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Regiospecific Ring Opening of Epoxides with Cyanotrimethylsilane on Solid Bases: Reaction Features, and Role of Metal Cations of Solid Bases

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A new attempt of utilizing solid acids and bases for ring opening of epoxides with Me_3SiCN was investigated. Solid strong bases such as calcium oxide and magnesium oxide catalyzed the regio- and chemoselective ring opening of epoxides with Me_3SiCN much more effectively than homogeneous catalysts. On CaO and MgO, the reactions of unsymmetrical epoxides with Me_3SiCN afforded 3-trimethylsiloxyalkanenitriles in high yields through regio- and stereoselective attack of cyanide ion on the less substituted epoxycarbon. Additionally, on CaO, 2,3-epoxy-1-alkanol derivatives were selectively converted to the corresponding C-3 opened products by the attack of cyanide ion. In these cases no isocyanides were formed. It was suggested that CaO acted as a bifunctional catalyst; the lattice oxide anions of CaO activated Me_3SiCN, and simultaneously calcium ions promoted the ring opening of epoxyalkanol as Lewis acid sites.

Cyanotrimethylsilane (Me_3SiCN), which is considered as stabilized hydrogen cyanide, has been widely applied to organic synthesis.[1] Recently Me_3SiCN has been reported to react with epoxyalkanes in the presence of various Lewis acids to give 3-trimethylsiloxyalkanenitriles or 2-trimethylsiloxyalkyl isocyanides.[2] "Hard" acids such as $AlCl_3$,[3,4] Et_2AlCl,[3,5] $Al(O^iPr)_3$,[5] $LuCl_3$,[6] and $Ti(O^iPr)_4$[7] promote the reaction of epoxides with Me_3SiCN to afford 3-trimethylsiloxyalkanenitriles. In contrast, 2-trimethylsiloxyalkyl isocyanides are predominantly produced in the presence of "Soft" acids such as $ZnCl_2$,[8] ZnI_2,[8] $Pd(CN)_2$,[5] and $SnCl_2$.[5] In acid-promoted nitrile formation via ring openings of unsymmetrical epoxides, however, the problems of low regioselectivity and contamination of isocyanides are often encountered.[5]

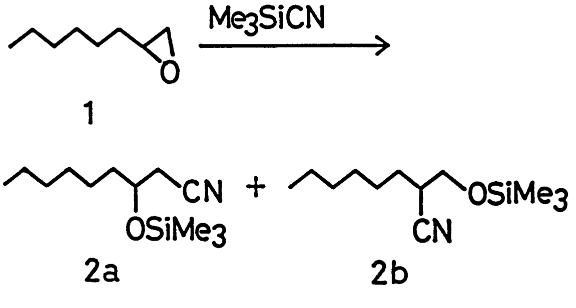
We have attempted to utilize inorganic solid acids and bases such as zeolites[9] and clay montmorillonite[10] for several types of liquid-phase organic reactions. These heterogeneous organic reactions on inorganic solids are becoming very useful for the following reasons:[11] (1) They are operationally simple, with product isolation involving only filtration and solvent evaporation, (2) they are often more selective and milder than the corresponding homogeneous reactions, (3) a synergistic reaction-promoting effect by acid and base sites is expected because both acid and base sites can exist independently on the surface of solid.

Recently we found that inorganic solid bases could efficiently activate Me_3SiCN to react with carbonyl compounds to afford 3-trimethylsiloxyalkanenitriles.[12] On the basis of this finding, we applied several types of solid bases as promoters to ring openings of unsymmetrical epoxides and 2,3-epoxy-1-alkanol derivatives with Me_3SiCN, and reported in a rapid communication that certain solid bases such as CaO and MgO greatly activated the ring opening of epoxides to produce exclusively 3-trimethylsiloxyalkanenitriles in a highly regioselective manner.[13] Regioselective ring opening of 2,3-epoxy-1-alkanol derivatives with nucleophiles is an intriguing synthetic subject since easily available, optically pure 2,3-epoxy-1-alkanols are important building blocks for synthesis of natural products.[14] In this context, we have previously demonstrated a highly regioselective ring opening of 2,3-epoxy-1-alkanols with several inorganic nucleophiles supported on a solid acid of calcium ion-exchanged Y-typed zeolite, in which the calcium ions bound in zeolite regulated the ring opening by forming a five-membered chelate complex with 2,3-epoxy-1-alkanol.[9b,9c]

In this paper, we describe the details of ring opening of epoxides promoted by inorganic solid bases such as CaO and MgO, comparing with the effects by other soluble promoters of $Al(O^iPr)_3$ and $^nBu_4NF$. In addition, we discuss the role of the metal cations of solid bases in regioselective ring opening of 2,3-epoxy-1-alkanol, based on a spectroscopic evidence for the formation of a five-membered chelate complex of Eu^{3+} with 2,3-epoxy-1-alkanol.

Results and Discussion

1) Reactions of Unsymmetrical Epoxides with Me_3SiCN. The reaction of 1,2-epoxyoctane (**1**) with Me_3SiCN was examined in the presence of various solid catalysts in heptane, and the results are listed in Table 1 (Eq. 1). On solid bases such as CaO, MgO, hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$),[15] and CaF_2, the ring opening of the epoxide was accelerated to produce 3-(trimethylsiloxy)nonanenitrile (**2a**) in over 97% regiose-



(1)

Table 1. Ring Opening of 1,2-Epoxyoctane (**1**) with Me_3SiCN

Run	Solid catalyst	Solvent	Condition Temp/°C (Time/h)	Yield %	**2a**:**2b**
1	CaO[a)]	Heptane	R.T. (0.5)	98	97:3
2	MgO[a)]	Heptane	R.T. (0.5)	97	98:2
3	HAp[a,b)]	Heptane	R.T. (1.5)	97	98:2
4	CaF_2[a)]	Heptane	R.T. (72)	96	99:1
5	SiO_2[a)]	Heptane	R.T. (5)	0	
6	Fe-Mont[a,e)]	Heptane	R.T. (5)	0	
7	$Al(O^iPr)_3$[b)]	Hexane	R.T. (72)	91	97:3
8	$^nBu_4NF$[c)]	THF	Reflux (4)	96	>99:1

a) **1** (1 mmol), Me_3SiCN (2 mmol), and solid catalyst (0.2 g) were used. b) **1** (1 mmol), Me_3SiCN (1.5 mmol), and $Al(O^iPr)_3$ (1.5 mmol) were used. c) **1** (1 mmol), Me_3SiCN (3 mmol), and $^nBu_4NF$ (3 mmol) were used. d) Hydroxyapatite. e) Iron (III) ion-exchanged montmorillonite.

