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Reduction of Carbonyl Compounds with Hydrosilanes on Solid Acid and Solid Base

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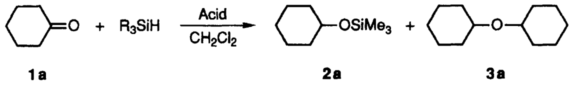
Hydrosilylations of carbonyl compounds were performed on the surfaces of solid acids and bases. Strongly acidic clays efficiently catalyzed the reduction of aldehydes and ketones with trialkylsilanes (e.g. Et_3SiH) to afford symmetrical ethers or hydrocarbons, depending upon the characters of substituents around carbonyl groups. Reduction-resistant ketone like 4,4′-dimethoxybenzophenone was found to be reduced with Et_3SiH under the catalytic influence of the highly acidic clay. In contrast, trialkoxysilanes (e.g. $(EtO)_3SiH$) became labile in contact with solid base like hydroxyapatite, reducing a variety of carbonyl compounds to yield alkoxy(triethoxy)silane in good yields. It was revealed that besides fluoride salts, solid bases bearing mild basicity and relatively large surface areas can activate the trialkoxysilane enough for reduction of carbonyl functions.

Hydrosilanes are synthetic equivalents of molecular hydrogen, and hence utilized in organic synthesis as a reducing agent owing to its mild reactivity and easy manipulation in laboratories.[1] The reduction of carbonyl compounds with hydrosilanes is currently performed using a variety of homogeneous catalysts and promoters: transition metal complexes like the Wilkinson catalyst $[RhCl(PPh_3)_3]$,[2] liquid acids (e.g. CF_3CO_2H,[3] $BF_3 \cdot OEt_2$,[4] and CF_3SO_3H[5])), inorganic and organic fluorides (e.g. KF,[6] CsF,[6] tetrabutylammonium fluoride (TBAF),[7] and tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF)[7]). Liquid acids, such as CF_3CO_2H and CF_3SO_3H, catalyze or promote the reactions of carbonyl compounds with hydrosilanes (R_3SiH), such as triethylsilane and dimethylphenylsilane, to afford alcohols, symmetrical ethers and/or hydrocarbons, depending upon the substituents around the carbonyl group and the reaction conditions.[3—5] On the other hand, under the influence of fluorides, hydrosilanes, such as triethoxysilane and dimethylphenylsilane, convert carbonyl compounds into the corresponding alcohols.[6,7] Pentacoordinate hydridosilicates which are derived from tetracoordinate hydrosilanes with alkoxide anions can also reduce carbonyl compounds to alcohols.[8]

We have been concerned with organic reactions on solid acids (e.g. zeolites,[9] clays[10]) and solid bases,[11] and applied the solid catalysts to organic syntheses. In our previous communication,[12] we reported solid acid- and base-catalyzed hydrosilylation under heterogeneous conditions. Here we fully discuss the efficient catalysis by solid acids and bases in the reactions of carbonyl compounds with hydrosilanes, relating the catalysis to acidity and basicity of the solid catalysts.

Results and Discussion

Solid Acid-Catalyzed Reduction of Carbonyl Compounds with Triethylsilane.



(1)

Table 1 summarizes the reduction of cyclohexanone with hydrosilanes in dichloromethane promoted by montmorillonites or trifluoromethanesulfonic acid (CF_3SO_3H). Cyclohexanone (**1a**) underwent reduction on treatment with triethylsilane (Et_3SiH) in the presence of acidic iron-ion exchanged montmorillonite (Fe-Mont),[10b] affording dicyclohexyl ether (**3a**) predominantly,[13] and cyclohexyloxy(triethyl)silane (**2a**) in a small amount (Run 1). Liquid acid, CF_3SO_3H also promoted the reduction to afford **3a** with a *catalytic* use (10 mol%) of the acid (Run 2), and **2a** with a *stoichiometric* use (110 mol%) (Run 3). It is meaningful to point out that the Fe-Mont-mediated reduction resembles the CF_3SO_3H-*catalyzed* one in terms of the product distribution. The primary reduction product **2a** seems to react promptly with another molecule of **1a** activated by the acid catalyst to give a symmetrical ether **3a**. On the contrary, the fact that a *stoichiometric* use of CF_3SO_3H results in the selective formation of **2a** implies that on treatment of an equivalent amount of CF_3SO_3H, all the molecules of **1a** are simultaneously activated with the acid in a one-to-one mode, being in turn converted into **2a** by an attack of Et_3SiH.

