,[6] that is, acetonitrile ≫ hexane ≥ benzene > CH_2Cl_2.

Table VI summarizes the results of the one-pot reaction with other carbonyl compounds. No reaction with ketone took place and the reaction was very slow with the aromatic aldehyde, benzaldehyde, and the α,β-unsaturated aldehyde, crotonaldehyde. On the other hand, the reaction with an aliphatic aldehyde proceeded smoothly to give the corresponding O-trimethylsilylated cyanohydrin in high yields. The reaction with isobutyraldehyde and trimethylacetaldehyde was slower because of steric hindrance. The present results are quite different from that reported by Nishiyama et al.,[4a] in which an analogous compound, trimethylsilyl isothiocyanate, reacts with aldehydes to give isothiocyanate-substituted ethers.

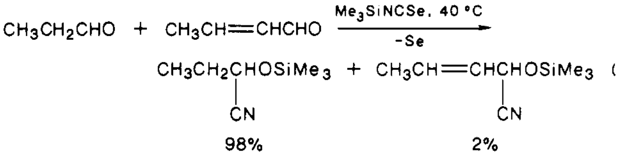
Complete chemoselectivity was observed in the reaction with a 1:1 mixture of hexanal and 2-heptanone. The aldehyde adduct was the sole product (eq 3). Similarly, extremely high chemoselectivities were observed in the reaction with a 1:1 mixture of hexanal and benzaldehyde (eq 4) and a 1:1 mixture of propionaldehyde and crotonaldehyde (eq 5). Unfortunately, substantially no chemoselectivity was observed in the reaction with a 1:1 mixture of hexanal and isobutyraldehyde (eq 6).



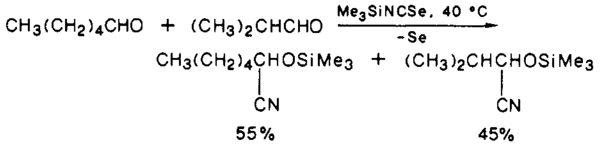
$$CH_3(CH_2)_4CHO + CH_3(CH_2)_4COCH_3 \xrightarrow[-Se]{Me_3SiNCSe} \underset{100\%}{\underset{CN}{CH_3(CH_2)_4\underset{|}{C}HOSiMe_3}} \quad (3)$$



$$CH_3(CH_2)_4CHO + PhCHO \xrightarrow[-Se]{Me_3SiNCSe,\ 40\ °C} \underset{98\%}{\underset{CN}{CH_3(CH_2)_4\underset{|}{C}HOSiMe_3}} + \underset{2\%}{\underset{CN}{Ph\underset{|}{C}HOSiMe_3}} \quad (4)$$



$$CH_3CH_2CHO + CH_3CH{=}CHCHO \xrightarrow[-Se]{Me_3SiNCSe,\ 40\ °C} \underset{98\%}{\underset{CN}{CH_3CH_2\underset{|}{C}HOSiMe_3}} + \underset{2\%}{\underset{CN}{CH_3CH{=}CH\underset{|}{C}HOSiMe_3}} \quad (5)$$



$$CH_3(CH_2)_4CHO + (CH_3)_2CHCHO \xrightarrow[-Se]{Me_3SiNCSe,\ 40\ °C} \underset{55\%}{\underset{CN}{CH_3(CH_2)_4\underset{|}{C}HOSiMe_3}} + \underset{45\%}{\underset{CN}{(CH_3)_2CH\underset{|}{C}HOSiMe_3}} \quad (6)$$

Although I have no explanation for the reaction mechanism, it is clear that $Me_3SiNCSe$ is a useful reagent for the chemoselective cyanosilylation of aldehydes.

Experimental Section

Materials. All the solvents were dried with molecular sieves 4A. Alkylsilyl chlorides, carbonyl compounds, $ZnCl_2$, and 18-crown-6 were used as obtained. KSeCN was dried at 90 °C under vacuum (~0.05 mmHg) for 4 h. KSeCN/XAD-4 was prepared by a method similar to that used for NaN_3/XAD-4.[7] Since silyl isoselenocyanates were strongly sensitive to moisture and air, reactions were carried out under a nitrogen atmosphere.