Table 2. Chemical Properties of Solid Acids and Bases

Solid	S.A./$m^2\,g^{-1}$[a)]	Acid or base strength[b)]
CaO	65	$H_- \geqslant +18.4$
MgO	316	$H_- \geqslant +18.4$
HAp	55	$+15.0 > H \geqslant +9.3$
CaF_2	6	c)
SiO_2	585	$+3.3 \geqslant H_o + 1.5$
Fe-Mont	37	$-8.2 \geqslant H_o$

a) Specific surface area. b) Maximum acid or base strength were measured by use of Hammett indicators in benzene. c) H_- of CaF_2 could not be determined.

lectivity (Run 1—4). The catalytic activity of solid base decreased in the order of $CaO \fallingdotseq MgO > HAp \gg CaF_2$, correlating to their intrinsic base strengths (Table 2). In contrast to the solid bases, strongly acidic montmorillonite (Fe-Mont), as well as weakly acidic silica (SiO_2), showed no catalytic activity for the ring opening (Run 5, 6). When Me_3SiCN and a soluble Lewis acid such as $Al(O^iPr)_3$ or $^nBu_4NF$ were treated with **1**, reaction rates were largely reduced compared with the cases of CaO and MgO (Run 7, 8).

Since silicon has strong affinities for fluoride ion and oxide ion, when combined with fluoride ion or oxide ion, silicon can expand its coordination number from the normal value of four to five or six to form penta- or hexacoordinated compounds.[16)] These penta- and hexacoordinate silicon compounds have higher reactivities than the ordinary tetracoordinate silicon compounds. On the other hand, the basic sites on CaO and MgO were reported to be the surface lattice oxygen (O^{2-}) species.[17)] It can be, therefore, presumed that a strongly basic site of O^{2-} on the surface of CaO or MgO coordinates to Me_3SiCN to release a cyanide ion, resulting in nucleophilic ring opening of epoxides (Chart 1).[18)]

Next, the reaction of **1** with Me_3SiCN on MgO was examined with respect to the influence of the reaction solvent (Table 3). The reaction rate was remarkably decreased when dimethoxyethane (DME) was used. A polar solvent such as DME may strongly adsorb on the surface of MgO to weaken the interaction between Me_3SiCN and MgO.

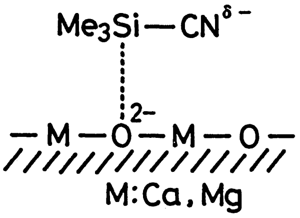


Chart 1.

Table 3. Effects of Solvent in the Reaction of **1** with Me_3SiCN on MgO[a)]

Run	Solvent	Time/h[b)]	Yield/%	**2a**:**2b**
1	Heptane	0.5	97	98:2
2	Benzene	0.5	97	98:2
3	CH_2Cl_2	0.5	97	99:1
4	DME	3	95	96:4

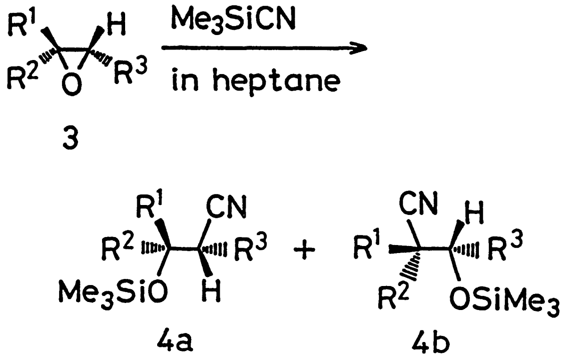
a) Ring-opening reaction was carried out at room temperature. b) Reaction was monitored by TLC and GC: Reaction was carried out until **1** was consumed.

Table 4. Ring Opening of Unsymmetrical Epoxides with Me_3SiCN

Run	Solid catalyst	R^1	R^2	R^3	Time h	Yield %	**4a**:**4b**
1	CaO[a)]	CH_3	CH_3	H	0.5	98	>99: 1
2	MgO[a)]	CH_3	CH_3	H	0.5	78	>99: 1
3	CaO[a)]	CH_3	$-(CH_2)_4-$		4.5	95	99: 1
4	MgO[a)]	CH_3	$-(CH_2)_4-$		3	96	98: 2
5	$Al(O^iPr)_3$[b)]	CH_3	$-(CH_2)_4-$		96	91	76:24
6	CaO[a)]	CH_3	CH_3	CH_3	24	84	94: 6
7	MgO[a)]	CH_3	CH_3	CH_3	24	84	96: 4
8	$Al(O^iPr)_3$[b)]	CH_3	CH_3	CH_3	48	82	51:49

a) Epoxide (1 mmol), Me_3SiCN (2 mmol), and solid catalyst (0.2 g) in heptane, at room temperature. b) Epoxide (1 mmol), Me_3SiCN (1.5 mmol), and $Al(O^iPr)_3$ (1.5 mmol), in heptane, at room temperature.

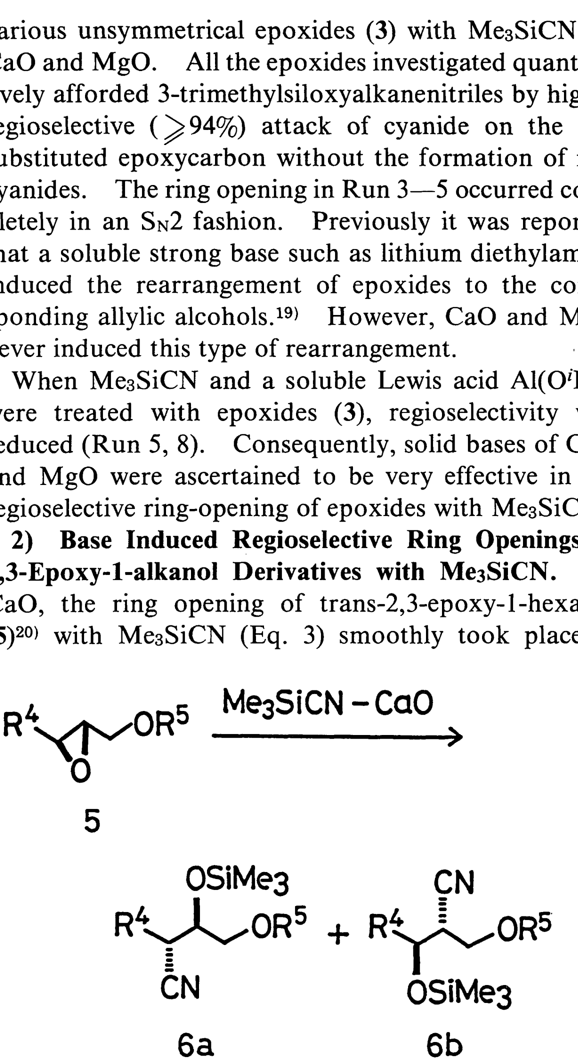
The synthetic potential of the present method was demonstrated by the successful employment of other epoxides (Eq. 2). Table 4 shows the ring openings of various unsymmetrical epoxides (**3**) with Me_3SiCN on CaO and MgO. All the epoxides investigated quantitatively afforded 3-trimethylsiloxyalkanenitriles by highly regioselective ($\geqslant$94%) attack of cyanide on the less substituted epoxycarbon without the formation of isocyanides. The ring opening in Run 3—5 occurred completely in an S_N2 fashion. Previously it was reported that a soluble strong base such as lithium diethylamide induced the rearrangement of epoxides to the corresponding allylic alcohols.[19] However, CaO and MgO never induced this type of rearrangement.