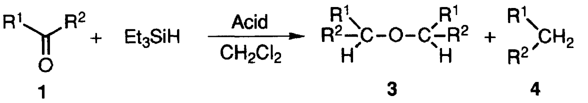
Table 1. Acid- Catalyzed Reduction of Cyclohexanone with Hydrosilanes[a)]

Run	Catalyst[b)] (Amount)	Hydrosilane	Time	Yield/%	
			h	**2a**	**3a**
1	Fe-Mont (0.2 g)	Et_3SiH	0.5	7	81
2	CF_3SO_3H (0.1 mmol)	Et_3SiH	0.5	4	80
3	CF_3SO_3H (1.1 mmol)	Et_3SiH	0.3	67	4
4	Fe-Mont (0.2 g)	$PhMe_2SiH$	1.5	0	84
5	Fe-Mont (0.2 g)	$(EtO)_3SiH$	20	0	0
6	Na-Mont (0.2 g)	Et_3SiH	47	0	0
7	SiO_2 (0.2 g)	Et_3SiH	21	0	0

a) Cyclohexanone (1 mmol) was treated with hydrosilane (1.1 mmol) and a catalyst in CH_2Cl_2 (6 ml) at room temperature. b) Solids were dried under the following conditions before use: at 120 °C/0.5 Torr for 3 h toward cation-exchanged montmorillonites, at 500 °C/0.5 Torr for 2 h toward SiO_2.

In the acid-catalyzed reduction, Et_3SiH was the most reactive among the three reductants, Et_3SiH, $PhMe_2SiH$, and $(EtO)_3SiH$: The electron-donating effect of alkyl substituents enhances the nucleophilicity of hydride at silicon, while electronegative oxygens on $(EtO)_3SiH$ provide an inverse effect on the hydride.

Strong acidity is required for a solid acid to boost the reduction. Weakly acidic solids, such as sodium ion-exchanged montmorillonite (Na-Mont) and SiO_2, exhibited no catalysis. In Table 2 are listed maximum acid strengths and specific surface areas of the solid acids employed in the present study.



a: $R^1, R^2 = -(CH_2)_5-$.
b: $R^1 = Ph, R^2 = Me$.
c: $R^1 = R^2 = Ph$.
d: $R^1 = Ph, R^2 = H$.
e: $R^1 = Hexyl, R^2 = H$.
f: $R^1 =$ *trans*-Ph-CH=CH, $R^2 = Me$.
g: $R^1 = Ph, R^2 = MeO$.

(2)

As shown in Table 3, the strongly acidic clays, Fe-Mont and tin(IV) ion-exchanged montmorillonite (Sn-Mont)[10c] were applicable to reductions of diverse carbonyl compounds with Et_3SiH in dichloromethane.[14] The solid acids converted the carbonyl substrates into symmetrical ethers **3** or hydrocarbons **4**, depending upon the substrates: Benzaldehyde, heptanal, and cyclohexanone produced symmetrical ethers.[13] Acetophenone and benzopheone bearing phenyl groups adjacent to a carbonyl function underwent complete reduction to ethylbenzene and diphenylmethane, respectively (Run 3—7). In the reduction of cyclohexanone and benzophenone it was confirmed that there is no difference in product selectivity between solid acid- and liquid acid-catalyzed reactions (Run 1, 2, and 4—7). Concerning the reduction efficiency, however, the Sn-Mont-catalyzed reduction proceeds far more rapidly than the CF_3SO_3H-catalyzed one (Run 5 vs. Run 6).

