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# Solid Acid and Base-Catalyzed Cyanosilylation of Carbonyl Compounds with Cyanotrimethylsilane

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A new attempt was investigated to utilize inorganic solid acids and bases for the promotion of the reaction of cyanotrimethylsilane ($Me_3SiCN$) with carbonyl compounds. Strongly acidic solids, such as $Sn^{4+}$ ion-exchanged montmorillonite (Sn-Mont) and $Fe^{3+}$ ion-exchanged montmorillonite (Fe-Mont), as well as basic solids, such as calcium fluoride ($CaF_2$), hydroxyapatite (HAp), calcium oxide (CaO), and magnesium oxide (MgO), catalyzed the reaction of $Me_3SiCN$ with aldehydes and ketones to afford the corresponding 2-(trimethylsiloxy)alkanenitriles in good yields. The reactions of dimethyl acetals with $Me_3SiCN$ in the presence of solid acids afforded 2-methoxyalkanenitriles. In cyanosilylations of $\alpha,\beta$-unsaturated ketones two kinds of adducts were produced selectively, depending on the use of a solid acid or a solid base: 1,4-Adducts (trimethylsilyl enol ether forms) were selectively obtained in the presence of strong solid acids, such as Fe-Mont and Sn-Mont, while 1,2-adducts (trimethylsilyl ether forms) were predominantly formed in the presence of solid bases, such as HAp, CaO, and MgO. The solid acids and bases realized higher activities and selectivities in the cyanosilylation than did conventional homogeneous catalysts.

Liquid cyanotrimethylsilane ($Me_3SiCN$, bp 118 °C) has been widely utilized as a synthetic equivalent of gaseous HCN (bp 26 °C) in organic syntheses. The introduction of a cyano functionality to electrophilic substrates, such as carbonyl compounds, epoxides, Shiff bases, and oximes, has been performed using $Me_3SiCN$.[1)] The additions of $Me_3SiCN$ to aldehydes and ketones with the aid of Lewis acids, such as $ZnI_2$ and $AlCl_3$, were first reported independently by Evans[2)] and Lidy[3)] in 1973. Since then, a number of synthetic methods using various Lewis acids, such as $CF_3SO_3SiMe_3$,[4)] $SnCl_2$,[5a,5c)] $BF_3\cdot OEt_2$,[5a,5c)] $SnCl_4$,[6)] and $TiCl_4$,[7)] have been developed for the reactions of $Me_3SiCN$ with aldehydes, ketones, and acetals. Evans also discovered that solubilized anionic species, such as $K^+CN^-$/18-Crown-6 and ${}^nBu_4N^+CN^-$, can catalyze the cyanosilylation of aldehydes and ketones.[8)] It was recently reported that neutral transition metal compounds,[9)] such as $NiCl_2$, $CoCl_2$, and di-$\mu$-chloro-bis-(1,5-cyclooctadiene)dirhodium ($[Rh(cod)Cl]_2$), as well as bases, such as $Et_3N$[10)] and $La_3(OBu^t)_9$,[11)] and Yb $(CN)_3$,[50)] catalyze the reaction of $Me_3SiCN$ with carbonyl compounds. One-pot cyanosilylations of carbonyl compounds were also carried out by the combined use of $Me_3SiCl$ and KCN (or NaCN).[12)]

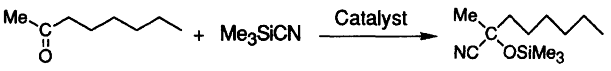
The cyanide addition to $\alpha,\beta$-unsaturated ketones (enones) can afford two regioisomers, 1,2-adducts and 1,4-adducts. Especially, conjugate additions were often applied in natural product syntheses, and several reagent systems have been developed: the Nagata reagents[13)] of HCN–$Et_3Al$ and $Et_2AlCN$ and the combined use of $Me_3SiCN$ and Lewis acids, such as $Et_3Al$, $ZnI_2$, and $AlCl_3$.[5b,5c)]

We have attempted to apply inorganic solid acids and bases, such as zeolites[14)] and clay montmorillonites,[15)] to liquid-phase organic reactions.[16)] The utilization of heterogeneous catalysts in liquid-phase reactions have the following advantages, compared with that of homogeneous catalysts: (1) Higher reactivities and selectivities are often realized, owing to the specific structures of solid surfaces where organic substrates are adsorbed, oriented, and activated. (2) A work-up procedure is only filtration of the solid catalysts, and the products are easily isolable.

In general, cyanosilylations of carbonyl compounds have so far been performed under homogeneous conditions, except for the sole example under heterogeneous conditions by the use of KCN (NaCN) doped on Amberlite XAD resin (nonionic polymeric adsorbent) and $Me_3SiCl$.[12c)] In this study we applied solid acids and bases to the reaction of $Me_3SiCN$ with carbonyl compounds, and examined how the solids interact with and activate the organic substrates. In our preliminary reports[17)] we discussed how solid bases, such as calcium fluoride and hydroxyapatite, as well as a solid acid like $Fe^{3+}$ ion-exchanged montmorillonite, promote the cyanosilylation of aldehydes and ketones to afford trimethylsilyl ethers of the corresponding cyanohydrins in good yields. We also found that $Me_3SiCN$ reacts with $\alpha,\beta$-unsaturated ketones to give adducts in regioselective manners, depending on the use of a solid acid or a solid base: 1,4-Adducts are obtained in the presence of strong solid acids, such as $Fe^{3+}$ and $Sn^{4+}$ ions-exchanged montmorillonites, while 1,2-adducts are produced in the presence of solid bases, such as hydroxyapatite, calcium oxide, and magnesium oxide. Here, we disclose further results concerning the cyanosilylation of carbonyl compounds over various inorganic solids, and scrutinize novel interactions between solid bases and $Me_3SiCN$.

## Results and Discussion

**Reaction of 2-Octanone with $Me_3SiCN$ in the Presence of Solid Acids.** Various activated solid acids were mixed with 2-octanone (**1**) and $Me_3SiCN$ in $CH_2Cl_2$ at 0 °C in a suspended state. The results of the cyanosilylation are shown in Table 1.



**1** **2**

(1)

We found that in the additions of alllylic silanes and silyl enol ethers to carbonyl compounds, $Al^{3+}$ ion-exchanged montmorillonite was the most effective catalyst among the solid acids of mica, zeolite, silica-alumina and ion-exchanged resin.[15a,15d] We found that in the presence of $Al^{3+}$, $Fe^{3+}$, and $Sn^{4+}$ ions-exchanged montmorillonites (Al-Mont, Fe-Mont, Sn-Mont), $Me_3SiCN$ reacted with 2-octanone at 0 °C within 10 min to afffor d 2-methyl-2-(trimethylsiloxy)octanenitrile (**2**) in good yields. Al-Mont and Sn-Mont have strong acidity (below −8.2) according to the Hammett acid function.[18] In contrast, the reaction was slowly catalyzed by $Ca^{2+}$ ion-exchanged montmorillonite (Ca-Mont), which is far less acidic than Al-Mont and Sn-Mont, thus giving poorer yield of **2**. A very weak acid, $Na^+$ ion-exchanged montmorillonite (Na-Mont), showed no catalytic activity.

The reaction was incomplete over the strongly acidic zeolite, $Ca^{2+}$ ion-exchanged Y-type zeolite (CaY), after a prolonged reaction time (4.5 h). Very weak solid acids, $Na^+$ ion-type Y-zeolite (NaY) and $SiO_2$ could not accelerate the reaction.

Based on the results, it is apparent that Fe-Mont, Al-Mont, and Sn-Mont are the catalysts of choice for the cyanosilylation of carbonyl compounds, and that the present reactions are promoted by the action of clay montmorillonites bearing strong acidity. Clay montmorillonite has a lamellar structure: Repetitions of a unit layer comprising an octahedral alumina sheet sandwiched between two tetrahedral silica sheets (Fig. 1). Exchangeable cations stay in interlayers between aluminosilicate layers to neutralize the negative charges in the layers.[19] It is known that the acidic properties of cation-exchanged montmorillonites originate from protons, which are produced by the dissociation of water molecules coordinating to the cations in the interlayer (Eq. 2).[20]

$$M^{n+}(OH_2) \longrightarrow (M{-}OH)^{(n-1)+} + H^+ \qquad (2)$$

Therefore, the acid strengths of cation-exchanged montmorillonites are considered to depend on the electronegativity,[20a] polarization power,[20b] and hydration enthalpy of exchanged cations.[20c] It was reported that montmorillonites exchanged with multivalent cations, such as $Al^{3+}$ and $Fe^{3+}$ ions bearing high electronegativities, showed higher activities than Ca-Mont and Na-Mont in ester formations from carboxylic acids with alkenes,[21a] as well as in ether formations from alkenes with water.[21b] Our results agree with these precedents. Accordingly, it is reasonable to suppose that the cyanosilylation of carbonyl compounds using Sn-Mont, Fe-Mont, and Al-Mont proceed through the activation of carbonyl functions with strongly acidic proton sites on the montmorillonites. However, it was reported that a protic superacid, $CF_3SO_3H$ readily reacts with trimethylsilylating agents, such as allyltrimethylsilane[22a] and aryltrimethylsilane,[22b] to be converted into $CF_3SO_3SiMe_3$, which can fill the role of a Lewis acid[4,23] (Eq. 3).

(3)

We therefore attempted the cyanosilylation of heptanal, comparing the catalyses of $CF_3SO_3H$ and $CF_3SO_3SiMe_3$: $Me_3SiCN$ was added to a mixture of the acid and heptanal in $CH_2Cl_2$ at 0 °C. The results are shown in Table 2. Although $CF_3SO_3H$ is more acidic than $CF_3SO_3SiMe_3$ in terms of acid strength, the $CF_3SO_3H$-catalyzed reaction required the same reaction time as did the $CF_3SO_3SiMe_3$-catalyzed reaction, and both acid catalysts showed similar yields. These facts imply that $CF_3SO_3H$ is converted into $CF_3SO_3SiMe_3$ with $Me_3SiCN$ during the initial stage of the reaction, and that the resultant $CF_3SO_3SiMe_3$ catalyzes the cyanosilylation of heptanal. By analogy, we can speculate that the acidic montmorillonite-catalyzed reactions proceed via the activation of carbonyl groups by trimethylsilyl cation-like Lewis acid sites on the montmorillonite, which are produced through the reaction of acidic protons with $Me_3SiCN$. The catalytic cycle is completed via the addition of $Me_3SiCN$ to the carbenium ion intermediate and the regeneration of a Lewis acid site, as shown in Fig. 2.