(2)

When Me_3SiCN and a soluble Lewis acid $Al(O^iPr)_3$ were treated with epoxides (**3**), regioselectivity was reduced (Run 5, 8). Consequently, solid bases of CaO and MgO were ascertained to be very effective in the regioselective ring-opening of epoxides with Me_3SiCN.

2) Base Induced Regioselective Ring Openings of 2,3-Epoxy-1-alkanol Derivatives with Me_3SiCN. On CaO, the ring opening of trans-2,3-epoxy-1-hexanol (**5**)[20] with Me_3SiCN (Eq. 3) smoothly took place at room temperature to afford **6a** and **6b** in good total yield (86%) and good regioselectivity (89 : 11). We assume that such high regioselection is attributed to the formation of a five-membered chelate complex between two oxygen atoms of the epoxyalkanol and a calcium ion of CaO. This chelate formation directs the ring-opening site of epoxide.[9b,9c] When 2,3-epoxy-1-alkanol was acetylated beforehand and then treated with Me_3SiCN on CaO, more regioselective ring opening at the C-3 carbon ($\geqslant$90) was realized as shown in Table 5. This higher regioselectivity would be caused by the inductive effect of the acetyl group in addition to the above-mentioned chelate formation between Ca^{2+} and 2,3-epoxy-1-acetate. In Runs 1—4 the ring openings proceeded with inversion of configuration, and no isocyanides were formed. MgO, HAp, and CaF_2 showed lower activities than CaO.



(3)

Table 5. CaO-Directed Reactions of *trans*-2,3-epoxy-1-alkanol and Its Derivative with Me_3SiCN[a]

Run	R^4	R^5	Condition Temp/°C (Time/h)	Yield %	**6a** : **6b**
1	^{n}Pr	H	R.T. (4)	86	89 : 11
2	^{n}Pr	Ac	R.T. (4)	91	96 : 4
3	^{i}Pr	Ac	60 °C (1)	75	96 : 4
4	Cyclohexyl	Ac	60 °C (2)	84	97 : 3

a) CaO (0.5 g), epoxides (0.5 mmol), Me_3SiCN (1 mmol), in heptane.

Compared with heptane, benzene and CH_2Cl_2 induced not only lower rates but lower regioselectivities. Benzene and CH_2Cl_2 may restrain the chelate formation between an epoxyalkanol molecule and a calcium ion. Furthermore, no ring-opening reaction occurred in DME. This strongly negative effect of DME is probably due to chelation of a calcium ion on CaO, so that DME may prevent a calcium ion from electrophilic activation of oxirane ring toward nucleophilic attack. Thus a less polar solvent is preferable in order to increase reaction rate and regioselectivity.

Reportedly, $Ti(O^iPr)_4$ promotes the reaction of *trans*-2,3-epoxy-1-hexanol with Me_3SiCN under DME reflux conditions to give C-3 and C-2 opening products in 83 : 17 regioselectivity and 32% yield.[21] In another control experiment, no reaction occurred when the *trans*-2,3-epoxy-1-hexanol was refluxed in THF with Me_3SiCN (3 equiv) in the presence of $^nBu_4NF$ (3 equiv). CaO thus catalyzed the ring opening of epoxyalkanols much more efficiently and selectively than $Ti(O^iPr)_3$ and $^nBu_4NF$.

3) Investigation on Chelate Complex Formation between 2,3-Epoxy-1-alkanol and Ca^{2+}. In order to clarify the role of Ca^{2+} ions of CaO in the nucleophilic ring opening of 2,3-epoxy-1-alkanol, we tried to confirm a putative intermediate complex formed from Ca^{2+} and 2,3-epoxy-1-alkanol in solution by means of ^{1}H NMR spectroscopy.[22] Unfortunately, most of calcium salts were sparingly soluble in nonpolar organic solvents suitable for ^{1}H NMR spectroscopy (e.g. $CDCl_3$). Here we chose $Eu(fod)_3$ instead of Ca^{2+} salts based on the following three reasons. First, Eu^{3+} (0.98 Å) is almost the same as Ca^{2+} (0.99 Å) with respect to ionic radius. Second, the coordination properties of Eu^{3+} have been recognized to be very similar to those of Ca^{2+}: Eu^{3+}, as well as Ca^{2+}, has a strong affinity for oxygen ion.[23]

Third, Eu(fod)$_3$ is freely soluble in organic solvents such as $CDCl_3$.

Eu(fod)$_3$ has been used as a typical NMR shift reagent.[24] Paramagnetic ions such as Lu^{3+} exert stronger magnetic fields on NMR spectra and afford greater spectral spreading properties, when coordinated by organic compounds which possess Lewis base sites. Therefore, the influence of magnetic fields by Lu^{3+} falls away sharply with the distance from Lu^{3+}, and the induced shifts will be significant only if a nucleus is in close average proximity to Lu^{3+}.

Figure 1 demonstrates the changes of chemical shifts in the ^{1}H NMR spectra (200 MHz) of 1-hexanol and *trans*-2,3-epoxy-1-hexanol with the amount of Eu(fod)$_3$ in $CDCl_3$. As expected, the shift of each proton of 1-hexanol induced by Eu(fod)$_3$ attenuated along the following series: $H_1 > H_2 > H_3 > H_4 > H_5 > H_6$. However, the shifts observed in the case of *trans*-2,3-epoxy-1-hexanol decreased in the order of $H_3 > H_1 > H_2 > H_4 > H_5 > H_6$. An anormalous larger shift of H_3 suggests that H_3 of *trans*-2,3-epoxy-1-hexanol is located closer to Eu^{3+}. By the molecular model examination of a bidentate complex of Eu(fod)$_3$ with *trans*-2,3-epoxy-1-hexanol, we could ascertain that the proton at C-3 and Eu^{3+} became so closely spaced each other as to interact strongly (Chart 2). Consequently it is obvious that the epoxyalkanol forms a bidentate complex with Eu^{3+}.

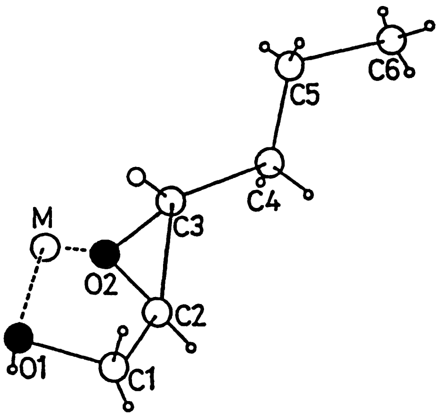


Chart 2.

The reaction of *trans*-2,3-epoxy-1-hexanol with Me_3SiCN in the presence of Eu(fod)$_3$[25] was rather slower and took about 20 h at 98 °C for completion. However, a good regioselectivity (88 : 12) and a good total yield of 80% were obtained as expected from the above mentioned complex formation. This regioselectivity was almost the same as that of the reaction on CaO.