The catalytic performance of Sn-Mont was completely suppressed upon the additon of 10 mol% of Et_3N in the reduction of benzophenone (Run 8). Therefore, the amount of active acid sites on the Sn-Mont surface is estimated to be less than 0.10 mmol per 0.2 g of Sn-Mont, and it was clarified that Sn-Mont behaves as an acid *catalyst* in the present reduction.[15]

In order to demonstrate that the Sn-Mont catalyst is applicable to reduction-resistant carbonyl compounds, the reduction of 4,4′-dimethoxybenzophenone (**5**) was attempted (Table 4).[16] Strongly acidic Sn-Mont catalyzed the reduction of **5** with Et_3SiH in 1,2-dichloroethane (bp 83 °C) under reflux to produce 4,4′-dimethoxydiphenylmethane (**6**) in 75% yield. In contrast, a stoichiometric use of CF_3SO_3H gave **6** in only 54% yield after 10 h because the reduction was observed to cease during the reaction. No catalyst deactivation was found in the Sn-Mont-mediated reduction.

On the basis of the results above, it is apparent that Sn-Mont is acidic enough to induce the reduction of various carbonyl compounds with Et_3SiH.

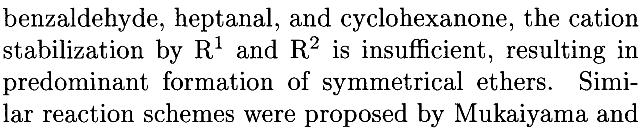
Although CF_3SO_3H ($H_0 = -14.6$) is more acidic than $CF_3SO_3SiMe_3$ in terms of acid strength, both acids gave the same catalytic activities toward the benzophenone reduction as shown in Runs 6 and 7 in Table 3, implying that the reduction might be brought about by the same active species, $CF_3SO_3SiR_3$ (R=Et or Me).

$$CF_3SO_3H + Et_3SiH \longrightarrow CF_3SO_3SiEt_3 + H_2 \qquad (3)$$

Acidic property of montmorillonite is derived from protons dissociated from the water coordinating with interlamellar cations.[17] H_2 evolution was observed when acidic Sn-Mont was mixed with Et_3SiH. Therefore, in the montmorillonite-catalyzed reduction, protic montmorillonite seems to be first converted into triethylsilylated clay, which fills a role of activation of a carbonyl function.

$$H^+\,[\text{Silicate}]^- + Et_3SiH \longrightarrow Et_3Si - [\text{Silicate}] + H_2 \qquad (4)$$

The reaction path is depicted in Scheme 1. The triethylsilylated montmorillonite provokes the hydrosilylation of a carbonyl function with Et_3SiH to afford (alkoxy)triethylsilane **2**. Product **2** then behaves as a nucleophile toward another activated carbonyl compound to yield symmetrical ether **3** via intermediate **9**. When R^1 and R^2 in **2** can sufficiently stabilize the cation adjacent to the triethylsiloxy group, **2** is transformed into an intermediary cation **10** via the interaction with the acidic montmorillonite, followed by prompt reduction with extra Et_3SiH to hydrocarbon **4**.



(5)

Methyl and phenyl groups in acetophenone and benzophenone direct the reduction to hydrocarbon formation because the two alkyl substituents can stabilize an adjacent cation. On the other hand, in the cases of benzaldehyde, heptanal, and cyclohexanone, the cation stabilization by R^1 and R^2 is insufficient, resulting in predominant formation of symmetrical ethers. Similar reaction schemes were proposed by Mukaiyama and Sakurai using hydrosilane with trityl perchlorate[18] or trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.[19]

The intrinsic acidity of a clay is controllable by simple cation exchange. We have demonstrated that Sn-Mont and Fe-Mont perform efficient acid catalysts in reactions of silicon-containing nucleophiles, in which the catalytic efficiency of the clays is attributable to their extremely high acid strength.[10,20] In other words, the advantage of using Sn-Mont and Fe-Mont in organic synthesis is that