**Estimation of the Amounts of Active Acid Sites on Sn-Mont and Fe-Mont.** In order to determine the amount of acid sites on Sn-Mont and Fe-Mont responsible for the activation of carbonyl functions, poisoning was performed using a probe base: A $CH_2Cl_2$ solution of a specified amount of $Et_3N$ was added to a suspension of Sn-Mont (0.2 g) or Fe-Mont (0.2 g) in $CH_2Cl_2$, and the mixture was stirred at 0 °C for 15 min. After poisoning, benzophenone (1 mmol) and $Me_3SiCN$ (1.2 mmol) were added successively, and the mixture was stirred at 0 °C. Figures 3 and 4 represent the results of poisoning with $Et_3N$ in the cyanosilylaiton of benzophenone on Sn-Mont and Fe-Mont. Both Sn-Mont and Fe-Mont were drastically deactivated upon the addition of a small amount of $Et_3N$. Sn-Mont was completely poisoned with 0.07 mmol of $Et_3N$, while Fe-Mont was poisoned with 0.02 mmol of $Et_3N$. Therefore, it was confirmed that these montmorillonites act as catalysts in the cyanosilylation of carbonyl compounds. The turnover numbers of the catalytic cycles are 14 for

Table 1. Cyanosilylation of 2-Octanone in the Presence of Various Inorganic Solid Acids[a)]

| Solid acid (Amount/g) | | Surface area $m^2\ g^{-1}$ | Maximum acid strength[b)] | Conditions Temp/°C (Time/h) | Yield % |
|---|---|---|---|---|---|
| None | | — | — | 0 (4.5) | 0[d)] |
| Sn-Mont | (0.2) | 280 | $-8.2 \geq H_0$ | 0 (0.2) | 97 |
| Fe-Mont | (0.2) | 26 | c) | 0 (0.2) | 96 |
| Al-Mont | (0.2) | 26 | $-8.2 \geq H_0$ | 0 (0.2) | 96 |
| Ca-Mont | (0.2) | 21 | $+1.5 \geq H_0 > +0.8$ | 0 (4.5) | 42[d)] |
| Na-Mont | (0.2) | 12 | $+3.3 \geq H_0 > +1.5$ | 0 (4.5) | 0[d)] |
| CaY | (0.5) | 680 | $-8.2 \geq H_0$ | 0 (4.5) | 40[d)] |
| NaY | (0.5) | 670 | $+1.5 \geq H_0 > +0.8$ | 0 (4.5) | 0[d)] |
| $CaSO_4$ | (0.5) | — | $+1.5 \geq H_0 > +0.8$ | 0 (4.5) | 4[d)] |
| $SiO_2$ | (0.5) | 585 | $+3.3 \geq H_0 > +1.5$ | 0 (4.5) | 0[d)] |

a) 2-Octanone (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) in $CH_2Cl_2$ (4 ml). Sn-, Fe-, Al-, Ca-, Na-Mont were dried at 120 °C and 0.5 Torr for 3 h. CaY, NaY, $SiO_2$, $CaSO_4$ were dried at 180 °C and 0.5 Torr for 2 h. b) Maximum acid strengths were determined with Hammett indicators in benzene. c) It is difficult to judge color changes of Hammett indicators because Fe-Mont is colored. d) These yields were estimated with GC (OV-1, 25 m).

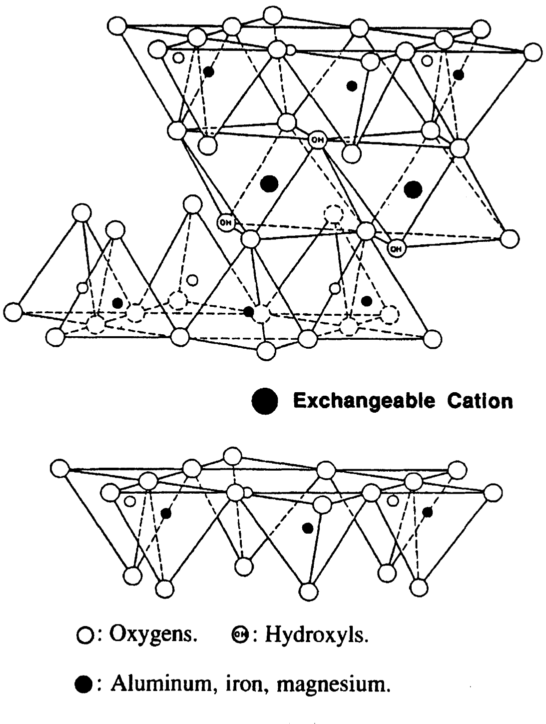


Fig. 1. Structure of clay montmorillonite.

Table 2. $CF_3SO_3H$ and $CF_3SO_3SiMe_3$-Catalyzed Cyanosilylation of Heptanal[a)]

| Catalyst | Temp/°C | (Time/h) | Yield/% |
|---|---|---|---|
| $CF_3SO_3H$ | 0 | (2) | 84 |
| $CF_3SO_3SiMe_3$ | 0 | (2) | 86 |

a) Heptanal (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) and catalyst (0.01 mmol) in $CH_2Cl_2$ (4 ml).

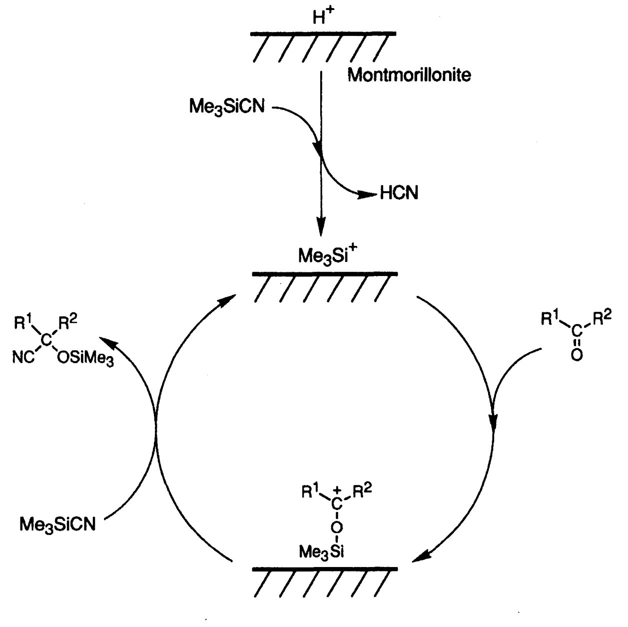


Fig. 2. Reaction mechanism of montmorillonite-catalyzed cyanosilylation of carbonyl compounds.

Sn-Mont and 50 for Fe-Mont, respectively. The amounts of active acid sites per unit weight of montmorillonite for the cyanosilylation are 0.35 mmol $g^{-1}$ on Sn-Mont and 0.10 mmol $g^{-1}$ on Fe-Mont.

**Cyanosilylation of 2-Octanone in the Presence of Solid Bases.** As shown in Table 3, we discovered that calcium fluoride ($CaF_2$), calcium metasilicate ($CaSiO_3$), and hydroxyapatite (HAp) can also promote the reaction of $Me_3SiCN$ with 2-octanone (Runs 1,2, and 3), although the solids are weaker acids than are $SiO_2$, Na-Mont, and NaY given in Table 1. Table 4 summarizes the maximum strengths of the acidity and basicity of the solids in Table 3, measured by means of

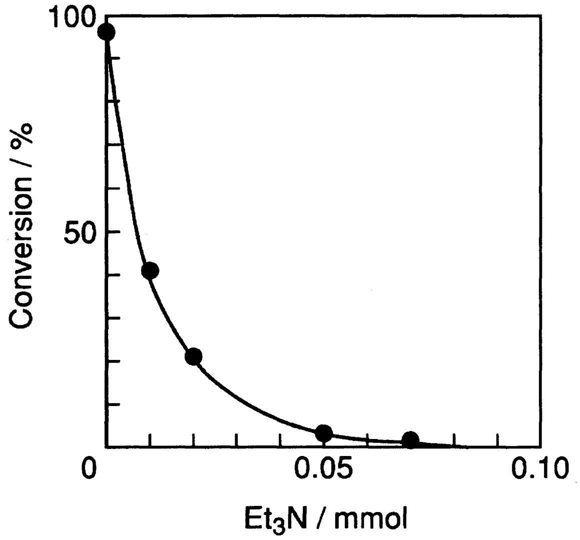


Fig. 3. Poisoning effects on the cyanosilylation of benzophenone on Sn-Mont. Sn-Mont (0.20 g) was dried at 120 °C and 0.5 Torr for 3 h. Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) in $CH_2Cl_2$ (5 ml) at 0 °C for 2 min after poisoning Sn-Mont with $Et_3N$.

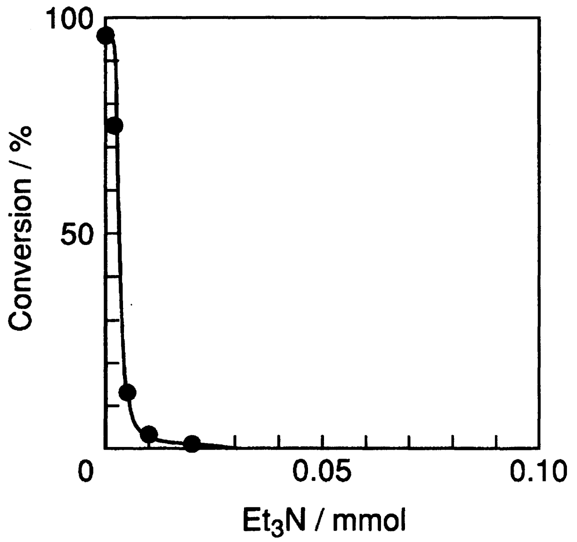


Fig. 4. Poisoning effects on the cyanosilylation of benzophenone on Fe-Mont. Fe-Mont (0.20 g) was dried at 120 °C and 0.5 Torr for 3 h. Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) in $CH_2Cl_2$ (5 ml) at 0 °C for 20 min after poisoning Fe-Mont with $Et_3N$.

Hammett indicators.[18)]

HAp has a chemical formula of $Ca_{10}(PO_4)_6(OH)_2$, and has both basic and acidic properties, and is well-known as a main component of biological hard tissue, such as teeth and bone.[24)] $CaSiO_3$ is also known to have a basic character.[25)] The basic properties of HAp and $CaSiO_3$ were confirmed with Hammett indicators, as shown in Table 4. Metal fluorides have frequently been utilized as base agents in organic synthesis.[26)]

On the basis of these facts, it is rational to assume that the cyanosilylation of 2-octanone on $CaF_2$, $CaSiO_3$, and HAp is promoted by a base catalysis, not by an acid catalysis. In order to further clarify the catalysis of $CaF_2$ and HAp, the cyanosilylation of 2-octanone was examined using other metal halides and metal phosphates. Among the metal halides, such as KF, CsF, $CaCl_2$, KCl, and KI, only fluorides are active (Table 3, Runs 4—8). Considering that solubilized anions, such as complexes of 18-Crown-6 with KCN, $KN_3$, KSCN, and KOMe, are effective promoters for cyanosilylations of ketones,[8)] and that the above-mentioned fluorides are sparingly soluble in $CH_2Cl_2$, the fluoride anion sites on the solid surfaces of $CaF_2$, KF, and CsF seem to be responsible for the activation of $Me_3SiCN$. Concerning the metal phosphates, only basic phosphates, such as HAp and $K_3PO_4$,[27)] showed high catalytic activities (Runs 3 and 11 in Table 3). In contrast, acidic phosphates, such as $CaHPO_4$[28)] and $Ni_3(PO_4)_2$,[29)] showed hardly any activities (Runs 9 and 10 in Table 3), although they are more acidic than HAp and $K_3PO_4$. HAp has basic OH groups.[24b)] A basic site of $K_3PO_4$ is $PO_4^{3-}$.[27)] It can be summarized that rapid cyanosilylations using HAp and $K_3PO_4$ can be ascribed to the catalytic functions of basic $OH^-$ and $PO_4^{3-}$ on HAp and $K_3PO_4$.

Consequently, it is reasonable to expect that much stronger bases, calcium oxide (CaO)[30)] and magnesium oxide (MgO),[30)] can facilitate the cyanosilylation of 2-octanone more promptly compared with $CaF_2$ and HAp (Runs 12 and 13 in Table 3). The catalyses of CaO and MgO have been demonstrated on a variety of organic reactions: the isomerization of olefins;[31)] the hydrogenation of olefins;[32)] the addition of amines to dienes;[33)] and the aldol condensation of acetone.[34)] As expected, CaO and MgO, especially freshly prepared from $Ca(OH)_2$ and $Mg(OH)_2$, demonstrate remarkable acceleration of the cyanosilylation.

It was reported that CaO and MgO prepared from $Ca(OH)_2$ and $Mg(OH)_2$ at the temperatures ranging from 400 to 600 °C in vacuo have stronger basicities and larger surface areas than do commercially available CaO and MgO.[30,31b,33)] Strong solid bases, such as CaO and MgO, readily adsorb $CO_2$ and $H_2O$ in air on the surfaces to form carbonates and hydroxides.[30b,35)] $Ca(OH)_2$, $Mg(OH)_2$, and $CaCO_3$ catalyze the cyanosilylation very slowly, compared with CaO and MgO, as shown in Table 3 (Runs 15—17). Therefore, fresh CaO and MgO should be prepared prior to use, so as to obtain high catalytic activities in the present cyanosilylation.