$Ca(OTf)_2$ is easily prepared by adding triflic acid to a suspension of calcium carbonate in dry methanol.[26] $Ca(OTf)_2$ though not soluble in $CHCl_3$ is freely soluble in methanol and DMSO. By using $Ca(OTf)_2$ dissolved

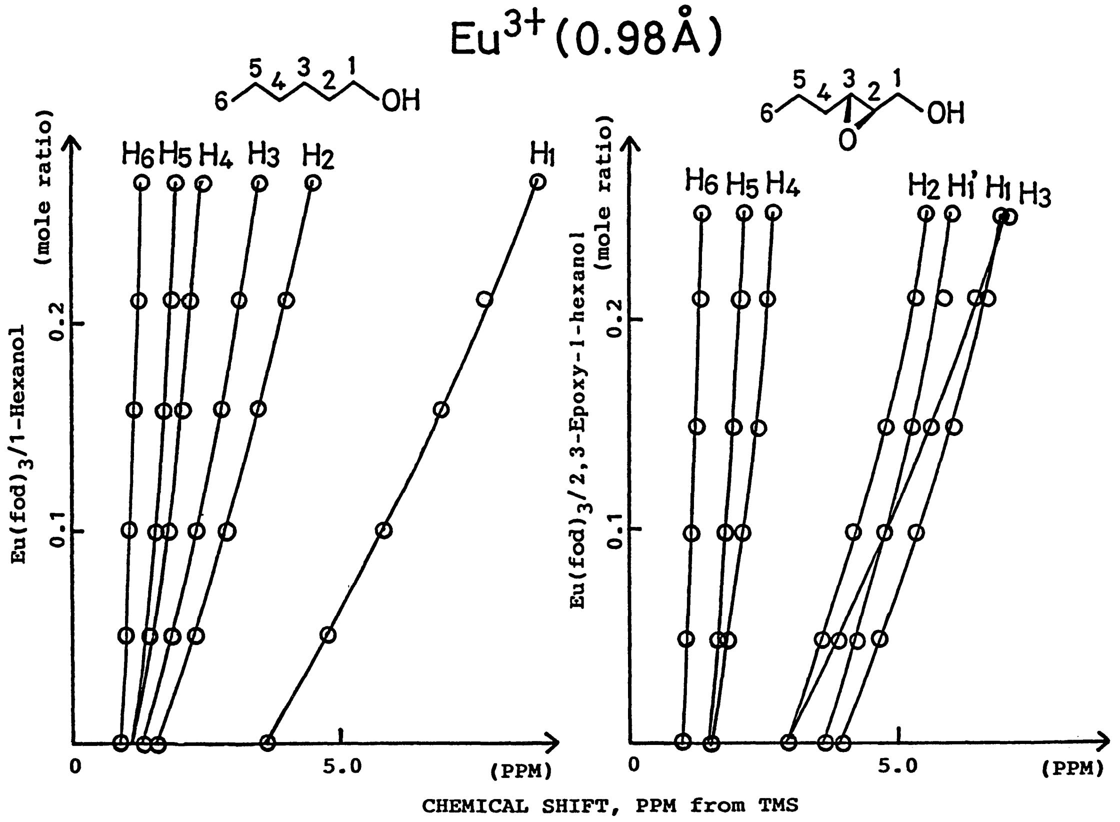


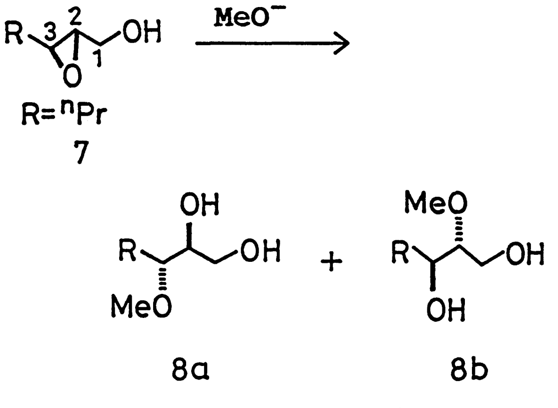
Fig. 1. Chemical shifts as a function of added Eu(fod)$_3$ to 1-Hexanol or 2,3-Epoxy-1-hexanol in 0.55 ml $CDCl_3$. 200 MHz spectra of 1-Hexanol or 2,3-Epoxy-1-hexanol with Eu(fod)$_3$ was measured at room temperature.

Table 6. Reactions of *trans*-2,3-Epoxy-1-hexanol (7) with MeO^-

Run	Promoter	Nucleophile	Condition	Yield %	**8a** : **8b**
1	$Ca(OTf)_2$	MeOH[a)]	$CHCl_3$, 50 °C, 3 h	82	79:21
2		MeONa[b)]	THF, 50 °C, 18 h	36	64:36

a) 7 (1 mmol), MeOH (5 mmol), and $Ca(OTf)_2$ (1 mmol), in $CHCl_3$. b) 7 (1 mmol), and MeONa (3 mmol), in THF.

in MeOH–$CHCl_3$ (1 : 30), we could examine homogeneous ring opening of epoxyalkanol (Eq. 4). When



(4)

MeOH and $Ca(OTf)_2$ were treated with *trans*-2,3-epoxy-1-hexanol (7) in $CHCl_3$, a C-3 : C-2 ratio was as high as 79:21 (Table 6). On the other hand, when 7 and MeONa were vigorously mixed in THF in the absence of any calcium salt, a lower C-3 : C-2 ratio of 64 : 36 (**8a** : **8b**) was obtained (Table 6). Evidently calcium ions could enhance the regioselectivity at C-3 acting as homogeneous Lewis acids.

On the basis of the spectroscopic study using $Eu(fod)_3$ and a comparative experiment using $Ca(OTf)_2$, it is concluded that the calcium ions on the surface of CaO regulate the ring-opening site, probably by forming bidentate chelate complexes with 2,3-epoxy-1-alkanol molecules.

Additionally, compared with the homogeneous Lewis acid-promoted reactions (e.g. $Al(O^iPr)_3$, $Ti(O^iPr)_4$ and $Eu(fod)_3$), CaO-promoted ring openings proceeded more efficiently and regioselectively because CaO served as a bifunctional catalyst; the oxide anions on CaO activated Me_3SiCN, and simultaneously the calcium ions on CaO activated epoxyalkanol as Lewis acids regulating the ring-opening site.

Conclusion

The present synthetic method using inorganic solid base catalysts provides a convenient and simple procedure for the regioselective ring opening of epoxides with Me_3SiCN. Especially the strong base solids such as CaO and MgO enable milder reaction conditions (room temperature, neutral reaction medium), higher regiospecific transformation, and easier product isolation than Lewis acids ever used in the corresponding homogeneous reactions. Further studies are underway to utilize base solids in various types of liquid-phase organic reactions which involve organosilicon reagents.