Table 2. Physical Properties of Solid Acids and Bases

Solid	Surface area/$m^2\,g^{-1}$	Maximum acid or base strength
Sn-Mont	280	$-8.2 \geq H_0$
Fe-Mont	26	$-8.2 \geq H_0$
Na-Mont	12	$+3.3 \geq H_0 > +1.5$
SiO_2	585	$+3.3 \geq H_0 > +1.5$
CaO	65	$+33.0 > H_- \geq +26.5$
Hydroxyapatite (HAp)	55	$+18.4 > H_- \geq +15.0$
$Ca(OH)_2$	15	$+18.4 > H_- \geq +15.0$
CaF_2	6	$+7.2 > H_-$

Table 3. Acid-Catalyzed Reactions of Various Carbonyl Compounds with Et_3SiH[a]

Run	Substrate	Catalyst[b]	Temp/°C (Time/h)	Product	Yield %
1	Cyclohexanone (**1a**)	Fe-Mont	R.T. (0.5)	**3a**	81
2		CF_3SO_3H	R.T. (0.5)	**3a**	80
3	Acetophenone (**1b**)	Fe-Mont	R.T. (4)	**4b**	72[d]
4	Benzophenone (**1c**)	Fe-Mont	R.T. (60)	**4c**	98
5		Sn-Mont	R.T. (2)	**4c**	98
6		CF_3SO_3H	R.T. (24)	**4c**	94
7		$CF_3SO_3SiMe_3$	R.T. (24)	**4c**	94
8		Sn-Mont/Et_3N[c]	R.T. (2)	**4c**	1[d]
9	Benzaldehyde (**1d**)	Fe-Mont	R.T. (0.3)	**3d**	80
10	Heptanal (**1e**)	Sn-Mont	R.T. (0.1)	**3e**	85
11	Benzylideneacetone (**1f**)	Sn-Mont	R.T. (6)		C.M.[e]
12	Methyl benzoate (**1g**)	Sn-Mont	40 (12)		0[f]

a) Substrate (1 mmol) was treated with Et_3SiH (in Runs 1,2,9,10: 1.1 mmol; in Runs 3—8: 2.2 mmol; in Runs 11, 12: 3 mmol) and a catalyst in CH_2Cl_2 (5 ml) at room temperature (R.T.) or 40 °C. b) 0.2 g of Fe-Mont and Sn-Mont were used. 0.10 mmol (10 mol%) of CF_3SO_3H and $CF_3SO_3SiMe_3$ were used. c) Sn-Mont was poisoned with 0.10 mmol of Et_3N, and then used. d) The yields were estimated with GC (OV-1, 25 m). e) Although the products were complex mixtures, the conjugate addition of hydrides to enone was confirmed with ^1H NMR and IR. f) Methyl benzoate was recovered in 98% yield.

Table 4. Reduction of 4,4′-Dimethoxybenzophenone[a]

Acid (Amount)	Temp/°C (Time/h)	Isolated yield/%
Sn-Mont (0.2 g)	83 (20)	75[b]
CF_3SO_3H (1 mmol)	83 (10)	54[c]
CF_3SO_3H (0.1 mmol)	83 (20)	24[c]

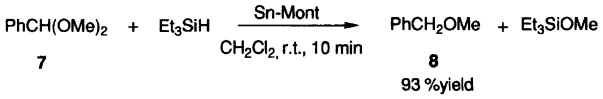
a) 4.4′-Dimethoxybenzophenone (1 mmol) was treated with Et_3SiH (5 mmol) and an acid in 1,2-dichloroethane (6 ml) under reflux. b) The reaction was quenched at 82% conversion of **5** with GC analysis. At higher conversion levels, complex mixtures were obtained owing to side reactions. c) The reduction ceased after 2 h.

the clays can display higher acidity in organic solvents compared to liquid acids, e.g. CF_3SO_3H.

Wolff-Kishner and Clemmensen reductions are classical processes for reducing carbonyl to methylene functions. Modern reagent systems have so far been developed for reductions of aromatic ketones: for instance, $LiAlH_4$–$AlCl_3$,[21] $NaBH_4$–CF_3CO_2H,[22] $NaBH_4$–$AlCl_3$,[23] R_3SiH–CF_3CO_2H,[3c] Et_3SiH–$BF_3{\cdot}OEt_2$,[4b] and Et_3SiH–CF_3SO_3H[5] are representative. In most cases, large amounts of reductants and acid promoters are necessary.