**Cyanosilylation of Various Carbonyl Compounds in the Presence of Solid Acids and Bases.** The solid-catalyzed process was applied to the reactions of $Me_3SiCN$ with representative aliphatic and aromatic aldehydes and ketones in Tables 1, 3, 5, and 6. Among

Table 3. Cyanosilylation of 2-Octanone Using Various Basic Inorganic Solids[a]

| Run | Solid | (Amount/g) | Surface area m$^2$ g$^{-1}$ | Conditions Temp/°C (Time/h) | Yield % |
|---|---|---|---|---|---|
| 1 | $CaF_2$ | (0.5) | 6 | 0 (4.5) | 94 |
| 2 | $CaSiO_3$ | (0.5) | 112 | 0 (4.5) | 95 |
| 3 | HAp | (0.5) | 55 | 0 (0.5) | 96 |
| 4 | KF | (0.5) | <0.3 | 0 (4.5) | 20[e] |
| 5 | CsF | (0.5) | <0.3 | 0 (4.5) | 13[e] |
| 6 | $CaCl_2$ | (0.5) | — | 0 (4.5) | 0[e] |
| 7 | KCl | (0.5) | — | 0 (4.5) | 0[e] |
| 8 | KI | (0.5) | — | 0 (4.5) | 0[e] |
| 9 | $CaHPO_4$ | (0.5)[b] | — | 0 (4.5) | 2[e,f] |
| 10 | $Ni_3(PO_4)_2$ | (0.5)[b] | — | 20 (17) | 0[e,f] |
| 11 | $K_3PO_4$ | (0.5)[c] | 0.4 | 0 (7.5) | 93[f] |
| 12 | CaO | (0.2)[d] | 65 | 0 (0.2) | 96 |
| 13 | MgO | (0.2)[d] | 316 | 0 (0.2) | 97 |
| 14 | BaO | (0.5) | — | 0 (4.5) | 60[e] |
| 15 | $Ca(OH)_2$ | (0.2) | 15 | 0 (4.5) | 86[e] |
| 16 | $Mg(OH)_2$ | (0.2) | 18 | 0 (4.5) | 53[e] |
| 17 | $CaCO_3$ | (0.5) | — | 0 (4.5) | 18[e] |

a) 2-Octanone (1 mmol), $Me_3SiCN$ (1.2 mmol), and solid catalyst were mixed in $CH_2Cl_2$ (4 ml). Solids were pre-dried at 180 °C and 0.5 Torr for 2 h except for CaO, MgO, $Ca(OH)_2$, and $Mg(OH)_2$. b) Acidic phosphate. c) Basic phosphate. d) CaO and MgO were obtained by calcination from corresponding hydroxides at 500 °C and 0.5 Torr for 2 h. e) These yields were estimated with GC (OV-1, 25 m). f) Toluene as a solvent.

Table 4. Maximum Acid and Base Strengths of Various Inorganic Solids

| Solid | Calcination[a] temp/°C | Maximum acid strength[b] | Maximum base strength[b] |
|---|---|---|---|
| $CaF_2$ | 180 | $+6.8\geq H_0>+4.0$ | $+7.2>H_-$ |
| $CaSiO_3$ | 180 | $+1.5\geq H_0>+0.8$ | $+15.0>H_-\geq+9.3$ |
| HAp | 180 | $+3.3\geq H_0>+1.5$ | $+15.0>H_-\geq+9.3$ |
| HAp | 400 | $+1.5\geq H_0>+0.8$ | $+18.4>H_-\geq+15.0$ |
| $K_3PO_4$ | 180 | $+4.0\geq H_0>+3.3$ | $+18.4>H_-\geq+15.0$ |
| $Ni_3(PO_4)_2$ | 180 | $+1.5\geq H_0>+0.8$ | $+7.2>H_-$ |
| $CaHPO_4$ | 180 | $+1.5\geq H_0>+0.8$ | $+7.2>H_-$ |
| MgO[c] | 500 | $H_0>+6.8$ | $+26.5>H_-\geq+22.3$ |
| CaO[c] | 500 | $H_0>+6.8$ | $+33.0>H_-\geq+26.5$ |
| BaO | 180 | $H_0>+6.8$ | $+18.4>H_-\geq+15.0$ |
| $Ca(OH)_2$ | — | $H_0>+6.8$ | $+18.4>H_-\geq+15.0$ |
| $Mg(OH)_2$ | — | $H_0>+6.8$ | $+9.3>H_-\geq+7.2$ |
| $CaCO_3$ | 180 | $H_0>+6.8$ | $+7.2>H_-$ |

a) Calcined at 0.5 Torr for 2 h. b) Maximum acid and base strengths were determined by use of various Hammett indicators in benzene. c) Calcined from metal hydroxide.

heptanal, benzaldehyde, 2-octanone, acetophenone, and benzophenone, benzophenone was found to have the least reactivity toward $Me_3SiCN$. Therefore, we first describe a comparison among solid catalysts, and solvent effects, as well as a comparison between heterogeneous and homogeneous catalysts in the cyanosilylation of benzophenone.

When $Sn^{4+}$, $Fe^{3+}$, $Al^{3+}$, $Zn^{2+}$ ions-exchanged montmorillonites were compared, the Sn-Mont-catalyzed reaction completed in the shortest reaction time (Table 5), because the acidity order of the clays is Sn-Mont > Fe-Mont > Al-Mont > Zn-Mont in $CH_2Cl_2$.[20c]

In the solid-catalyzed cyanosilylation the solvent nature is closely associated with the solid catalysis. Table 7 demonstrates the solvent effect on the CaO-catalyzed cyanosilylation of benzophenone. As the dielectric constant increases, the reaction rate declines: hexane≈toluene≫1,2−dimethoxyethane(DME) > dichloromethane > acetonitrile. A polar solvent seems to hinder the interaction between $Me_3SiCN$ and a base site on the solid surface, due to competitive adsorption of massive polar solvents on the solid. Normally, a re-

Table 5. Cyanosilylation of Various Carbonyl Compounds in the Presence of Solid Acid and Homogeneous Acid Catalysts[a]

| Substrate | Catalyst (Amount) | Temp/°C (Time/h) | Yield[b] % |
|---|---|---|---|
| Heptanal | Fe-Mont (0.2 g) | 0 (0.3) | 93 (5) |
| | $ZnI_2$ (1 mol%) | 0 (0.2) | 93 (4) |
| | TMSOTf (1 mol%)[c] | 0 (2) | 87 (8) |
| Benzaldehyde | Fe-Mont (0.2 g) | 0 (0.2) | 96 |
| Acetophenone | Fe-Mont (0.2 g) | 0 (0.2) | 96 |
| Benzophenone | Sn-Mont (0.05 g) | 0 (0.1) | 99 |
| | Fe-Mont (0.05 g) | 0 (0.5) | 99 |
| | Al-Mont (0.05 g) | 0 (0.5) | 98 |
| | Zn-Mont (0.05 g) | 0 (1.8) | 98 |
| | $ZnI_2$ (10 mol%) | 0 (14) | 98 |
| | $ZnI_2$ (10 mol%) | 25 (2) | 98 |
| | TMSOTf (10 mol%)[c] | Reflux (20) | 51[d] |
| | $BF_3\cdot OEt_2$(5 mol%) | 0 (1) | 93[e] |

a) Substrate (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) in $CH_2Cl_2$ (4 ml). b) Figures in parentheses represent yields of by-products. c) Trimethylsilyl trifluoromethanesulfonate. d) Determined with GC (OV-1, 25 m). e) Cyanohydrin was obtained as another product in 5% yield.

Table 6. Cyanosilylation of Various Carbonyl Compounds in the Presence of Solid Base and Homogeneous Anionic Catalysts[a]

| Substrate | Catalyst[b] | Solvent | Temp/°C (Time/h) | Yield[c] % |
|---|---|---|---|---|
| Heptanal | $CaF_2$ | $CH_2Cl_2$ | 0 (0.2) | 96 (0) |
| | $CaSiO_3$ | $CH_2Cl_2$ | 0 (0.2) | 92 (5) |
| | HAp (180)[d] | $CH_2Cl_2$ | 0 (0.2) | 87 (11) |
| | CaO | $CH_2Cl_2$ | 0 (0.2) | 87 (11) |
| | MgO | $CH_2Cl_2$ | 0 (0.2) | 82 (13) |
| | KCN/18-crown-6 | $CH_2Cl_2$ | 0 (0.2) | 90 (9) |
| Benzaldehyde | $CaF_2$ | $CH_2Cl_2$ | 0 (0.5) | 99 |
| | HAp (180)[d] | $CH_2Cl_2$ | 0 (0.3) | 95 |
| | CaO | $CH_2Cl_2$ | 0 (0.2) | 96 |
| | MgO | $CH_2Cl_2$ | 0 (0.2) | 95 |
| Acetophenone | $CaF_2$ | $CH_2Cl_2$ | 0 (5) | 98 |
| | HAp (180)[d] | $CH_2Cl_2$ | 0 (1.3) | 96 |
| | HAp (400)[e] | $PhCH_3$ | 0 (0.1) | 96 |
| | CaO | $CH_2Cl_2$ | 0 (1.8) | 96 |
| | CaO | $PhCH_3$ | 0 (0.1) | 97[f] |
| | MgO | $CH_2Cl_2$ | 0 (1.8) | 96 |
| | MgO | $PhCH_3$ | 0 (0.1) | 95[f] |
| Benzophenone | $CaF_2$ | $CH_2Cl_2$ | Reflux (4) | 40[g] |
| | HAp (180)[d] | $CH_2Cl_2$ | 20 (18) | 94 |
| | HAp (400)[e] | $CH_2Cl_2$ | 0 (4) | 97 |
| | HAp (400)[e] | $PhCH_3$ | 0 (0.3) | 98 |
| | CaO | $CH_2Cl_2$ | 0 (6) | 99 |
| | CaO | $PhCH_3$ | 0 (1.6) | 98 |
| | MgO | $CH_2Cl_2$ | 0 (6) | 97 |
| | MgO | $PhCH_3$ | 0 (0.8) | 99 |
| | KCN/18-crown-6 | $PhCH_3$ | 25 (8) | 96 |

a) Substrate (1 mmol) was treated with $Me_3SiCN$ (1.2 mmol) in solvent (4 ml). b) $CaF_2$ (0.5 g), $CaSiO_3$ (0.5 g), HAp (0.5 g), CaO (0.2 g), MgO (0.2 g), and KCN/*cis*-dicyclohexano-18-crown-6 (10 mol%) were used. c) Figures in parentheses represent yields of by-products. d) Dried at 180 °C and 0.5 Torr for 2 h. e) Dried at 400 °C and 0.5 Torr for 2 h. f) Contaminated with a trace amount of silyl enol ether (CaO: 0.5%, MgO: 1%). g) Determined with GC (OV-1, 25 m).

Table 7. Solvent Effect on CaO-Catalyzed Cyanosilylation of Benzophenone[a)]

| Solvent | Dielectric constant (20 °C) | Conditions Temp/ °C | (Time/h) | Yield % |
|---|---|---|---|---|
| *n*-Hexane | 1.9 | 0 | (2) | 98 |
| $PhCH_3$ | 2.4 | 0 | (2) | 99 |
| DME[b)] | 7.0 | 0 | (4) | 92[c)] |
| $CH_2Cl_2$ | 9.1 | 0 | (4) | 75[c)] |
| $CH_3CN$ | 37.5 | 0 | (4) | 35[c)] |

a) Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.6 mmol) and CaO (0.2 g) in solvent (hexane: 6 ml, other solvents: 4 ml). CaO was prepared from $Ca(OH)_2$ by calcination at 500 °C and 0.5 Torr for 2 h. b) 1,2-Dimethoxyethane. c) The cyanosilylation was quenched after 4 h, and yields were compared with GC (OV-1).