Experimental

Measurement. Infrared (IR) spectra were measured in $CDCl_3$ or CCl_4 with a JASCO IR-810 spectrometer. The ^1H NMR spectra were measured in $CDCl_3$ with Hitachi R-600 (60 MHz) and Varian GEMINI 200 (200 MHz) spectrometers. Tetramethylsilane (TMS) was used as an internal standard. The chemical shifts are given in δ (ppm) downfield from TMS, and the coupling constants are in hertz. Gas chromatographic analyses were carried out with a Shimadzu GC-8A instrument with a flame ionization detector and a capillary column (OV-1 bonded, 25 m and PEG-HT bonded, 25m).

Materials. MgO and CaO were prepared by calcining their hydroxide (Kishida Chemical Co.) at 500 °C/0.5 Torr (1 Torr=133.322 Pa), for 2 h. Hydroxyapatite[15)] (HAp, $Ca_{10}(PO_4)_6(OH)_2$, Nacalai Tesque, Inc.) was dried at 500 °C/0.5 Torr for 2 h. CaF_2 (Kishida Chemical Co.) and Silica (Fuji-Davison B-Type) were dried at 200 °C/0.5 Torr for 2 h. Iron (III) ion-exchanged montmorillonite (Fe–Mont) was prepared from sodium ion exchanged montmorillonite (Kunipia-F, Kunimine Co.) by ion exchange.[10b)] Fe-Mont was dried at 120 °C/0.5 Torr for 3 h.

Organic solvents were dried over molecular sieves 3A.

(2*S*,3*S*)-2,3-Epoxy-1-alkanols were prepared from trans allylic alcohols by Sharpless asymmetric epoxidation process.[27)]

$Ca(CF_3SO_3)_2$. Trifluoromethanesulfonic acid (5 ml, 0.06 mol) was slowly added to a suspension of calcium carbonate (2 g, 0.02 mol) in dry methanol (20 ml) at room temperature. The reaction mixture was stirred at room temperature for 20 min, then at reflux for 2 h. It was concentrated under reduced pressure, and then the resulting white cake was dried at 130 °C/1 Torr for 3 h to give 6.6 g of calcium triflate (98% yield).

Acid and Base Strength Measurements of Solids. The method of measurement corresponded to Walling's method.[28)] The following Hammett indicators (pK_a value) were employed; 4-nitroaniline (+18.4), 2,4-dinitroaniline (+15.0), phenolphthalein (+9.3), bromothymol blue (+7.2), 4-(dimethylamino)azobenzene (butter yellow) (+3.3), 4′-amino-2,3′-dimethylazobenzene (+2.0), 4-(phenylazo)-*N*-phenylaniline (+1.5), crystal violet (+0.8), and anthraquinone (− 8.2).

The color of the indicator adsorbed on the solid was visually observed after the addition of about 5 ml of dry benzene and one drop of a 0.1% solution of the indicator in benzene to 0.1 g of a solid.

Reactions of Unsymmetrical Epoxides with Me_3SiCN and Inorganic Solids. To a suspended mixture of the solid catalyst (0.2 g) and heptane (2 ml) were added a heptane solution

(3 ml) of epoxide (1 mmol), and $\mathrm{Me_3SiCN}$ (2 mmol), successively. The mixture was stirred under the conditions listed in Tables 1, 3, and 4. As work-up, ether (5 ml) was added, the solid catalyst was filtered off through a Celite pad and washed with ether. The filtrate was distilled on a Kugelrohr apparatus to yield the products. The regioisomeric ratios of the products were determined by ^{1}H NMR (200 MHz) and capillary GC (OV-1, 25 m).

Reaction of 1,2-Epoxyoctane with $\mathrm{Me_3SiCN}$ and $^{n}\mathrm{Bu_4NF}$. A solution of $^{n}\mathrm{Bu_4NF}$ in THF (1.1 M, 1 M=1mol dm^{-3}) was stored over activated 3A molecular sieves powders. (Activation of powdered 3A molecular sieves involved heating at 200 °C and 0.5 Torr pressure for at least 3 h.) Under a nitrogen atmosphere, the solution of $^{n}\mathrm{Bu_4NF}$ (3 mmol) was added to a solution of a 1,2-epoxyoctane (1 mmol) and $\mathrm{Me_3SiCN}$ (3 mmol) in THF (5 ml) at room temperature. The mixture was stirred at 60 °C for 4 h. The THF was removed by evaporation, and the residue was diluted with $\mathrm{Et_2O}$. The reaction mixture was washed with water and the organic layer was dried over anhydrous $\mathrm{Na_2SO_4}$. The organic layer was evaporated and distilled by a Kugelrohr apparatus to yield the products.

Reactions of Unsymmetrical Epoxides with $\mathrm{Me_3SiCN}$ and $\mathrm{Al(O^{\mathit{i}}Pr)_3}$. Under a nitrogen atmosphere, a mixture of $\mathrm{Al(O^{\mathit{i}}Pr)_3}$ (1.5 mmol) and $\mathrm{Me_3SiCN}$ (1.5 mmol) in hexane (5 ml) was stirred for 2 h at room temperature. An epoxide (1 mmol) was added and the mixture was stirred at room temperature. Then $\mathrm{Me_3SiCN}$ (8 mmol) was added and the mixture was stirred at room temperature for 20 h. As work-up, a mixture of ice and 3M NaOH was added, and the mixture was extracted with ether. The ethereal solution was washed with brine and dried over anhydrous $\mathrm{Na_2SO_4}$. The organic layer was evaporated and distilled by a Kugelrohr apparatus to yield the products.

3-(Trimethylsiloxy)nonanenitrile. Bp 110 °C (bath temperature)/0.5 Torr; IR ($\mathrm{CCl_4}$) 1253, 2251 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.15 (s, 9H, $\mathrm{CH_3Si}$), 0.88 (t, 3H, J=7.7 Hz, $\mathrm{CH_3}$), 1.10—1.44 (br, 8H, $\mathrm{(CH_2)_4}$), 1.44—1.64 (m, 2H, $\mathrm{CH_2COSi}$), 2.44 (d, 2H, J=7.7 Hz, $\mathrm{CH_2CN}$), 3.9 (dddd, 1H, J=5.1, 5.1, 5.1 Hz, CHOSi); ^{13}C NMR δ=−0.1, 13.8, 22.4, 25.0, 26.1, 28.9, 31.5, 37.0, 68.4, 118.0. Found: C, 63.54; H, 11.33; N, 6.15%. Calcd for $\mathrm{C_{12}H_{25}NOSi}$: C, 63.38; H, 11.08; N, 6.16%.

***c*-2-Methyl-2-(trimethylsiloxy)-*r*-1-cyclohexanecarbonitrile:** Bp 135 °C (bath temperature)/20 Torr; IR ($\mathrm{CCl_4}$) 1253, 2249 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.14 (s, 9H, $\mathrm{CH_3Si}$), 1.42 (s, 3H, $\mathrm{CH_3}$), 1.35—1.80 (m, 7H, -($\mathrm{CH_2}$)-), 1.88—2.06 (m, 1H), 2.60 (dd, 1H, J=7.0, 4.0 Hz, CHCN); ^{13}C NMR ($\mathrm{CDCL_3}$) δ=2.1, 21.5, 22.4, 25.8, 26.2, 37.7, 41.0, 73.0, 121.3. Found: C, 62.77; H, 10.21; N, 6.62%. Calcd for $\mathrm{C_{11}H_{12}NOSi}$: C, 62.50; H, 10.01; N, 663%.