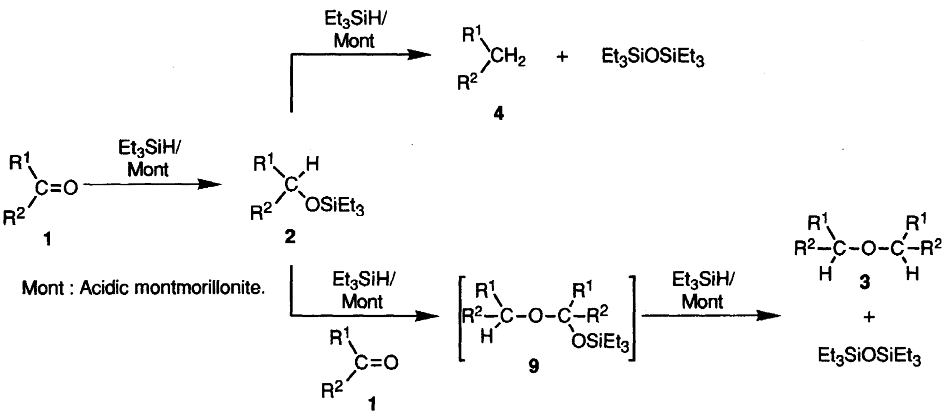
Sn-Mont was found ineffective in the reduction of enones and enoates with Et_3SiH (Runs 11 and 12 in Table 3).

Sn-Mont smoothly catalyzed the reaction of benzaldehyde dimethyl acetal (**7**) with Et_3SiH to yield unsymmetrical ether **8** in good yield. The same reaction has been carried out by using acid catalysts, such as $CF_3SO_3SiMe_3$,[24] Ph_3CClO_4,[18] Me_3SiI,[25] Nafion-H.[26]



$$\underset{\mathbf{7}}{PhCH(OMe)_2} + Et_3SiH \xrightarrow[CH_2Cl_2,\ r.t.,\ 10\ min]{Sn\text{-}Mont} \underset{\substack{\mathbf{8} \\ 93\ \%yield}}{PhCH_2OMe} + Et_3SiOMe \tag{6}$$

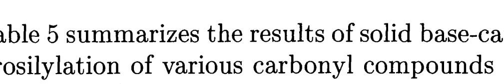
Solid Base-Catalyzed Hydrosilylation of Carbonyl Compounds with Triethoxysilane. As shown in Table 1, Et_3SiH is very active, while $(EtO)_3SiH$ is inert to carbonyl groups under acidic



Scheme 1. Reduction of carbonyl compounds with Et_3SiH on acidic montmorillonite.

conditions. Under basic reaction conditions, however, $(EtO)_3SiH$ seems to be a preferred reducing agent because the hydrosilylation with $(EtO)_3SiH$ has been reported by using fluoride sources, in which an intermediary, pentacoordinate hydridosilicate species is postulated to be a real reductant.[6)]

We have already found that organosilicon compounds bearing electronegative substituents (e.g. Me_3SiCN,[11)] Me_3SiN_3,[27)] Me_3SiCl[27)]) can be activated on the surface of solid bases, such as CaO, MgO, hydroxyapatite, and CaF_2, to participate in nucleophilic addition to epoxides and carbonyl compounds. By analogy, hydrosilanes are expected to be adsorbed and activated by solid bases.



11 12

a: R^1 = Hexyl, R^2 = H.
b: R^1 = Ph, R^2 = H.
c: R^1 = Hexyl, R^2 = Me.
d: R^1, R^2 = $-(CH_2)_5-$.
e: R^1 = Ph, R^2 = Me.
f: R^1 = R^2 = Ph.
g: R^1 = Ph, R^2 = OEt.
h: R^1 = Pentyl, R^2 = OMe; h': R^1 = Pentyl, R^2 = H.
i: R^1 = *trans*-Ph-CH=CH-, R^2 = H.
j: R^1 = *trans*-Ph-CH=CH-, R^2 = Me.