Reaction of Me_3SiCl with KSeCN in Various Solvents. A mixture of Me_3SiCl (0.54 g, 5 mmol), KSeCN (1.3 g, 9 mmol), a solvent (10 mL), and toluene as an internal standard was stirred for the indicated time at room temperature. The resulting mixture was analyzed by GLC (silicone SE-30, 10%, 1 m × 3 mm, 60 °C).

$Me_3SiNCSe$ (1): bp 75–76 °C (30 mmHg); IR (hexane) 2040 cm^{-1} (Si–NCSe); MS, m/z 179 (M^+, ^{80}Se), 177 (M^+, ^{78}Se), 99 ($M^+ - Se$), 84 ($M^+ - Se - CH_3$). Anal. Calcd for C_4H_9NSeSi: Se, 44.34. Found: Se, 43.2.

$Ph_2HSiNCSe$ (6). A mixture of Ph_2HSiCl (1.64 g, 7.5 mmol), KSeCN (1.3 g, 9 mmol), and hexane (10 mL) was stirred for 7 h at room temperature. The solid material was filtered and washed with CH_2Cl_2. After removal of the solvent, the residue was distilled under vacuum, giving only 0.83 g (38% yield) of **6**, because of its decomposition during distillation, where evolution of gas was observed and a higher boiling unidentified residue was obtained: bp 140–143 °C (0.6 mmHg); mp 43–45 °C; IR (hexane) 2175 (w) (Si–SeCN), 2034 cm^{-1} (Si–NCSe). Anal. Calcd for $C_{13}H_{11}NSeSi$: Se, 27.41. Found: Se, 26.5.

t-$BuMe_2SiNCSe$ (3). A mixture of t-$BuMe_2SiCl$ (1.13 g, 7.5 mmol), KSeCN (1.3 g, 9 mmol), and CH_2Cl_2 (10 mL) was stirred for 48 h at 40 °C. The same treatment as for **6** gave 1.27 g (77% yield) of **3**, bp 77–78 °C (8 mmHg), redistillation of which gave pure **3**: IR (hexane) 2040 cm^{-1} (Si–NCSe); MS, m/z 221 (M^+, ^{80}Se), 219 (M^+, ^{78}Se), 141 ($M^+ - Se$), 126 ($M^+ - Se - CH_3$). Anal. Calcd for $C_7H_{15}NSeSi$: Se, 35.88. Found: Se, 35.2.

$Me_2Si(NCSe)_2$ (7). A mixture of Me_2SiCl_2 (0.55 g, 4.3 mmol), KSeCN (1.3 g, 9 mmol), and CH_2Cl_2 (10 mL) was stirred for 5 h at room temperature. The same treatment for **6** gave 0.92 g (80% yield) of **7**, bp 92–94 °C (1.2 mmHg), redistillation of which gave pure **7**: mp 44–47 °C; IR (hexane) ca. 2040, 2000 cm^{-1}; MS,

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Table IV. Reaction of Hexanal with $Me_3SiNCSe$[a]

solvent	catalyst	time, h	temp, °C	yield,[b] %
CH_3CN	–	48	RT[c]	<1
	$ZnCl_2$[d]	24	40	~15
hexane	–	48	40	<1
	$ZnCl_2$[d]	24	40	~85

[a] Reactions were carried out with $Me_3SiNCSe$ (5 mmol), hexanal (5 mmol), and a solvent (10 mL). [b] Determined by GLC with *n*-tridecane as an internal standard. [c] Room temperature. [d] 0.3 mmol.

Table V. One-Pot Reaction of Hexanal with $Me_3SiNCSe$ in Various Solvents[a]

solvent	catalyst	time, h	temp, °C	yield,[b] %
CH_3CN	$ZnCl_2$[c]	48	RT[e]	~5
	$ZnCl_2$[c]	24	40	17
CH_2Cl_2	–	24	40	42
	$ZnCl_2$[c]	24	40	69
	KSeCN/XAD-4[d]	24	40	61
benzene	–	24	40	55
	$ZnCl_2$[c]	24	40	60
hexane	–	24	40	78
	$ZnCl_2$[c]	20	40	>95
	KSeCN/XAD-4[d]	24	40	>95
	18-crown-6[c]	24	40	70