Table 8. Solvent Effect on Sn-Mont-Catalyzed Cyanosilylation of Benzophenone[a)]

| Solvent | Conditions Temp/ °C | (Time/h) | Yield % |
|---|---|---|---|
| $CH_2Cl_2$ | 0 | (0.1) | 99 |
| $PhCH_3$ | 0 | (0.2) | 98 |
| DME[b)] | 20 | (24) | 49[c)] |
| $CH_3CN$ | 20 | (24) | 20[c)] |

a) Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.6 mmol) and Sn-Mont (0.05 g) in solvent (4 ml). Sn-Mont was dried at 120 °C and 0.5 Torr for 3 h. b) 1,2-Dimethoxyethane. c) The cyanosilylation was quenched after 24 h, and yields were compared with GC (OV-1).

action catalyzed by homogeneous promoters, such as fluoride anions, requires aprotic polar solvents, such as tetrahydrofuran, DME, and acetonitrile, to dissolve the promoters. There is a distinct difference in the requirements for a reaction solvent between heterogeneous and homogeneous reactions.

On solid acids, the reaction proceeds quickly in $CH_2Cl_2$ and toluene at 0 °C, but slowly in dimethoxyethane and acetonitrile, even at 20 °C, as shown in Table 8. Dichloromethane is the most suitable in the solid acid-catalyzed cyanosilylation.

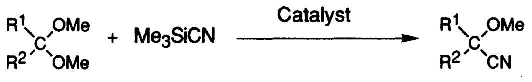
When the catalytic abilities for the cyanosilylation of benzophenone are compared between solid and homogeneous promoters, the superiority of the solid catalysis is apparent, as shown in Tables 5 and 6. Most of heterogeneous catalyst systems listed in the Tables enable the cyanosilylation to proceed at lower reaction temperatures, or to complete more rapidly, as compared with the use of conventional, homogeneous catalysts.

We must comment on the reaction of heptanal bearing active hydrogens: When strong solid acids or bases were applied, a small amount of undetermined by-products with high boiling points were formed. In order to suppress the formation of any by-product, $CaF_2$ bearing both weakly basic and acidic properties was found to be the catalyst of choice for inducing the cyanosilylation quantitatively.

In addition to the carbonyl compounds mentioned above, enolizable ketones also undergo cyanosilylation on a solid acid and base. For instance, ethyl acetoacetate in $CH_2Cl_2$ was cyanosilylated on Sn-Mont and HAp at room temperature for 8 h to afford ethyl 3-cyano-3-(trimethylsiloxy)butanoate in 79 and 76% yield, respectively.[50)]

As a summary, it was revealed that strongly acidic clays (Sn-Mont, Fe-Mont) and solid bases (CaO, MgO, HAp, and $CaF_2$) are appropriate solid catalysts for reactions of saturated carbonyl compounds with $Me_3SiCN$. In addition, these heterogeneous systems have another experimental advantage in that the work-up only requires filtration of the solids without any neutralization and extraction procedures.

**Cyanation of Acetals.** Table 9 shows the results of the reactions of various dimethyl acetals with $Me_3SiCN$ in the presence of solid catalysts (Eq. 4).



3 4

(4)

Acetals are reactive toward nucleophiles only when coming into contact with acid. In order to elucidate the difference in the catalytic roles of Fe-Mont, CaO, MgO, HAp, $CaSiO_3$, and $CaF_2$, the reactions of benzaldehyde dimethyl acetal with $Me_3SiCN$ were conducted using the solids in $CH_2Cl_2$ at 0 °C. In the presence of strongly acidic Fe-Mont, the acetal reacted with $Me_3SiCN$ smoothly to give 2-methoxy-2-phenylethanenitrile in 96% yield (Run 2). In contrast, CaO, MgO, HAp, $CaSiO_3$, and $CaF_2$ showed no promotion for the reaction, although HAp, $CaSiO_3$, and $CaF_2$ have weakly acidic sites, as shown in Table 4. This fact indicates that the acid strengths of those solids are not enough to activate the acetal to react with $Me_3SiCN$.

Acidic Fe-Mont and Sn-Mont behaved as effective catalysts for the reactions of various dimethyl acetals with $Me_3SiCN$, affording the corresponding 2-methoxyalkanenitriles (**4**) in good yields. In the solid acid-

Table 9. Cyanation of Acetals[a)]

| Run | Dimethyl acetal |  | Catalyst | Conditions |  | Yield |
|---|---|---|---|---|---|---|
|  | R$^1$ | R$^2$ | (Amount/g) | Temp/°C | (Time/h) | % |
| 1 | Ph | H | Fe-Mont (0.2) | 0 | (0.2) | 92[c)] |
| 2 | Ph | H | Fe-Mont (0.2) | 0 | (0.5) | 96 |
| 3 | Ph | H | CaO (0.2) | 24 | (14) | 0[d)] |
| 4 | Ph | H | MgO (0.2) | 20 | (24) | 0[d)] |
| 5 | Ph | H | HAp (0.5)[b)] | 22 | (15) | 0[d)] |
| 6 | Ph | H | $CaSiO_3$ (0.5) | 25 | (24) | 0[d)] |
| 7 | Ph | H | $CaF_2$ (0.5) | 20 | (19) | 0[d)] |
| 8 | $n$-$C_6H_{13}$ | H | Fe-Mont (0.2) | 0 | (0.2) | 97 |
| 9 | $n$-$C_6H_{13}$ | Me | Fe-Mont (0.2) | 0 | (0.2) | 96 |
| 10 | Ph | Ph | Fe-Mont (0.2) | 0 | (2) | 99 |
| 11 | Ph | Ph | Sn-Mont (0.2) | 0 | (0.2) | 99 |

a) Acetal (1 mmol), $Me_3SiCN$ (1.6 mmol), and $CH_2Cl_2$ (5 ml) were used. The reaction was performed through the addition of acetal to a suspension of Fe-Mont and $Me_3SiCN$ in $CH_2Cl_2$. b) Calcined at 400 °C. c) The reaction was performed through the addition of $Me_3SiCN$ to a suspension of Fe-Mont and benzaldehyde dimethyl acetal in $CH_2Cl_2$. With this addition procedure, $\alpha$-trimethylsiloxy nitrile was obtained in 5% yield in addition to $\alpha$-methoxy nitrile. d) Acetal was recovered completely.

catalyzed cyanation of acetals, the addition of acetal to a suspended mixture of $Me_3SiCN$ and acidic clay is more preferable to the addition of $Me_3SiCN$ to a mixture of acetal and clay, since any contact of acetal with acidic clay in the absence of $Me_3SiCN$ caused a hydrolysis of the acetal with water contained in the clay, as shown in Runs 1 and 2 in Table 9.

It was reported that the addition of $Me_3SiCN$ to acetals was performed using $BF_3\cdot OEt_2$,[5a,5c] $SnCl_2$,[5a,5c] $SnCl_4$,[6] $NiCl_2$,[9] $CoCl_2$,[9] and $[Rh(cod)Cl]_2$.[9] As compared to the homogeneous acid catalyses, two solid acids (Fe-Mont and Sn-Mont) were found to have higher catalytic activities.

**Estimation of the Amounts of Active Basic Sites on CaO and Hydroxyapatite.** In order to determine the amount of base sites on solid bases responsible for the activation of $Me_3SiCN$, poisoning was performed using a probe acid in the following manner: A toluene solution with a specified amount of $CCl_3COOH$ was added to a suspension of HAp (0.50 g) or CaO (0.20 g) in toluene; the mixture was then stirred at 0 °C for 0.5 h. After poisoning, benzophenone (1 mmol) and $Me_3SiCN$ (1.6 mmol) were added successively; the mixture was then stirred at 0 °C. Figures 5 and 6 represent the results of poisoning with $CCl_3COOH$ in the cyanosilylation of benzophenone on HAp and CaO.

Both HAp and CaO were drastically deactivated with the addition of a small amount of $CCl_3COOH$: HAp was completely poisoned with 0.074 mmol of $CCl_3COOH$. As for CaO, a large drop in the catalytic activity was observed upon the addition of $CCl_3COOH$ in the range of 0 to 0.075 mmol. However, adding more acid could not stop the reaction completely. It seems that new oxide surfaces of CaO were exposed after some $(CCl_3COO)_2Ca$, which formed on the CaO surface, was dissolved into a toluene solution. In fact, white-brown powdery salts were obtained after evaporating the toluene solution part of the reaction mixture. Accordingly, the amount of active base sites on CaO could be estimated to be 0.056 mmol per 0.2 g of CaO by extrapolation of the poisoning curve in Fig. 6.

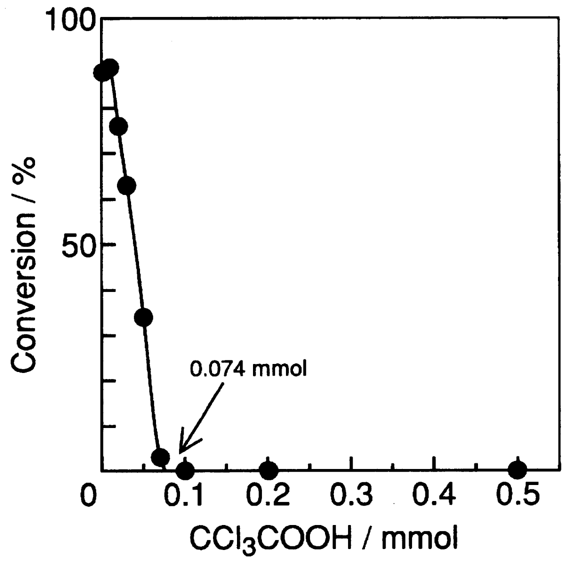


Fig. 5. Poisoning effects on the cyanosilylation of benzophenone on hydroxyapatite. HAp (0.50 g) was dried at 400 °C and 0.5 Torr for 2 h. Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.6 mmol) in $PhCH_3$ (6 ml) at 0 °C for 10 min after poisoning HAp with $CCl_3COOH$.

It was proved that HAp and CaO work as base catalysts in the cyanosilylation of carbonyl compounds. The turnover numbers of the catalytic cycles are 14 for HAp and 18 for CaO. The amounts of effective base sites per unit weight of the solid bases are 0.15 mmol g$^{-1}$ on HAp and 0.27 mmol g$^{-1}$ on CaO.

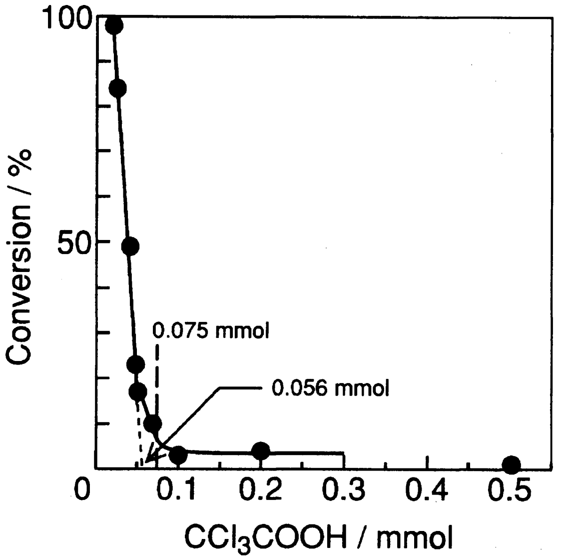
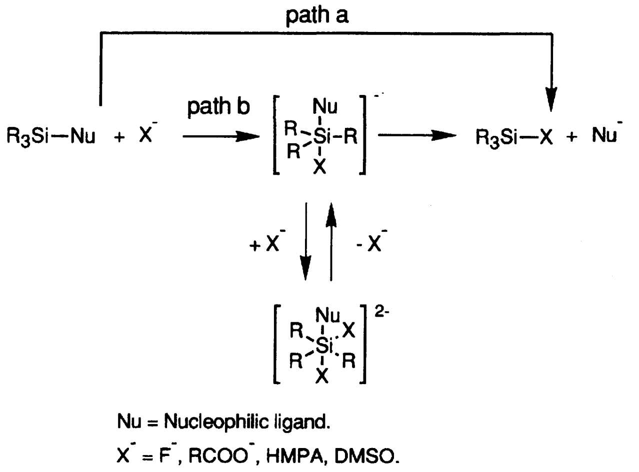


Fig. 6. Poisoning effects on the cyanosilylation of benzophenone on CaO. CaO (0.20 g) was prepared from $Ca(OH)_2$ at 500 °C and 0.5 Torr for 2 h. Benzophenone (1 mmol) was treated with $Me_3SiCN$ (1.6 mmol) in $PhCH_3$ (6 ml) at 0 °C for 0.5 h after poisoning CaO with $CCl_3COOH$.