(7)

Table 5 summarizes the results of solid base-catalyzed hydrosilylation of various carbonyl compounds in heptane solvent.[28)] Under basic conditions, only hydrosilylation of carbonyl functions took place, exclusively affording alkoxy(triethoxy)silane without any formation of symmetrical ethers and hydrocarbons.

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$),[29)] which is known as a main component of teeth and bone, exhibited remarkable catalysis on the hydrosilylation of aldehydes, ketones, esters, and enones with $(EtO)_3SiH$. A strong solid base, CaO, also promoted the addition of the hydrosilane to a carbonyl function, but side reactions like self-condensations of carbonyl compounds concurred owing to high base strength of CaO. $Ca(OH)_2$ and CaF_2 were inactive because of low basicities and small specific surface areas of the solids. The basic properties and specific surface areas of the solids employed are listed in Table 2. Consequently, the effectiveness of HAp as a base catalyst for the hydrosilylation is ascribed to its mild basicity and sufficient surface area. Hydroxide ions (OH^-) in HAp take part in basic functions.[29,30)]

$(EtO)_3SiH$ was found to be the only reductant applicable to hydrosilylation on solid bases. The electronegative oxygens at silicon enable $(EtO)_3SiH$ to interact with a base site on solid base in a pentacoordinate mode, as shown in Fig. 1, and a hydride in $(EtO)_3SiH$ undergoes activation enough to attack a carbonyl function.

Although ester carbonyl functions were inert to hydrosilane under acidic conditions, ethyl benzoate and methyl hexanoate suffered hydrosilylation in the presence of solid base, producing benzyloxy(triethoxy)silane and hexyloxy(triethoxy)silane, respectively.

α,β- Unsaturated carbonyl compounds such as cinnamaldehyde and benzylideneacetone were likewise hydrosilylated on HAp, yielding 1,2-reduction products in a triethoxylsilyl ether form.

In the present solid base-hydrosilane system, chemoselective reduction is possible: For instance, when an equimolar mixture of benzaldehyde and acetophenone, or of acetophenone and ethyl benzoate was applied to reduction with $(EtO)_3SiH$ (1 equiv) in heptane at 90 °C by use of HAp, benzaldehyde and acetophenone in each system were reduced with 100% selectivity.

In precedents of *heterogeneous* hydrosilylation, fluoride salts, such as KF and CsF, were employed as activators for hydrosilane with or without aprotic polar solvent, taking advantage of good affinity between fluoride and silicon. In the present study, we could unveil the facts that basic materials other than fluoride salts can also activate hydrosilane enough to reduce diverse carbonyl functions in nonpolar solvent so long as the solid base has medium basicity and relatively large surface area, and that in particular, hydroxyapatite is a preferred solid base catalyst for hydrosilylation.

Experimental

Measurement. The ^1H NMR spectra were recorded with a Hitachi R-600 (60 MHz) or a Varian GEMINI

Table 5. Solid Base-Catalyzed Hydrosilylation of Various Carbonyl Compounds with Hydrosilanes