2,3-Dimethyl-3-(trimethylsiloxy)butanenitrile. Bp 130 °C (bath temperature)/30 Torr; IR ($\mathrm{CCl_4}$) 1253, 2251 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.12 (s, 9H, $\mathrm{CH_3Si}$), 1.28 (d, 3H, J=7.1 Hz, $\mathrm{CH_3CCN}$), 1.38 (s, 6H, $\mathrm{CH_3COSi}$), 2.69 (q, 1H, J=7.1 Hz, CHCN); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=2.0, 12.8, 26.7, 27.6, 39.1, 73.7, 122.0. Found: C, 58.17; H, 10.31; N, 7.64%. Calcd for $\mathrm{C_9H_{19}NOSi}$: C, 58.32; H, 10.33; N, 7.56%.

3-Methyl-3-(trimethylsiloxy)butanenitrile. Bp 120 °C (bath temperature)/30 Torr; IR ($\mathrm{CCl_4}$) 1253, 2251 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.14 (s, 9H, $\mathrm{CH_3Si}$), 1.38 (s, 6H, $\mathrm{CH_3COSi}$), 2.45 (s, 2H, $\mathrm{CH_2CN}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=2.0, 29.3, 33.8, 71.7, 118.0. Found: C, 56.08; H, 10.10; N, 8.11%. Calcd for $\mathrm{C_8H_{17}NOSi}$: C, 56.09; H, 10.00; N, 8.18%

Reactions of (2*S*,3*S*)-2,3-Epoxy-1-alkanol Derivatives with $\mathrm{Me_3SiCN}$ and Inorganic Solids. To a suspended mixture of an inorganic solid (0.5 g) and heptane (2 ml) was added a heptane (3 ml) solution of (2*S*,3*S*)-2,3-epoxy-1-alkanol (0.5 mmol) and the mixture was stirred under the conditions listed in Table 5. As work-up, ether (3 ml) was added, the inorganic solid was filtered off through a Celite pad and washed with ether. After organic solvents were evaporated, the reaction mixture was diluted with methanol (3 ml), and 5 equivalents of potassium fluoride was added. The mixture was stirred at 25 °C for 14 h in order to desilylate the organic products. The regioselectivity of the reaction was based on GC (OV-1; 25 m) and ^{1}H NMR (200 MHz) analysis of the unpurified reaction mixture after acetylation. The hydroxy carbonitriles were treated with $\mathrm{Ac_2O}$ (0.5 ml) and pyridine (0.5 ml) in $\mathrm{CH_2Cl_2}$ (1 ml) in the presence of catalytic 4-(*N*,*N*-dimethylamino)pyridine. After the reaction was complete, the reaction mixture was washed with 1 M HCl solution (3 ml) and brine (3 ml), dried over anhydrous $\mathrm{Na_2SO_4}$, and distilled with a Kugelrohr apparatus to yield dihydroxy carbonitriles.

The two regioisomers of dihydroxy carbonitriles were identical with those obtained from the reactions of epoxyalkanols with $\mathrm{Me_3SiCN}$–$\mathrm{Ti(O^{\mathit{i}}Pr)_4}$ by GC (OV-1; 25 m) and ^{1}H NMR (200 MHz) analyses.

Reaction of (2*S*,3*S*)-2,3-Epoxy-1-alkanol with $\mathrm{Me_3SiCN}$ and $\mathrm{Ti(O^{\mathit{i}}Pr)_4}$. Under a nitrogen atmosphere, $\mathrm{Ti(O^{\mathit{i}}Pr)_4}$ (1.5 mmol) was added to solution of an epoxyalkanol (1 mmol) and $\mathrm{Me_3SiCN}$ (3 mmol) in DME (5 ml) at room temperature. The mixture was stirred at 80 °C until the epoxyalkanol was consumed. After 5% $\mathrm{H_2SO_4}$ (5 ml) was added, the two phase mixture was stirred vigorously until two clear layers formed. The dihydroxy carbonitriles were extracted with AcOEt and dried over anhydrous $\mathrm{Na_2SO_4}$. The regioselectivity of the reaction was based on GC (OV-1; 25 m) and ^{1}H NMR (200 MHz) analysis of the unpurified reaction mixture after acetylation.

Reaction of (2*S*,3*S*)-2,3-Epoxy-1-hexanol with $\mathrm{Me_3SiCN}$ and $\mathrm{Eu(fod)_3}$. Under a nitrogen atmosphere, $\mathrm{Eu(fod)_3}$ (1 mmol) was added to solution of a 2,3-epoxy-1-hexanol (1 mmol) and $\mathrm{Me_3SiCN}$ (3 mmol) in heptane (4 ml) at room temperature. The reaction mixture was stirred at 98 °C for 20 h. After 5% $\mathrm{H_2SO_4}$ (5 ml) was added, the two phase mixture was stirred vigorously for 1 h at room temperature. The dihydroxy carbonitriles were extracted with AcOEt, and then dried over anhydrous $\mathrm{Na_2SO_4}$. The regioselectivity was determined as described above.

(2*R*,3*R*)-3-Cyano-1,2-hexanediol. Bp 170 °C (bath temperature)/1 Torr; IR ($\mathrm{CCl_4}$) 2250, 3400 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.98 (br t, 3H, $\mathrm{CH_3}$), 1.10—2.00 (br, 4H, $\mathrm{(CH_2)_2}$), 2.50—3.05 (m, 1H, CHCN), 3.30—4.20 (br m, 5H, $\mathrm{CH_2OH}$, CHOH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=13.3, 20.3, 29.7, 35.0, 63.8, 71.1, 120.5. Found: C, 58.52; H, 9.05; N, 9.73%. Calcd for $\mathrm{C_7H_{13}O_2N}$: C, 58.72; H, 9.15; N, 9.78%.

(2*R*,3*R*)-3-Cyano-1,2-hexanediol Diacetate. This product was obtained from (2*R*,3*R*)-3-cyano-1,2-hexanediol by acetylation. Bp 150 °C (bath temperature)/1 Torr; IR ($\mathrm{CCl_4}$) 1760, 2250 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.94 (t, 3H, J=6.8 Hz, $\mathrm{CH_3}$), 1.25—1.80 (br, 4H, $\mathrm{(CH_2)_2}$), 2.06 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.85—3.00 (m, 1H, CHCN), 4.17 (dd, 1H, J=12.5, 5.2 Hz, C(H)HOAc), 4.44 (dd, 1H, J=12.5, Hz, 3.3 Hz, C(H)HOAc), 5.05 (ddd, 1H, J=5.2, 5.2, 3.3 Hz, CHOAc); ^{13}C NMR ($\mathrm{CDCl_3}$), δ=13.1, 20.1, 20.4, 20.5, 30.1, 33.2, 62.2, 69.7, 118.6, 170.0, 170.6.