**Reaction Mechanism of Solid Base-Catalyzed Cyanosilylation.** The reactions of silicon nucleophiles with electrophiles provoked by fluoride anions proceed via the direct formation of anionic nucleophiles through fluorodesilylation[36,40a] (path a) or via the formation of hypervalent silicon intermediates with penta- or hexa-coordination states (path b), which result from the coordination of fluorides to silicon nucleophiles (Eq. 5).[37,40e,41b]



(5)

For instance, diverse fluorides, such as tetrabutylammonium fluoride (TBAF),[40b] tris(dialkylamino)sulfonium difluorotrimethylsilicate (TASF),[40c] and CsF,[40d] catalyze the additions of various organosilicon nucleophiles,[36b] such as allylsilanes,[38,39] silyl enol ethers,[40] silyl ketene acetal,[40] and hydrosilanes,[41] to carbonyl compounds via the above-mentioned activation mechanisms. Several silicon compounds in hypervalent states were isolated and confirmed with $^{29}Si$ NMR and X-ray diffractometry studies.[42] It was also found that isolated penta-coordinated silicon compounds, such as allylsilicates[38,43,44] and hydridosilicates,[43,45] can participate in nucleophilic additions to carbonyl compounds. Besides fluoride ions, nucleophilic oxygens of carboxylate ions,[46] hexamethylphosphoric triamide (HMPA),[41b,46] and dimethyl sulfoxide[46] are known to have strong affinities toward silicon and to activate organosilicons.

It was recently reported that tetrabutylammonium cyanide can coordinate to $Me_3SiCN$ to form tetrabutylammonium dicyanotrimethylsilicate (Eq. 6), which was isolated and characterized well.[47]

$$Me_3SiCN + Bu_4N^+CN^- \rightleftharpoons [Me_3Si(CN)_2]^- \cdot N^+Bu_4 \qquad (6)$$

The base sites on the solid bases listed in Table 3 are fluoride ions on metal fluorides, $OH^-$ on HAp, $PO_4^{3-}$ on $K_3PO_4$, and lattice oxide anions ($O^{2-}$) on CaO and MgO.[48]

Based on the activation mechamism of organosilicons with the siliconophiles mentioned above, it is reasonable to consider that the base sites on the solid bases coordinate with $Me_3SiCN$ to form hypervalent silicate, as shown in Fig. 7, followed by releasing nucleophilic cyanide to carbonyl functions.[51,52] A similar activation mechanism of organosilicons via penta-coordinated species was proposed by Corriu et al. in solid CsF-catalyzed reactions using tetraalkoxysilanes.[41a]

To recognize the intermediate state of $Me_3SiCN$ on a solid base, an adsorption experiment of $Me_3SiCN$ on CaO was attempted. CaO was chosen as a representative solid base, due to its high catalytic activity for cyanosilylation, large specific surface area, and simple crystal structure.

$Me_3SiCN$ (1.043 mmol) was mixed with CaO (0.198 g) in 1-chlorooctane (solvent, 5.0 ml) together with nonane (internal standard for GC analysis) at 20 °C. The amounts of $Me_3SiCN$ and hexamethyldisiloxane ($Me_3SiOSiMe_3$) formed in the supernatant solution

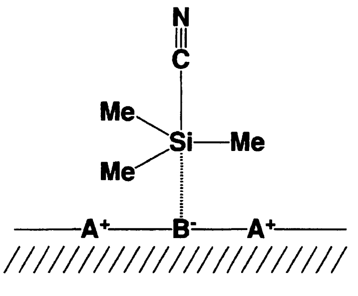


Fig. 7. Activation of $Me_3SiCN$ on solid bases. $A^+$: Cation site. $B^-$: Anion site ($F^-$, $OH^-$, $PO_4^{3-}$, $O^{2-}$).

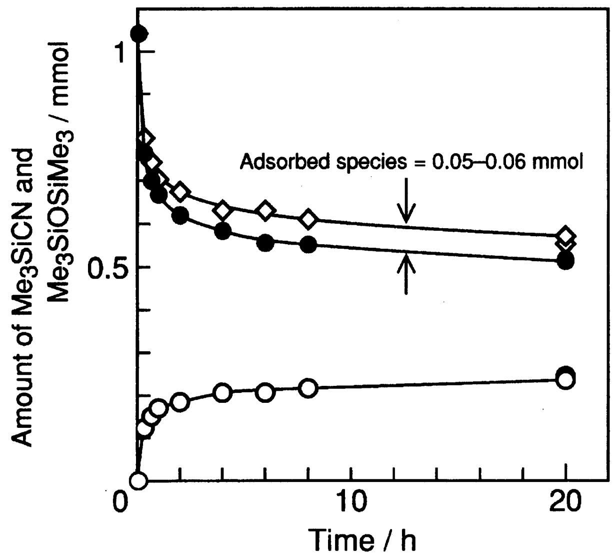


Fig. 8. Time-dependent adsorption of $Me_3SiCN$ on CaO. $Me_3SiCN$ (1.043 mmol) was mixed with CaO (0.198 g) in 1-chlorooctane (5.0 ml) at 20 °C. (●) Amounts of $Me_3SiCN$. (○) Amounts of $Me_3SiOSiMe_3$. (◇) Amounts of $Me_3SiCN$ calculated by subtracting the quantity of $Me_3SiCN$ required for the formation of $Me_3SiOSiMe_3$ from the original $Me_3SiCN$ amount (1.043 mmol).

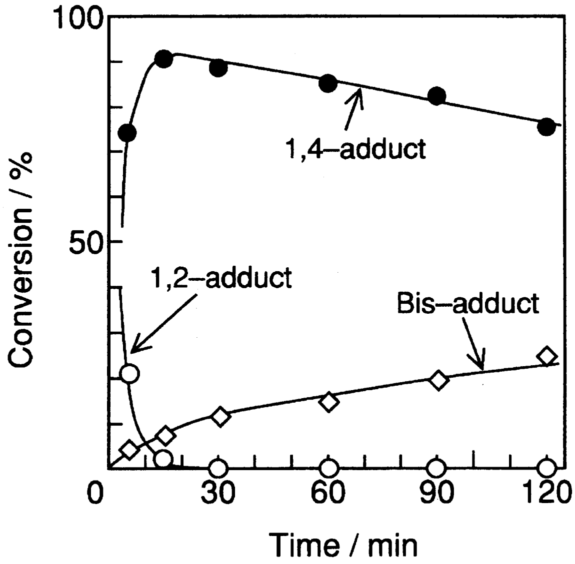
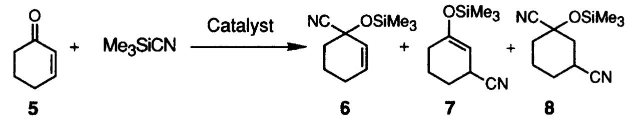


Fig. 9. Time-dependent product distribution in cyanosilylation of 2-cyclohexen-1-one catalyzed by Fe-Mont. Fe-Mont (0.2 g), 2-cyclohexen-1-one (1 mmol), and $Me_3SiCN$ (1.6 mmol) were mixed in $CH_2Cl_2$ (4 ml) at 0 °C.

were analyzed with a capillary GC (OV-1, 25 m) at intervals. Figure 8 represents the adsorption of $Me_3SiCN$ on CaO. The black and white circles indicate the amounts of $Me_3SiCN$ and $Me_3SiOSiMe_3$ in a solution part of the mixture, respectively. The $Me_3SiCN$ amount in the solution decreased with time, and the formation of $Me_3SiOSiMe_3$ was concurrent: $Me_3SiOSiMe_3$ was assumed to form via hydrolysis of two moles of $Me_3SiCN$ with one mole of $H_2O$ remaining in CaO. The white diamond marks show the residual amounts of $Me_3SiCN$, which are calculated by subtracting the quantity of $Me_3SiCN$ required for the formation of $Me_3SiOSiMe_3$ from the original $Me_3SiCN$ amount (1.043 mmol). These calculated values (◇) do not coincide with the observed ones (●). In a separate adsorption experiment, no adsorption of $Me_3SiOSiMe_3$ on CaO was confirmed. Accordingly, the discrepancy (0.05—0.06 mmol) between the calculated and observed amounts of $Me_3SiCN$ above can be attributed to the adsorption of $Me_3SiCN$ on CaO. This value of the adsorbed species well corresponds to the amount of active base sites on CaO (0.056 mmol) estimated by the poisoning test in Fig. 6.

**Reaction of 2-Cyclohexen-1-one with $Me_3SiCN$ in the Presence of Solid Acids and Bases.** Table 10 shows results of the cyanosilylation of 2-cyclohexen-1-one (**5**) using various catalysts. 2-Cyclohexen-1-one reacted with $Me_3SiCN$ to afford three products: 1-trimethylsiloxy-2-cyclohexene-1-carbonitrile (**6**, 1,2-adduct), 3-trimethylsiloxy-2-cyclohexene-1-carbonitrile (**7**, 1,4-adduct), and 1-trimethylsiloxy-1,3-cyclohexanedicarbonitrile (**8**, bis-adduct) (Eq. 7). Compound **8** was produced via the extra cyanosilylation of 3-oxocyclohexane-1-carbonitrile formed through hydrolysis of **7**.



(7)

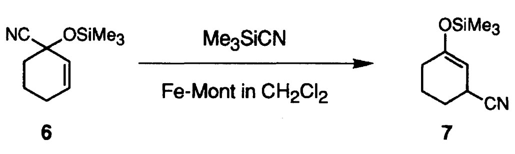
As mentioned before, the acid strength of cation-exchanged montmorillonite depends on electron negativity, polarizing power, and hydration enthalpy of the cation exchanged.[20] Thus, the acidity order of cation-exchanged montmorillonites is estimated to be Sn-Mont > Fe-Mont > Al-Mont > Ni-Mont. The reaction using Ni-Mont predominantly afforded the 1,2-adduct, **6** (Run 1). In contrast, the 1,4-adduct **7** was obtained regioselectively in the presence of stronger solid acids, such as Al-Mont and Fe-Mont (Runs 2 and 3). Dichloromethane was found to be the best solvent to produce a 1,4-adduct among the five solvents in Runs 3—7. In order to clarify the origin of the attainment of high 1,4-regioselectivity in the Fe-Mont-catalyzed reaction, the cyanosilylation of 2-cyclohexen-1-one was periodically monitored with GC, as shown in Fig. 9. Besides 1,4-adduct, 1,2-adduct was also produced during the extremely initial stage, and was promptly isomerized to the 1,4-adduct with the aid of a strong acid catalysis of Fe-Mont. In fact, it was confirmed that the 1,2-adduct (1 mmol, 1,2/1,4 = 98/2) was converted into the 1,4-