Run	Substrate	Solid base[b]	Hydrosilane	Temp/°C (Time/h)	Product	Yield %
1	Heptanal (**11a**)	HAp	(EtO)$_3$SiH	90(4)	**12a**	81
2	Benzaldehyde (**11b**)	HAp	(EtO)$_3$SiH	90(2)	**12b**	72
3		CaO	(EtO)$_3$SiH	90(1)	**12b**	59
4	2-Octanone (**11c**)	HAp	(EtO)$_3$SiH	90(1)	**12c**	93
5		CaO	(EtO)$_3$SiH	90(2)	**12c**	71
6	Cyclohexanone (**11d**)	HAp	(EtO)$_3$SiH	90(1)	**12d**	99
7		CaO	(EtO)$_3$SiH	90(2)	**12d**	61
8		CaO	PhMe$_2$SiH	90(8)		0[c]
9		CaO	Et$_3$SiH	90(8)		0[c]
10		CaO	(EtO)$_3$SiH	90(2)	**12d**	24[d]
11		CaO	(EtO)$_3$SiH	40(2)		0[e]
12	Acetophenone (**11e**)	HAp	(EtO)$_3$SiH	90(5)	**12e**	72
13		HAp	PhMe$_2$SiH	90(20)		0
14		HAp	Et$_3$SiH	90(23)		0
15		CaO	(EtO)$_3$SiH	90(7)	**12e**	70
16		Ca(OH)$_2$	(EtO)$_3$SiH	90(21)		0
17		CaF$_2$	(EtO)$_3$SiH	90(21)		0
18	Benzophenone (**11f**)	HAp	(EtO)$_3$SiH	90(1)	**12f**	82[f]
19		CaO	(EtO)$_3$SiH	90(1)	**12f**	72[f]
20	Ethyl benzoate (**11g**)	HAp	(EtO)$_3$SiH	90(20)	**12b**	97[g]
21	Methyl hexanoate (**11h**)	HAp	(EtO)$_3$SiH	90(24)	**12h′**	44[g]
22	Cinnamaldehyde (**11i**)	HAp	(EtO)$_3$SiH	90(2)	**12i**	70[h]
23	Benzylideneacetone (**11j**)	HAp	(EtO)$_3$SiH	90(3)	**12j**	94[h]

a) Substrate (1 mmol) and hydrosilane (1.5 mmol) were mixed with a catalyst (0.5 g) in heptane (6 ml). b) HAp and CaF$_2$ were dried at 500 °C and 0.5 Torr for 2 h. CaO was prepared from Ca(OH)$_2$ by calcination at 500 °C and 0.5 Torr for 2 h. Ca(OH)$_2$ was an untreated sample. c) Condensation (aldol) reactions were observed. d) Toluene as solvent. e) CH$_2$Cl$_2$ as solvent. f) Obtained as an alcohol form. g) 3 mmol of (EtO)$_3$SiH was used. h) 1,2-Reduction product (100%).

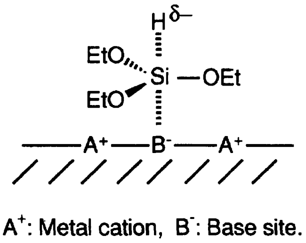


Fig. 1. (EtO)$_3$SiH activated on a base site of solid base.

200 (200 MHz) spectrometer. The ^{13}C NMR spectra were recorded with a Varian GEMINI 200 (50 MHz) spectrometer. The NMR spectra were measured in CDCl$_3$ 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 dectector and a capillary column (OV-1 Bonded, 25 m).

Materials (Catalysts and Reagents). Cation-exchanged montmorillonites were prepared from purified sodium ion-exchanged montmorillonite, "Kunipia-F" supplied by Kunimine Industries Co., Japan and passed through a 60 mesh sieve. Ion exchange was performed according to the procedure shown in Ref. 11b using aqueous solutions of corresponding salts (SnCl$_4$·xH$_2$O (x=4—5) for Sn-Mont, and Fe(NO$_3$)$_3$·9H$_2$O for Fe-Mont).

Powdery hydroxyapatite (HAp, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, Nacalai Tesque Inc.) and CaF$_2$ (Kishida Chemical Co.) were dried at 500 °C and below 0.5 Torr for 2 h in an electric furnace. CaO was prepared from Ca(OH)$_2$ (Kishida Chemical Co.) by calcination at 500 °C and below 0.5 Torr (1 Torr=133.322 Pa) for 2 h in an electric furnace.

Commercially available Et$_3$SiH, PhMe$_2$SiH, and (EtO)$_3$SiH were distilled and used. CF$_3$SO$_3$H and CF$_3$SO$_3$SiMe$_3$ were purchased and purified by distillation before use. Commercial aldehydes, ketones, esters, and enones 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). Organic solvents were dried over molecular sieves 4A.