(2*R*,3*R*)-3-Cyano-3-cyclohexyl-1,2-propanediol Diacetate. Bp 190 °C (bath temperature)/0.5 Torr; IR ($\mathrm{CCl_4}$) 1758, 2249 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.00—2.00 (br, 11H, cyclohexyl), 2.10 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.84 (dd, 1H, J=7.9, 6.0 Hz, CHCN), 4.18 (dd, 1H, J=12.4, 5.6 Hz, C(H)HOAc), 4.55 (dd, 1H, J=12.4, 2.6 Hz, C(H)HOAc), 5.23 (ddd, 1H, J=7.9, 5.6, 2.6 Hz, CHOAc); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=20.4, 20.5, 25.4, 25.5, 25.6, 29.2, 31.1, 35.8, 39.8, 62.8, 67.7, 117.7, 170.0, 170.6. Found: C, 63.13; H, 8.14; N, 5.51%. Calcd for $\mathrm{C_{14}H_{21}O_4N}$: C, 62.90; H, 7.92; N, 5.24%.

(2*R*,3*R*)-3-Cyano-4-methyl-1,2-pentanediol Diacetate. Bp 130 °C (bath temperature)/0.5 Torr; IR ($\mathrm{CCl_4}$) 1760, 2250 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.09 (d, 3H, J=7.2 Hz $\mathrm{CH_3}$), 1.13 (d, 3H, J=7.2 Hz, $\mathrm{CH_3}$), 2.12 (s, 6H, Ac), 2.86 (dd, 1H, J=8.4, 5.5 Hz, CHCN), 4.18 (dd, 1H, J=12.2, 4.8 Hz, C(H)HOAc), 4.57 (dd, 1H, J=12.2, 3.0 Hz, C(H)HOAc), 5.21 (ddd, 1H, J=8.4, 4.8, 3.0 Hz, CHOAc); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=18.3, 20.4, 20.5, 20.8, 26.6, 40.5, 62.9, 68.2, 117.4, 170.0, 170.6. Found: C, 57.96; H, 7.69; N, 6.25%. Calcd for $\mathrm{C_{11}H_{17}O_4N}$: C, 58.14; H, 7.54; N, 6.16%.

Reaction of (2*S*,3*S*)-2,3-Epoxy-1-hexanol with MeOH and Ca(OTf)$_2$. Under a nitrogen atmosphere, $\mathrm{Ca(OTf)_2}$ (1 mmol) was added to solution of a 2,3-epoxy-1-hexanol (1 mmol) and $\mathrm{CH_3OH}$ (5 mmol) in $\mathrm{CHCl_3}$. The reaction mixture was stirred at 50 °C for 3 h. It was diluted with $\mathrm{Et_2O}$ (5 ml), washed with $\mathrm{H_2O}$ (3 ml), and the organic phase was dried over anhydrous $\mathrm{Na_2SO_4}$. The regioselectivity was based on GC (PEG-HT, 25 m) and ^{1}H NMR (200 Hz) analysis of the unpurified reaction mixture after acetylation.

Reaction of (2*S*,3*S*)-2,3-Epoxy-1-hexanol with MeONa. Under a nitrogen atmosphere, sodium hydride (3 mmol) was slowly added to solution of MeOH (3 mmol) in THF (2 ml). The solution was stirred for 0.5 h and solution of an epoxyalkanol (1 mmol) in THF was added to it. The reaction mixture was stirred at 60 °C for 18 h. It was then diluted with AcOEt (3 ml) and washed with water (3 ml), and the organic phase was dried over anhydrous $\mathrm{Na_2SO_4}$. The regioselectivity was determined as described above.

(2*R*,3*R*)-3-Methoxy-1,2-hexanediol. 140 °C (bath temperature)/0.6 Torr; IR ($\mathrm{CCl_4}$) 2830, 3450 (br), 3630 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.70—1.16 (br t, 3H, $\mathrm{CH_3}$), 1.16—1.80 (br m, 4H, $\mathrm{(CH_2)_2}$), 2.57 (s, 2H, OH), 3.42 (s, 3H, $\mathrm{OCH_3}$), 3.60—4.10 (m, 4H, CHOMe, $\mathrm{CH_2OH}$, CHOH); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=14.0, 18.5, 32.1 , 58.4, 63.2, 72.3, 83.4. Found: C, 56.52; H, 10.80%. Calcd for $\mathrm{C_7H_{16}O_3}$: C, 56.73; H, 10.88%.

(2*R*,3*R*)-3-Methoxy-1,2-hexanediol Diacetate. This product was obtained from (2*R*,3*R*)-3-methoxy-1,2-hexanediol by acetylation. 140 °C (bath temperature)/1 Torr; IR ($\mathrm{CCl_4}$) 1750, 2830 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.90 (tr, 3H, J=6.6 Hz, $\mathrm{CH_3}$), 1.20—1.65 (br m, 4H, $\mathrm{(CH_2)_2}$), 2.03 (s, 3H, Ac), 2.07 (s, 3H, Ac), 3.25—3.45 (m, 1H, CHOMe), 3.38 (s, 3H, $\mathrm{OCH_3}$), 4.11 (dd, 1H, J=12.1, 7.6 Hz, C(H)HOAc), 4.34 (dd, 1H, J=12.1, 3.0 Hz, C(H)HOAc), 5.12 (ddd, 1H, J=7.6, 4.2, 3.0 Hz, CHOAc); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=13.8 18.4, 20.6, 20.8, 32.7, 58.4, 62.6, 72.7, 80.2, 170.6, 171.0.

References

1) a) W. C. Groutas and D. Felker, *Synthesis,* **1980**, 861; b) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983), p. 6.

2) a) M. T. Reetz and I. Chatziiosifidis, *Angew. Chem., Int. Ed. Engl.,* **20**, 1017 (1981); b) T. Sasaki, A. Nakanishi, and M. Ohno, *J. Org. Chem.,* **46**, 5445 (1981); c) M. T. Reetz, I. Chatziiosifidis, H. Künzer, and H. Müller-Starke, *Tetrahedron,* **39**, 961 (1983).

3) J. C. Mullis and W. P. Weber, *J. Org. Chem.,* **47**, 2873 (1982).

4) W. Lidy and W. Sundermeyer, *Tetrahedron Lett.,* **1973**, 1449.

5) K. Imi, N. Yanagihara, and K. Utimoto, *J. Org. Chem.,* **52**, 1013 (1987).

6) A. E. Vougioukas and H. B. Kagan, *Tetrahedron Lett.,* **28**, 5513 (1987).

7) a) M. Caron and K. B. Sharpless, *J. Org. Chem.,* **50**, 1557 (1985); b) M. Emziane, P. Lhoste, and D. Sinou, *J. Mol. Catal.,* **49**, L23 (1988).