[a] All reactions were carried out with KSeCN (9 mmol), Me_3SiCl (5 mmol), hexanal (5 mmol), and a solvent (10 mL). [b] Determined by GLC. [c] 0.3 mmol. [d] KSeCN (9 mmol)/XAD-4 (2.0 g) was used in place of KSeCN (9 mmol). [e] Room temperature.

m/z 270 (M^+, ^{80}Se, ^{80}Se), 268 (M^+, ^{80}Se, ^{78}Se), 266 (M^+, ^{78}Se, ^{78}Se), 190 (M^+ – Se, ^{80}Se), 188 (M^+ – Se, ^{78}Se). Anal. Calcd for $C_4H_6N_2SeSi$: Se, 58.96. Found: Se, 57.8.

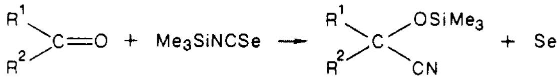
One-Pot Reaction of $Me_3SiNCSe$ with Hexanal in Various Solvents. After a mixture of KSeCN (1.3 g, 9 mmol), Me_3SiCl (0.54 g, 5 mmol), and a solvent (10 mL) was stirred for 7 h at room temperature, hexanal (0.50 g, 5 mmol) and tridecane (as an internal standard) were added to the mixture. The resulting mixture was stirred for the indicated time at 40 °C and analyzed by GLC (silicone SE-30, 10%, 1 m × 3 mm, 60 and 120 °C).

One-Pot Reaction of $Me_3SiNCSe$ with Carbonyl Compounds. GLC retention times and/or IR spectra of all the products were in agreement with those of the corresponding products obtained from the reaction with Me_3SiCN.[6]

Hexanal Cyanohydrin Trimethylsilyl Ether. After a mixture of KSeCN (4.32 g, 27 mmol), Me_3SiCl (2.43 g, 22.5 mmol), and hexane (30 mL) was stirred for 7 h at room temperature, hexanal (2.46 g, 24.6 mmol) and $ZnCl_2$ (0.08 g) were added to the mixture. The resulting mixture was stirred for 24 h at 40 °C. After the mixture had been cooled to room temperature, the solid material was filtered and washed with CH_2Cl_2. After removal of the solvent, the residue (4.63 g, ca. 100% yield) was distilled under reduced pressure, giving 4.09 g (91% yield) of product, bp 90–91 °C (10 mmHg). Redistillation, using a 70-mm column (with 5 mm × 5 mm rasching rings), gave the pure cyanohydrin ether: bp 89.0–89.5 °C (8 mmHg); IR (neat) 1256, 1128, 1100, 876, 848, 752 cm^{-1}, no CN; ^1H NMR ($CDCl_3$) δ 0.208 (s, 9 H), 0.906 (t, 3 H, $J = 6$ Hz), 1.1–1.9 (m, 8 H), 4.386 (t, 3 H, $J = 6$ Hz); MS, *m/z* 199 (M^+), 184 ($M^+ - CH_3$), 157.

Isobutyraldehyde Cyanohydrin Trimethylsilyl Ether. After a mixture of KSeCN (4.32 g, 27 mmol), Me_3SiCl (2.43 g, 22.5 mmol), and hexane (30 mL) was stirred for 7 h at room temperature, isobutyraldehyde (1.77 g, 24.6 mmol) and $ZnCl_2$ (0.08 g) were added. The resulting mixture was stirred for 48 h at 40 °C. The same treatment for hexanal gave 3.81 g (99% yield) of the crude product. The residue was distilled under reduced pressure to give 3.36 g (87% yield) of the cyanohydrin ether. Redistillation, using a 70-mm column (with 5 mm × 5 mm rasching rings), afforded the pure compound: bp 65.5–66.0 °C (14 mmHg); IR (neat) 1256, 1104, 872, 848, 752 cm^{-1}, no CN; ^1H NMR ($CDCl_3$) δ 0.208 (s, 9 H), 1.033 (dd, 6 H, $J = 6.5$, 1.8 Hz), 1.5–2.3 (m, 1 H), 4.158 (d, 1 H, $J = 5.6$ Hz); MS, *m/z* 171 (M^+), 156 ($M^+ - CH_3$), 129.