Table 10. Cyanosilylation of 2-Cyclohexen-1-one in the Presence of Various Catalysts[a)]

| Run | Catalyst[b)] | Solvent | Temp/°C | Yield/% | | |
|---|---|---|---|---|---|---|
| | | | (Time/h) | **6**+**7** | **6**/**7** | **8** |
| 1 | Ni-Mont | $CH_2Cl_2$ | 0 (0.3) | 86 | 61/39 | 3 |
| 2 | Al-Mont | $CH_2Cl_2$ | 0 (0.4) | 78 | 8/92 | 8 |
| 3 | Fe-Mont | $CH_2Cl_2$ | 0 (0.4) | 84 | 8/92 | 5 |
| 4 | Fe-Mont | $CH_3CN$ | 0 (0.4) | 73 | 80/20 | 10 |
| 5 | Fe-Mont | DME[c)] | 0 (0.4) | 85 | 43/57 | 4 |
| 6 | Fe-Mont | *n*-Hexane | 0 (0.4) | 85 | 57/43 | 1 |
| 7 | Fe-Mont | $PhCH_3$ | 0 (0.4) | 86 | 36/64 | 2 |
| 8 | Sn-Mont | $CH_2Cl_2$ | 0 (0.2) | 73 | 1/>99 | 16 |
| 9 | Sn-Mont/MS4A | $CH_2Cl_2$ | 0 (0.2) | 94 | 0/100 | 1 |
| 10 | $ZnI_2$ | $CH_2Cl_2$ | 0 (0.4) | 90 | 73/27 | 1 |
| 11 | $ZnI_2$ | $CH_2Cl_2$ | 40 (6) | 75 | 4/96 | 11 |
| 12 | $CF_3SO_3SiMe_3$ | $CH_2Cl_2$ | 0 (0.4) | 90 | 74/26 | 0 |
| 13 | $CF_3SO_3SiMe_3$ | $CH_2Cl_2$ | 40 (8) | 92 | 66/34 | 1 |
| 14 | HAp | $PhCH_3$ | 0 (5) | 30[d)] | 81/19 | 49 |
| 15 | HAp | $PhCH_3$ | −40 (2) | 80 | >99/1 | 5 |
| 16 | CaO | $PhCH_3$ | −40 (0.3) | 88 | >99/1 | 1 |
| 17 | MgO | $PhCH_3$ | −40 (0.5) | 80 | >99/1 | 2 |
| 18 | KCN/18-crown-6 | $PhCH_3$ | 25 (2) | 91 | 97/3 | 0.2 |

a) 2-Cyclohexen-1-one (1 mmol) was treated with $Me_3SiCN$ (1.6 mmol) in solvent (4 ml). b) Amounts of cation-exchanged montmorillonite, MS4A, CaO, and MgO were 0.2 g. HAp (0.5 g) was used. Amounts of $ZnI_2$, $CF_3SO_3SiMe_3$, and KCN/*cis*-dicyclohexano-18-crown-6 were 10 mol%. c) 1,2-Dimethoxyethane. d) The reaction was quenched at 79% conversion.

adduct (conversion 92%, 1,2/1,4=11/89) when treated with $Me_3SiCN$ (2 mmol) in the presence of Fe-Mont (0.2 g) at 0 °C for 2 h (Eq. 8). Interestingly, this isomerization did not take place without $Me_3SiCN$. The rate of isomerization from 1,2- to 1,4-adducts was increased in proportion to the amount of $Me_3SiCN$ added. For instance, in the presence of 0.1, 1.0, and 2.0 mmol of $Me_3SiCN$ in $CH_2Cl_2$, the conversions of **6** to **7** were 3, 22, and 40%, respectively, after 30-min of contact with Fe-Mont. Based on these findings, it can be concluded that the isomerization of **6** to **7** is brought about not via a direct transfer of a cyano group from 1- to 3-position in **6**, but by an attack of another $Me_3SiCN$ on 3-position, concurrently liberating a cyano group at the 1-position to give **7**.



(8)

The selective formation of 1,4-adduct is possible only in dichloromethane; other solvents, such as acetonitrile, 1,2-dimethoxyethane, hexane, and toluene, are not adequate.

The most acidic montmorillonite, Sn-Mont affords the 1,4-adduct **7** exclusively. However, the bis-adduct **8** was also produced as a by-product via an extra cyanosilylation of 3-oxocyclohexanecarbonitrile, which was produced from **7** with residual water in Sn-Mont (Run 8). When molecular sieves 4A were added to the reaction system, the hydrolysis was suppressed, and the yield of **7** greatly improved up to 94% (Run 9).

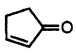
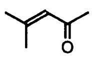
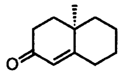
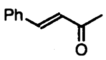
In the presence of homogeneous catalysts, $ZnI_2$ and $CF_3SO_3SiMe_3$, the 1,2-adduct **6** was produced predominantly under the same reaction conditions (Runs 10 and 12). The isomerization barely occurred at 0 °C. In the $ZnI_2$-catalyzed reaction, the 1,4-adduct **7** was finally obtained selectively at a higher reaction temperature of 40 °C, and after longer reaction time of 6 h (Run 11), compared with the Sn-Mont-catalyzed reaction. As for $CF_3SO_3SiMe_3$, isomerization hardly took place, even under reflux (Run 13).

On the other hand, the 1,2-adduct was regioselectively produced in toluene at −40 °C by use of solid base catalysts, such as HAp, CaO, and MgO. On the basic solids, the isomerization of 1,2-adduct did not occur at −40 °C (Runs 15, 16, and 17). This solid base system is evidently efficient in selective 1,2-adduct formation when compared with a conventional, homogeneous system of $K^+CN^-$/18-Crown-6 in Run 18.

**Reactions of $Me_3SiCN$ and Various α,β-Unsaturated Ketones.** For the purpose of unveiling the usefulness and limitations of the solid-catalyzed cyanosilylations, several α,β-unsaturated ketones were applied (Table 11).

4-Methyl-3-penten-2-one and 6-methylbicyclo[4.4.0]-dec-1-en-3-one ((*R*)-(−)-4,4a,5,6,7,8-hexahydro-4a-methylnaphthalen-2(3*H*)-one, **9**) underwent cyanosilylation to give 1,2- and 1,4-adducts in highly regioselective

Table 11. Cyanosilylation of Various $\alpha,\beta$-Unsaturated Ketones[a)]

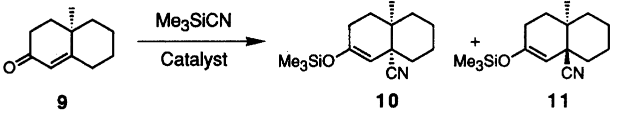
| Substrate | Catalyst | Solvent | Temp/°C (Time/h) | Yield % | Ratio 1,2-/1,4- |
|---|---|---|---|---|---|
|  | Fe-Mont/MS4A | $CH_2Cl_2$ | −10 (0.7) | 84 | 2/98 |
| | CaO | $PhCH_3$ | −45 (0.8) | Complex mixture | |
|  | Fe-Mont/MS4A | $CH_2Cl_2$ | 0 (10) | 94 | 1/>99 |
| | CaO | $PhCH_3$ | −40 (0.7) | 93 | 100/0 |
|  | Sn-Mont/MS4A | $CH_2Cl_2$ | −20 (4) | 97 | 1/99 (28/72)[b)] |
| | CaO | $PhCH_3$ | −40 (2) | 95 | 100/0 |
|  | Sn-Mont/MS4A | $CH_2Cl_2$ | 0 (0.2) | 97 | >99/1 |
| | CaO | $PhCH_3$ | −40 (0.5) | 97 | 100/0 |

a) Solid catalyst (0.2 g), MS4A (0.2 g), substrate (1 mmol), and $Me_3SiCN$ (1.6—3.0 mmol) were mixed in solvent (5 ml). b) *cis* : *trans* Ratio was shown in parenthesis. Homogeneous methods: HCN–$Et_3Al$ (tetrahydrofuran, 25 °C, 8 h), quantitative yield, *cis* : *trans*=29 : 71.[13d)]; $Me_3SiCN$–$Et_3Al$ (toluene, 25 °C, 20 h), quantitative yield, *cis* : *trans*=31 : 69.[5c)]

ways, depending upon the use of an acid or base.

The conjugate hydrocyanation of cyclic $\alpha,\beta$-unsaturated ketones has been utilized in total syntheses of complex natural products. Nagata and his co-workers discovered efficient hydrocyanation methods involving the combined use of hydrogen cyanide and alkylaluminum (HCN–$R_3Al$) or alkylcyanoaluminum ($R_2AlCN$).[13)] These methods require a stoichiometric amount of aluminum reagents. Compound **9** underwent conjugate hydrocyanation by use of HCN–$Et_3Al$ or $Et_2AlCN$, and the *cis* : *trans* ratio of 1,4-adduct was controlled by the choice of either kinetic or thermodynamic control:[13d)] The more valuable *trans* 1,4-adduct was predominant (*cis*: *trans*=29 : 71) under kinetic conditions, in which the quantitative hydrocyanation was performed in tetrahydrofuran at 25 °C in the presence of HCN and 5 equivalents of $Et_3Al$.

Utimoto and his co-workers reported a new method using $Me_3SiCN$ instead of HCN:[5b,5c)] The cyanosilylation of **9** with $Me_3SiCN$ and 2 equivalents of $Et_3Al$ in toluene at 25 °C quantitatively gave **10** and **11** in a ratio of 29 : 71. They also discovered a catalytic process using $Me_3SiCN$ and Lewis acid catalysts without a solvent, affording **11** (56—67% selectivities).[5c)]



**9** **10** **11**

(9)

In comparison with the above precedents, the cyanosilylation of **9** using solid catalyst, Sn-Mont/MS4A proceeds smoothly at a lower temperature to afford 1,4-adducts, **10** and **11**, exclusively in a *cis* : *trans* ratio of 28 : 72. On the basis of the fact that the *cis*-isomer **10** is thermodynamically more stable than the *trans*-isomer **11**, the present acid clay-promoted cyanosilylation of **9** seems to be kinetically controlled. The effectiveness of the solid acid catalysis and the exclusive formation of the 1,4-adduct with a high yield are facts worth mentioning concerning the introduction of a cyanide group to angular positions of polycyclic compounds.

The cyanosilylation of 2-cyclopenten-1-one on CaO yields a complex mixture of 1,2-, 1,4-, and bis-adducts, since 1,2-adduct is very labile. 4-Phenyl-3-buten-2-one exclusively gives 1,2-adduct, even by use of a strong solid acid, Sn-Mont. The isomerization of 1,2- to 1,4-adduct is too slow.

A work-up of the heterogeneous reaction system simply demands filtering the solids off. Removal of excess aluminum reagents is occasionally a tedious work-up process.

## Experimental

**Measurement.** The $^1$H NMR spectra were recorded with Hitachi R-600 (60 MHz) and Varian GEMINI 200 (200 MHz) spectrometers. The $^{13}$C NMR spectra were recorded with Varian GEMINI 200 (50 MHz) or Varian VXR 500 (125 MHz) spectrometers. The NMR spectra were measured in $CDCl_3$ or $C_6D_6$ with tetramethylsilane (TMS) as an internal standard. The infrared (IR) spectra were recorded in $CCl_4$ with a JASCO IR-810 spectrometer. The gas chromatograms were obtained on a Shimadzu GC-8A with a flame ionization detector and a capillary column (OV-1 Bonded, 25 m, OV-17 Bonded, 50 m, or PEG-HT Bonded, 25 m).

**Measurements of Specific Surface Area, and Acid and Base Strengths of Solids.** The solids were predried at specified temperatures prior to measurements. The specific surface areas were determined by the BET method with a Shibata Surface Analyzer (Model 4200). The maximum acid and base strengths were determined by use of appropriate Hammett indicators according to the following procedure.[18b,18c] The pre-dried solid (0.1 g) was immersed in dry benzene (2 ml) in a vial. One drop of a 0.1 wt% benzene solution of a Hammett indicator was added; the color change of the indicator on the solid surface was judged after 12 h.