8) a) P. G. Gassman and T. L. Guggenheim, *J. Am. Chem. Soc.,* **104**, 5849 (1982); b) P. G. Gassman and R. S. Gremban, *Tetrahedron Lett.,* **25**, 3259 (1984); c) P. G. Gassman and L. M. Haberman, *ibid.,* **26**, 4971 (1985); d) P. G. Gassman, K. Okuma, A. Lindbeck, and R. Allen, *ibid.,* **27**, 6307 (1986); e) P. G. Gassman and L. M. Haberman, *J. Org. Chem.,* **51**, 5010 (1986).

9) a) M. Onaka, M. Kawai, and Y. Izumi, *Bull. Chem. Soc. Jpn.,* **59**, 1761 (1986); b) M. Onaka, K. Sugita, and Y. Izumi, *J. Org. Chem.,* **54**, 1116 (1989); c) M. Onaka, K. Sugita, H. Takeuchi, and Y. Izumi, *J. Chem. Soc., Chem. Commun.,* **1988**, 1173.

10) a) M. Onaka, R. Ohno, M. Kawai, and Y. Izumi, *Bull. Chem. Soc. Jpn.,* **60**, 2689 (1987); b) M. Kawai, M. Onaka, and Y. Izumi, *ibid.,* **61**, 1237 (1988); c) M. Kawai, M. Onaka, and Y. Izumi, *ibid.,* **61**, 2157 (1988); d) M. Onaka, R. Ohno, and Y. Izumi, *Tetrahedron Lett.,* **30**, 747 (1989); e) M. Onaka, T. Mimura, R. Ohno, and Y. Izumi, *ibid.,* **30**, 6341 (1989).

11) Recently various porous inorganic solids such as zeolite, silica, and alumina are widely utilized to organic reactions. a) Review: G. H. Posner, *Angew. Chem., Int. Ed. Engl.,* **17**, 487 (1978); b) Review: A. Mckillop and D. W. Young, *Synthesis,* **1979**, 401, 481; c) Review: A. Cornelis and P. Laszlo, *ibid.,* **1985**, 909.

12) M. Onaka, K. Higuchi, K. Sugita, and Y. Izumi, *Chem. Lett.,* **1989**, 1393.

13) To the best our knowledge, this base-catalyzed method is the first example in the reaction of epoxides with $\mathrm{Me_3SiCN}$: K. Sugita, A. Ohta, M. Onaka, and Y. Izumi, *Chem. Lett.,* **1990**, 481.

14) a) K. B. Sharpless, C. H. Behrens, T. Katsuki, A. W. Lee, V. S. Martin, M. Takatani, S. M. Viti, J. Walker, and S. S. Woodard, *Pure Appl. Chem.,* **55**, 589 (1983); b) C. H. Behrens and K. B. Sharpless, *Aldrichimica Acta,* **16**, 67 (1983); c) C. H. Behrens, S. Y. Ko, K. B. Sharpless, and F. J. Walker, *J. Org. Chem.,* **50**, 5687 (1985); d) C. H. Behrens and K. B. Sharpless, *J. Org. Chem.,* **50**, 5696 (1985); e) A. Pfenninger, *Synthesis,* **1986**, 89.

15) J. A. S. Bett, L. G. Christner, and W. K. Hall, *J. Am. Chem. Soc.,* **89**, 5535 (1967).

16) The reactions involving pentacoordinate silicate intermediates have been reported in regio- and stereocontrolled organic synthesis: a) M. Kumada, K. Tamao, and J. Yoshida, *J. Organomet. Chem.,* **239**, 115 (1982); b) M. Kira, K. Sato, and H. Sakurai, *J. Org. Chem.,* **52**, 948 (1987); c) G. Cerveau, C. Chuit, R. J. P. Corriu, and C. Reye, *J. Organomet. Chem.,* **328**, C17 (1987); d) A. Hosomi, S. Kohra, and Y. Tominaga, *J. Chem. Soc., Chem. Commun.,* **1987**, 1517; e) Review: H. Sakurai, *Synlett,* **1**, 1 (1989); f) M. Kira, K. Sato, and H.

Sakurai, *J. Am. Chem. Soc.*, **112**, 257 (1990).

17) The basic site on CaO or MgO was reported to be a surface lattice oxygen (O^{2-}): K. Tanabe and K. Saito, *J. Catal.*, **35**, 247 (1974).

18) Recently we identified the interaction between silicon of Me_3SiCN and O^{2-} on the CaO, by infrared spectrum on the CaO in the course of the above reaction: to be submitted for publication.

19) a) A. C. Cope and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3125 (1965); b) B. Rickborn and R. P. Thummel, *ibid.*, **34**, 3583 (1969); c) R. P. Thummel and B. Rickborn, *ibid.*, **92**, 2064 (1970).

20) When Me_3SiCN and CaO were treated with *cis*-2,3-epoxy-1-hexanol, the ring opening was completed within 1 h at room temperature, and a mixture of dihydroxy carbonitriles was isolated in 88% yield. A ^1H NMR analysis of the acetylated crude product revealed a C-3 : C-2 ratio of 97 : 3.

21) The reaction of *trans*-2,3-epoxy-1-hexanol with Nagata's reagent(Et_2AlCN) was reported to give high regioselectivity (94 : 6). See Ref. 7a.

22) In recent years, the solution structures of the complexes formed between 3-alkoxyalkanal and Lewis acid have been confirmed via NMR spectroscopy: a) G. E. Keck and S. Castellino, *J. Am. Chem. Soc.*, **108**, 3847 (1986); b) G. E. Keck, S. Castellino, and M. R. Wiley, *J. Org. Chem.*, **51**, 5478 (1986); c) G. E. Keck and S. Castellino, *Tetrahedron Lett.*, **28**, 281 (1987); d) M. T. Reetz, M. Hüllmann, and T. Seitz, *Anegw. Chem., Int. Ed. Engl.*, **26**, 477 (1987).

23) Review: F. S. Richardson, *Chem. Rev.*, **82**, 541 (1982).

24) a) Review: A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973); b) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 1038 (1974).

25) Lanthanide complexes have been utilized as Lewis-acid catalysts to various organic reactions. For a review: a) H. B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1986); For a Diels–Alder reaction: b) M. Bednarski and S. Danishefsky, *J. Am. Chem. Soc.*, **105**, 3716 (1983); c) J. Jurczak, A. Golebiowski, and T. Bauer, *Synthesis*, **1985**, 928; d) M. Quimpere and K. Jankowski, *J. Chem. Soc., Chem. Commun.*, **1987**, 676; e) M. M. Midland and M. M. Afonso, *J. Am. Chem. Soc.*, **111**, 4368 (1989); For a ring opening of epoxides: f) A. E. Vougioukas and H. B. Kagan, *Tetrahedron Lett.*, **28**, 6065 (1987); See, also Ref. 9.

26) E. J. Corey and K. Shimoji, *Tetrahedron Lett.*, **24**, 169 (1983).

27) Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, and K. B. Sharpless, *J. Am. Chem. Soc.*, **109**, 5765 (1987).

28) a) C. Walling, *J. Am. Chem. Soc.*, **72**, 1164 (1950); b) J. Take, N. Kikuchi, and Y. Yoneda, *J. Catal.*, **21**, 164 (1971).