Table VI. One-Pot Cyanosilylation Using $Me_3SiNCSe$[a]



R^1	R^2	solvent	time, h	temp, °C	yield,[b] %
CH_3CH_2	H	CH_2Cl_2	48	40	>95
		hexane	20	40	>95
$CH_3(CH_2)_4$	H	CH_2Cl_2	24	40	69
		hexane	24	40	~100 (91)[c]
$CH_3CH{=}CH$	H	hexane	72	60	22
$(CH_3)_2CH$	H	CH_2Cl_2	24	40	57
		hexane	24	40	86
		hexane	48	40	~99 (87)[c]
$(CH_3)_3C$	H	hexane	24	40	75
		hexane	48	40	>97 (84)[c]
C_6H_5	H	benzene	48	40	8
		hexane	40	60	30
CH_3CH_2	CH_3	hexane	24	40	0
$CH_3(CH_2)_4$	CH_3	hexane	24	40	0
$(CH_3)_2C{=}CH$	CH_3	hexane	72	40	0
C_6H_5	CH_3	benzene	48	40	0
		hexane	48	40	0

[a] Unless otherwise noted, reactions were carried out with KSeCN (9 mmol), Me_3SiCl (5 mmol), a carbonyl compound (5 mmol), $ZnCl_2$ (0.3 mmol), and a solvent (10 mL). [b] Determined by GLC. [c] Isolated yields. Reactions were carried out with KSeCN (27 mmol), Me_3SiCl (22.5 mmol), a carbonyl compound (24.6 mmol), $ZnCl_2$ (0.6 mmol), and a solvent (30 mL).

Trimethylacetaldehyde Cyanohydrin Trimethylsilyl Ether. This compound was isolated in 84% yield: bp 69–70 °C (15 mmHg); IR (neat) 1256, 1108, 868, 848, 752 cm^{-1}, no CN; ^1H NMR ($CDCl_3$) δ 0.208 (s, 9 H), 1.014 (s, 9 H), 3.982 (s, 1 H); MS, *m/z* 185 (M^+), 170 ($M^+ - CH_3$), 143.

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Registry No. **1**, 16966-40-8; **2**, 119336-64-0; **3**, 119336-65-1; **4**, 16966-42-0; **5**, 119336-66-2; **6**, 119336-67-3; **7**, 119336-68-4; KSeCN, 3425-46-5; Me_3SiCl, 75-77-4; $Me_2PhSiCl$, 768-33-2; *t*-$BuMe_2SiCl$, 18162-48-6; Et_3SiCl, 994-30-9; $MePh_2SiCl$, 144-79-6; Ph_2HSiCl, 1631-83-0; Me_2SiCl_2, 75-78-5; $Ph_2HSiSeCN$, 119336-69-5; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_4CHO$, 66-25-1; $CH_3CH{=}CHCHO$, 4170-30-3; $(CH_3)_2CHCHO$, 78-84-2; $(CH_3)_3CCHO$, 630-19-3; C_6H_5CHO, 100-52-7; $CH_3CH_2COCH_3$, 78-94-4; $CH_3(CH_2)_4COCH_3$, 110-43-0; $(CH_3)_2C{=}CHCOCH_3$, 141-79-7; $C_6H_5COCH_3$, 98-86-2; $CH_3CH_2CH(CN)OSiMe_3$, 24731-32-6; $CH_3(CH_2)_4CH(CN)OSiMe_3$, 40326-17-8; $CH_3CH{=}CHCH(CN)OSiMe_3$, 40326-20-3; $(CH_3)_2CHCH(CN)OSiMe_3$, 40326-16-7; $(CH_3)_3CCH(CN)OSiMe_3$, 88522-73-0; $C_6H_5CH(CN)OSiMe_3$, 25438-37-3; $ZnCl_2$, 7646-85-7; 18-crown-6, 17455-13-9; amberlite XAD-4, 37380-42-0.

Supplementary Material Available: Table III containing physical and spectral properties of silyl isoselenocyanates **1–7** (1 page). Ordering information is given on any current masthead page.

Pressure Effects in a Solvolysis Involving Extended π Participation

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Introduction

Knowledge and understanding of the effect of pressure on the rate and equilibrium constants of chemical reactions in solution have become increasingly widespread in recent