**Materials (Catalysts and Reagents).** Cation-exchanged montmorillonites were prepared according to the procedure shown in the next section, and dried at 120 °C and below 0.5 Torr (1 Torr=133.322 Pa) for 3 h in an oil bath. Powdery hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$, Nacalai Tesque Inc.) was dried at 180 and 400 °C and below 0.5 Torr for 2 h in an electric furnace. CaO and MgO were prepared from $Ca(OH)_2$ and $Mg(OH)_2$ (Kishida Chemical Co.) by calcination at 500 °C and below 0.5 Torr for 2 h in an electric furnace. Zeolite CaY (Cation contents: $Ca^{2+}$ 67%, $Na^+$ 33%) prepared by a treatment of NaY (Shokubai Kasei Co.:ZCP-50) with an aqueous $CaCl_2$ solution[14c] was dried at 180 °C and below 0.5 Torr for 2 h. $CaF_2$, calcium metasilicate ($CaSiO_3 \cdot xH_2O$, $x$=2—3), and $K_3PO_4$ (Kishida Chemical Co.) were dried at 180 °C and below 0.5 Torr for 2 h. $SiO_2$ (Fuji-Davison Chemical: B Type) was ground, passed through a 115-mesh screen, and dried at 180 °C and below 0.5 Torr for 2 h. Commercially available $CaSO_4 \cdot 2H_2O$, KF, CsF, $CaCl_2 \cdot 2H_2O$, KCl, KI, $CaHPO_4 \cdot 2H_2O$, and $Ni_3(PO_4)_2$ were ground, passed through an 80-mesh screen, and dried at 180 °C and below 0.5 Torr for 2 h. Commercial powdery BaO and $CaCO_3$ were dried at 180 °C and below 0.5 Torr for 2 h. Molecular sieves 4A (Fuji-Davison Chemical: Grade 612 4 Å) were ground, passed through an 80-mesh screen, and dried at 400 °C and below 0.5 Torr for 2 h before use.

Commercially available $Me_3SiCN$ was distilled and used. $CF_3SO_3H$, $CF_3SO_3SiMe_3$ and $BF_3 \cdot OEt_2$ were purchesed and purified by distillation before use. $ZnI_2$, *cis*-dicyclohexano-18-Crown-6, and KCN were purchased and used without further purification. Commercial aldehydes, ketones, and $\alpha,\beta$-unsaturated ketones were purified by distillation. Dimethyl acetals were prepared by the transacetalization of aldehydes and ketones with trimethyl orthoformate in the presence of Amberlyst-15 (Rohm & Haas Co.; strong acidic ion-exchange resin).[49]

Solvents (dichloromethane, toluene, hexane, 1,2-dimethoxyethane, and acetonitrile) were dried over molecular sieves 4A.

**Preparation of Ion-Exchanged Montmorillonites.** Sn-Mont, Fe-Mont, Al-Mont, Ni-Mont, Zn-Mont, and Ca-Mont were prepared from purified $Na^+$ ion-exchanged montmorillonite "Kunipia-F" (cation-exchange capacity=1.19 mequiv $g^{-1}$)supplied by Kunimine Industries Co., Japan by cation-exchange using aqueous solutions of corresponding salts, such as $SnCl_4 \cdot xH_2O$ ($x$= 4—5), $Fe(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $NiCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $CaCl_2 \cdot 2H_2O$. The preparation of $Fe^{3+}$ ion-exchanged montmorillonite (Fe-Mont) is shown as a typical example. (1) Powdery Kunipia-F (40 g) was gradually added to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (65 g=10 equivalents of cation-exchange capacity) in deionized water (400 ml), and stirred vigorously at room temperature (r.t.) for 2—4 h in a 1 $dm^3$ beaker. The stirring should be conducted mechanically using a motor and a stirring blade. (2) The resultant suspension was filtered on a Büchner funnel by suction. (After the clay being precipitated, the filtration was easily conducted.) (3) The clay was collected, suspended again in a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (65 g=10 equiv) in deionized water (400 ml) with vigorous stirring at r.t. for 2—4 h. The clay was filtered on the funnel by suction, and washed with deionized water (100 ml). (4) The clay was collected, and suspended in deionized water (400 ml) with stirring at r.t. for 1 h, and filtered on a suction funnel, then washed with deionized water (100 ml). (5) The washing procedure of (4) was repeated again. The pH of the filtrate was around 4. (6) The collected clay was again suspended in a mixture of deionized water (200 ml) and methanol (200 ml) with stirring at r.t. for 1 h, and filtered. The pH of the filtrate was around 7. If not, the procedure of (6) should be repeated. (7) The washed clay was again suspended in methanol (400 ml) with stirring at r.t. for 0.5 h, and filtered. (8) The filtered clay was dried at r.t. and 0.5 Torr for 12 h in a 300-ml round-bottom flask. Then the clay was ground in a mortar with a pestle and passed through a 60-mesh screen. The obtained Fe-Mont (35 g) was stored in a desiccator over anhydrous silica gel.

The ion-exchange procedure with an aqueous solution of metal salts must be repeated. Otherwise cation-exchange is incomplete. The ion-exchanged montmorillonite should be dried at 120 °C and below 0.5 Torr for 3 h prior to use.

**General Procedure for Solid Acid and Base-Catalyzed Reactions of $Me_3SiCN$ with Saturated Carbonyl Compounds.** In a 20 ml round-bottom flask solid acid or solid base (0.2—0.5 g) was dried or calcined at the specified conditions before use. The flask was cooled down under vacuum, and inert gas (argon or nitrogen) was introduced. A solvent (1 ml) was added, and cooled to 0 °C. (Normally dichloromethane was used in montmorillonite-catalyzed reactions, and toluene in solid base-catalyzed reactions as solvent.) A solution of carbonyl compound (1 mmol) in the solvent (3 ml) was added to the suspended catalyst. The mixture was allowed to stand at the temperature specified in Tables. After 5 min, $Me_3SiCN$ (1.2—1.6 mmol) was added by syringe. The resulting mixture was stirred under the conditions given in Tables. Completion of the reaction was confirmed with GC or TLC. The solid catalyst was filtered off through a Celite 545 pad and washed with ether (10—20 ml). 2-(Trimethylsiloxy)alkanenitriles were obtained after evaporation of the filtrate and distillatoin on a Kugelrohr apparatus. The product purity was analyzed by capillary GC (OV-1, 25 m).

**General Procedure for Clay Montmorillonite-Catalyzed Reactions of $Me_3SiCN$ with Acetals.** $Me_3SiCN$ (1.6 mmol) was added to a suspended mixture of dried Fe-Mont or Sn-Mont (0.2 g) and $CH_2Cl_2$ (1 ml) at 0 °C. After stirring for 1—2 min, a $CH_2Cl_2$ solution (3 ml) of dimethyl acetal (1 mmol) was introduced into the suspended mixture over a period of 5 min with stirring. The resulting mixture was stirred under the conditions listed in Table 9. The reaction was monitored with GC and TLC. As a work-up, the montmorillonite was filtered off through a Celite pad, and washed with ether (10—20 ml). The filtrate was evaporated and distilled on a Kugelrohr apparatus to yield 2-methoxyalkanenitriles. The product purities were analyzed by capillary GC (OV-1, 25 m).

**Michael Additions of $Me_3SiCN$ with $\alpha,\beta$-Unsaturated Ketones in the Presence of Fe-Mont or Sn-**

**Mont and MS4A.** Powdered molecular sieves 4A (0.2 g), pre-dried at 400 °C and 0.5 Torr for 1 h in an electric furnace, were added to the suspension of montmorillonite (Fe-Mont or Sn-Mont, 0.2 g, pre-dried at 120 °C and below 0.5 Torr for 3 h) in $CH_2Cl_2$ (2 ml). After the mixture had been stirred for 1 h at r.t. under nitrogen, the stirring was stopped. The mixture was then cooled down to the reaction temperature indicated in Tables, and $Me_3SiCN$ (1.6 mmol) and a solution of $\alpha,\beta$-unsaturated ketone (1 mmol) in $CH_2Cl_2$ (3 ml) were added successively. The resulting mixture was allowed to stand for 5 min, and then stirred under the conditions given in Tables 10 and 11. (While the stirring is interrupted, no reaction proceeds.) Completion of the isomerization of the 1,2-adduct to the 1,4-adduct was confirmed with GC. The solid catalyst was filtered off, and the filtrate was distilled to give the conjugate adduct in a silyl enol ether form. The regioselectivities of the products were determined by GC (OV-1, 25 m).

**Preparation of 1,2-Adducts from $\alpha,\beta$-Unsaturated Ketones in the Presence of Solid Bases.** To a suspended mixture of a solid base, such as CaO, MgO, and HAp (0.2—0.5 g), and toluene (1 ml) was added at −40 °C a solution of $\alpha,\beta$-unsaturated ketone in toluene (3 ml) and $Me_3SiCN$ (1.6 mmol), successively. The mixture was allowed to stand for 5 min, and was then stirred under the conditions listed in Tables 10 and 11. Consumption of the carbonyl compound was checked by GC or TLC. The solid catalyst was filtered off; the filtrate was distilled to yield 1,2-adduct. The regioisomeric ratios of the products were determined by capillary GC (OV-1, 25 m).

**$ZnI_2$-Catalyzed Reactions of $Me_3SiCN$ with Carbonyl Compounds.** In a flask $ZnI_2$ (0.01—0.10 mmol) was dried at 120 °C and below 0.5 Torr for 2 h before use. A $CH_2Cl_2$ solution (4 ml) of carbonyl compound (1 mmol) was added, and the mixture was stirred until $ZnI_2$ was dissolved at 0 °C under an inert gas atmosphere. $Me_3SiCN$ (1.2—1.6 mmol) was then added; the resulting solution was stirred under the conditions given in Tables. After the reaction was quenched by injecting $Et_3N$ (0.5 ml), the solution was diluted with ether (10 ml). Water (10 ml) was poured into the quenched solution, and the organic products were extracted with ether three times. The combined extract was washed with brine, and dried over anhydrous $Na_2SO_4$. After the solvent was evaporated, the products were obtained by distillation of the crude oil on a Kugelrohr apparatus.

**$BF_3\cdot OEt_2$ and $CF_3SO_3SiMe_3$-Catalyzed Reactions of Carbonyl Compounds.** To a solution of a carbonyl compound (1 mmol) in $CH_2Cl_2$ (3 ml) was added at 0 °C a $CH_2Cl_2$ (1 ml) solution of acid catalyst (0.01—0.10 mmol) and $Me_3SiCN$ (1.2—1.6 mmol) under a nitrogen atmosphere. The solution was then stirred under the conditions given in Table 5. As for $CF_3SO_3SiMe_3$, the solution was quenched with $Et_3N$ (0.5 ml), diluted with ether (10 ml), and poured into water. In the case of $BF_3\cdot OEt_2$, the reaction was quenched by adding an aqueous $NaHCO_3$ solution. The organic products were extracted with ether. The extract was washed with brine, dried over anhydrous $Na_2SO_4$, and distilled to yield the products.

**KCN/18-Crown-6-Catalyzed Reactions of Carbonyl Compounds with $Me_3SiCN$.** To a solution of *cis*-dicyclohexano-18-crown-6 (0.1 mmol) and KCN (0.1 mmol) in a solvent (toluene or $CH_2Cl_2$, 2.5 ml) was added at 0 °C a solution (1.5 ml) of a carbonyl compound (1 mmol) in the same solvent and $Me_3SiCN$ (1.6 mmol) under a nitrogen atmosphere. The resulting solution was then stirred under the conditions given in Tables. The solution was quenched with water (10 ml), and the organic products were extracted with ether. The extract was dried and distilled to yield the products.

**Poisoning Sn-Mont and Fe-Mont with $Et_3N$.** Sn-Mont and Fe-Mont (0.2 g) was dried at 120 °C and below 0.5 Torr for 3 h. In a nitrogen atmosphere, a dichloromethane solution (1.0 ml) of $Et_3N$ (0.002—0.07 mmol) was added to a suspended mixture of the Sn-Mont or Fe-Mont and $CH_2Cl_2$ (1.5 ml); the resulting mixture was stirred at 0 °C for 15 min. A solution of benzophenone (1 mmol) in $CH_2Cl_2$ (2.5 ml) was added; the mixture was allowed to stand at 0 °C for 5 min. After $Me_3SiCN$ (1.2 mmol) was added, the resultant suspension was stirred for 2 min (Sn-Mont) or for 20 min (Fe-Mont). Then the reaction was quenched with $Et_3N$ (0.1 ml). The conversion of benzophenone was determined by an analysis of the supernatant solution by capillary GC (OV-1, 25 m).

**Poisoning CaO and Hydroxyapatite with $CCl_3COOH$.** Hydroxyapatite (0.5 g) was dried at 400 °C and below 0.5 Torr for 2 h. CaO (0.2 g) was calcined from $Ca(OH)_2$ at 500 °C and below 0.5 Torr for 2 h. In a nitrogen atmosphere, a toluene solution (1.5 ml) of $CCl_3COOH$ (0.01—0.5 mmol) was added to a suspended mixture of the HAp or CaO and toluene (2 ml); the resulting mixture was stirred at 0 °C for 30 min. After adding a solution of benzophenone (1 mmol) in toluene (2.5 ml), the mixture was allowed to stand for 5 min. $Me_3SiCN$ (1.6 mmol) was added, and the resultant suspension was then stirred for 10 min (HAp) or for 30 min (CaO). The stirring was then stopped, and solid materials were precipitated. The conversion of benzophenone was determined by an analysis of the supernatant solution by capillary GC (OV-1, 25 m). Benzophenone and 2,2-diphenyl-2-(trimethylsiloxy)ethanenitrile were isolated through distillation to confirm the products.

**2-(Trimethylsiloxy)octanenitrile.** Bp 145 °C (bath temperature)/20 Torr; IR ($CCl_4$) no CN absorption, 1256 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta$=0.21 (s, 9H, $(CH_3)_3Si$), 0.89 (t, 3H, $J$=6.5 Hz, $CH_3$), 1.15—1.56 (br, 8H, $(CH_2)_4$), 1.70—1.88 (m, 2H, $CH_2CCN$), 4.39 (t, 1H, $J$=6.5 Hz, CHCN); $^{13}$C NMR ($CDCl_3$) $\delta$=−0.70, 13.76, 22.28, 24.29, 28.39, 31.37, 36.05, 61.37, 120.18. Found: C, 61.70; H, 10.90; N, 6.51%. Calcd for $C_{11}H_{23}NOSi$: C, 61.91; H, 10.86; N, 6.56%.

**2-Phenyl-2-(trimethylsiloxy)ethanenitrile.** Bp 150 °C (bath temperature)/20 Torr; IR ($CCl_4$) no CN absorption, 1257 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta$=0.24 (s, 9H, $(CH_3)_3Si$), 5.51 (s, 1H, CHCN), 7.36—7.55 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta$=−0.52, 63.59, 119.27, 126.46, 129.06, 129.46, 136.41. Found: C, 64.38; H, 7.65; N, 6.79%. Calcd for $C_{11}H_{15}NOSi$: C, 64.35; H, 7.36; N, 6.82%.

**2-Methyl-2-(trimethylsiloxy)octanenitrile.** Bp 135 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2230 (CN), 1254 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta$=0.24 (s, 9H, $(CH_3)_3Si$), 0.89 (t, 3H, $J$=6.6 Hz, $CH_3$), 1.21—1.40 (br, 6H, $(CH_2)_3$), 1.40—1.65 (m, 2H, $CH_2$), 1.56 (s, 3H, $CH_3CCN$), 1.65—1.78 (m, 2H, $CH_2CN$); $^{13}$C NMR ($CDCl_3$) $\delta$=1.06, 13.84, 22.37, 24.07, 28.76, 28.83, 31.47, 43.28, 69.66, 122.36. Found: C, 63.36; H, 11.15; N, 6.40%. Calcd for

$C_{12}H_{25}NOSi$: C, 63.38; H, 11.08; N, 6.16%.

**2-Phenyl-2-(trimethylsiloxy)propanenitrile.** Bp 145 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2234 (CN), 1255 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.18$ (s, 9H, $(CH_3)_3Si$), 1.86 (s, 3H, $CH_3$), 7.30—7.63 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta=0.80$, 33.41, 71.56, 121.74, 124.72, 128.76, 128.26, 142.15. Found: C, 65.76; H, 7.97; N, 6.17%. Calcd for $C_{12}H_{17}NOSi$: C, 65.70; H, 7.81; N, 6.39%.

**2,2-Diphenyl-2-(trimethylsiloxy)ethanenitrile.** Bp 140 °C (bath temperature)/0.5 Torr; IR ($CCl_4$) 2234 (CN), 1254 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.13$ (s, 9H, $(CH_3)_3Si$), 7.28—7.57 (m, 10H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$: 125 MHz NMR) $\delta=0.97$, 76.33, 120.64, 125.83, 128.48, 128.58, 141.85. Found: C, 72.56; H, 6.91; N, 5.07%. Calcd for $C_{17}H_{19}NOSi$: C, 72.55; H, 6.80; N, 4.98%.

**2-Methyoxyoctanenitrile.** Bp 130 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2236 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta=0.89$ (t, 3H, $J=6.6$ Hz, $CH_3$), 1.20—1.60 (br, m, 8H, $(CH_2)_4$), 3.49 (s, 3H, $CH_3O$), 4.04 (t, 1H, $J=6.5$ Hz, CHCN); $^{13}$C NMR ($CDCl_3$) $\delta=13.37$, 22.27, 24.44, 28.46, 31.33, 33.16, 57.84, 70.64, 118.28.

**2-Methoxy-2-phenylethanenitrile.** Bp 160 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2230 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta=3.53$ (s, 3H, $CH_3O$), 5.20 (s, 1H, CHCN), 7.35—7.56 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta=57.09$, 72.20, 117.02, 127.38, 129.12, 129.94, 133.36.

**2-Methyl-2-methoxyoctanenitrile.** Bp 125 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2230 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta=0.89$ (t, 3H, $J=6.4$ Hz, $CH_3$), 1.15—1.78 (br, m, 8H, $(CH_2)_4$), 1.52 (s, 3H, $CH_3$), 1.68—1.88 (m, 2H, $CH_2$), 3.43 (s, 3H, $CH_3O$); $^{13}$C NMR ($CDCl_3$) $\delta=13.80$, 22.32, 23.33, 23.57, 28.88, 31.40, 39.48, 52.98, 74.76, 120.07.

**2,2-Diphenyl-2-methoxyethanenitrile.** Bp 165 °C (bath temperature)/0.5 Torr; IR ($CCl_4$) 2234 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta=3.42$ (s, 3H, $CH_3O$), 7.28—7.58 (m, 10H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta=54.45$, 82.50, 118.29, 126.56, 128.85, 129.16, 138.85.

**1-Trimethylsiloxy-2-cyclohexene-1-carbonitrile.** Bp 150 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2235 (CN), 1650 (C=C), 1258 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.24$ (s, 9H, $(CH_3)_3Si$), 1.70—2.25 (m, 6H, $(CH_2)_3$), 5.75 (d, 1H, $J=9.8$ Hz, CHCCN), 5.97 (dt, 1H, $J=9.8$ 3.6 Hz, CH=C); $^{13}$C NMR ($CDCl_3$) $\delta=1.27$, 18.17, 24.13, 36.80, 66.76, 121.99, 127.75, 132.75. Found: C, 61.42; H, 8.57; N, 7.08%. Calcd for $C_{10}H_{17}NOSi$: C, 61.49; H, 8.77; N, 7.17%.

**3-Trimethylsiloxy-2-cyclohexene-1-carbonitrile.** Bp 150 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2235 (CN), 1662 (C=C), 1258 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($C_6D_6$) $\delta=0.11$ (s, 9H, $(CH_3)_3Si$), 1.10—1.30 (m, 2H, $CH_2$), 1.30—1.60 (m, 2H, $CH_2$), 1.70—1.84 (m, 2H, $CH_2$), 2.58—2.74 (m, 1H, CHCN), 4.68 (d, 1H, $J=4.0$ Hz, CH=C); $^{13}$C NMR ($C_6D_6$) $\delta=0.23$, 20.65, 26.32, 26.48, 29.60, 99.18, 122.04, 155.07. Found: C, 61.20; H, 8.72; N, 7.22%. Calcd for $C_{10}H_{17}NOSi$: C, 61.49; H,8.77; N, 7.17%.

**3-Trimethylsiloxy-2-cyclopentene-1-carbonitrile.** Bp 145 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2230 (CN), 1642 (C=C), 1257 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.22$ (s, 9H, $(CH_3)_3Si$), 2.00—2.80 (m, 4H, $(CH_2)_2$), 3.55 (m, 1H, CHCN), 4.59 (d, 1H, $J=3.5$ Hz, CH=C).

**2,4-Dimethyl-2-trimethylsiloxy-3-pentenenitrile.** Bp 110 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2230 (CN), 1667 (C=C), 1252 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.21$ (s, 9H, $(CH_3)_3Si$), 1.67 (s, 3H, $CH_3CCN$), 1.76 (d, 3H, $J=1.4$ Hz, $CH_3C$=C), 1.91 (d, 3H, $J=1.4$ Hz, $CH_3C$=C), 5.27 (m, 1H, CH=C).

**2,2-Dimethyl-4-trimethylsiloxy-3-pentenenitrile.** Bp 145 °C (bath temperature)/20 Torr; IR ($CCl_4$) 2235 (CN), 1670 (C=C), 1254 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($C_6D_6$) $\delta=0.27$ (s, 9H, $(CH_3)_3Si$), 1.22 (s, 6H, $(CH_3)_2C$), 1.55 (d, 3H, $J=1.0$ Hz, $CH_3C$=C), 4.09 (m, 1H, CH=C).

**2-Methyl-4-phenyl-2-trimethylsiloxy-3-butenenitrile.** Bp 150 °C (bath temperature)/0.5 Torr; IR ($CCl_4$) 2240 (CN), 1652 (C=C), 1258 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.24$ (s, 9H, $(CH_3)_3Si$), 1.75 (s, 3H, $CH_3$), 6.13 (d, 1H, $J=15.7$ Hz, CHCCN), 6.89 (d, 1H, $J=15.7$ Hz, PhCH), 7.25—7.47 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta=$ 1.15, 30.75, 69.95, 120.82, 127.04, 128.75, 128.92, 129.68, 131.12, 135.29. Found: C, 68.76; H, 7.74; N, 5.64%. Calcd for $C_{14}H_{19}NOSi$: C, 68.52; H, 7.80; N, 5.71%.

**6-Methyl-3-(trimethylsiloxy)bicyclo[4.4.0]dec-1-ene-3-carbonitrile.** Bp 120 °C (bath temperature)/0.5 Torr; IR($CCl_4$) 2225 (CN), 1654 (C=C), 1251 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($CDCl_3$) $\delta=0.24$ (s, 9H, $(CH_3)_3Si$), 1.11 (s, 3H, $CH_3$), 1.15—2.30 (m, 12H, $(CH_2)_4$, $(CH_2)_2$), 5.34 (br, s, 1H, CH=C); $^{13}$C NMR ($CDCl_3$) $\delta=1.35$, 21.79, 23.17, 27.81, 31.97, 33.49, 34.80, 35.93, 41.37, 68.81, 120.90, 122.13, 150.03. Found: C, 68.28; H, 9.74; N, 5.31%. Calcd for $C_{15}H_{25}NOSi$: C, 68.39, H, 9.56; N, 5.32%.

**6-Methyl-3-(trimethylsiloxy)bicyclo[4.4.0]dec-2-ene-1-carbonitrile.** A mixture of *cis* and *trans* isomers was obtained (*cis*: *trans*=28:72). Bp 160 °C (bath temperature)/0.5 Torr; IR ($CCl_4$) 2225 (CN), 1658 (C=C), 1255 cm$^{-1}$ ($(CH_3)_3Si$); $^1$H NMR ($C_6D_6$) $\delta=0.15$ (*cis*) and 0.16 (*trans*) (s, 9H, $(CH_3)_3Si$), 0.68 (*trans*) and 1.12 (*cis*) (s, 3H, $CH_3$), 1.03—1.52 (m, 8H, $(CH_2)_4$), 1.60—2.12 (m, 4H, $(CH_2)_2$), 4.64 (*trans*) and 4.73 (*cis*) (br s, 1H, CH=C); $^{13}$C NMR ($C_6D_6$) (*trans* isomer) $\delta=0.38$, 15.95, 20.75, 22.92, 28.00, 30.95, 34.86, 35.19, 35.44, 44.03, 106.15, 123.55, 154.85. Found: C, 68.23; H, 9.72; N, 5.29%. Calcd for $C_{15}H_{25}NOSi$: C, 68.39; H, 9.56; N, 5.32%.

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