General Procedure for Clay Montomorillonite-Catalyzed Reactions of Carbonyl Compounds with Et$_3$SiH. In a 20-ml round-bottom flask Sn-Mont or Fe-Mont (0.2 g) was dried at 120 °C and below 0.5 Torr for 3 h in an oil bath. Under argon atmosphere, to a suspended mixture of the montmorillonite and CH$_2$Cl$_2$ (1 ml) were added CH$_2$Cl$_2$ (2.5 ml) solutions of carbonyl compound (1 mmol) and Et$_3$SiH (1.1—5.0 mmol) at room temperature successively. In the reaction of 4,4′-dimethoxybenzophenone 1,2-dichloroethane was used as a solvent. The resulting mixture was stirred under the conditions shown 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), and the filtrate was evaporated. The products were purified on a silica-gel column or by distillation on a Kugelrohr apparatus.

CF_3SO_3H and $CF_3SO_3SiMe_3$-Catalyzed Reactions of Carbonyl Compounds with Et_3SiH. Under argon atmosphere, to a solution of a liquid acid (0.10—1.1 mmol) in solvent (2 ml) were added solutions of carbonyl compound (1 mmol) and Et_3SiH (1.1—5.0 mmol) in the same solvent (2 ml) at room temperature successively. The solution was stirred under the conditions listed in Tables. After the reaction was quenched with Et_3N (0.5 ml), the mixture was diluted with ether (10 ml) and then poured into water. The organic products were extracted with ether. The extract was washed with brine, and dried over anhydrous Na_2SO_4. The products were purified with a silica-gel column or by distillation on a Kugelrohr apparatus.

Poisoning of Sn-Mont with Et_3N. Poisoning of Sn-Mont with Et_3N was performed in the following manner: A CH_2Cl_2 (1 ml) solution of Et_3N (0.10 mmol) was added to a suspension of Sn-Mont (0.2 g) in CH_2Cl_2 (1.5 ml), and the mixture was stirred at room temperature for 15 min. After the poisoning, CH_2Cl_2 solutions (2.5 ml) of benzophenone (1 mmol) and Et_3SiH (2.2 mmol) were added successively, and the mixture was stirred at room temperature for 2 h.

General Procedure for Solid Base-Catalyzed Reactions of Carbonyl Compounds with $(EtO)_3SiH$. In a 20-ml round-bottom flask solid bases were dried or calcined under the specified conditions before use. Under argon atmosphere to a suspended mixture of the solid base and heptane (1 ml) were added the heptane (2.5 ml) solutions of carbonyl compound (1 mmol) and $(EtO)_3SiH$ (1.5—3.0 mmol) at room temperature successively. The resultant mixture was stirred under the conditions shown in Table 5. Completion of the reaction was confirmed with GC or TLC. As work-up, solid catalyst 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 alkoxy(triethoxy)silane.

Cyclohexyloxy(triethyl)silane (2a): Bp 125 °C (bath temperature)/20 Torr; IR (CCl_4) 1238 (CH_2Si), 1092 cm^{-1} (C–O–Si); ^1H NMR ($CDCl_3$) $\delta=0.59$ (q, 6H, $J=7.8$ Hz, $CH_3C\underline{H}_2Si$), 0.96 (t, 9H, $J=7.8$ Hz, $C\underline{H}_3CH_2Si$), 1.05—1.95 (br, 10H, $(CH_2)_5$), 3.56 (br, 1H, CH).

Dicyclohexyl Ether (3a): Bp 125 °C (bath temperature)/20 Torr; IR (CCl_4) 1088 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ=1.00—2.05 (br, 20H, $(CH_2)_5$), 3.32 (br, 2H, CH). (Found: C, 79.10; H, 12.39%)

Dibenzyl Ether (3d): Bp 120 °C (bath temperature)/0.5 Torr; IR (CCl_4) 1455 (CH_2), 1090 and 1070 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) $\delta=4.56$ (s, 4H, CH_2), 7.34 (s, 10H, C_6H_5).

Ethylbenzene (4b): Bp 90 °C (bath temperature)/100 Torr; IR (CCl_4) 1455 cm^{-1} (CH_2); ^1H NMR ($CDCl_3$) $\delta=$ 1.23 (t, 3H, $J=7.4$ Hz, CH_3), 2.65 (q, 2H, $J=7.4$ Hz, CH_2), 7.22 (s, 5H, C_6H_5).

Diphenylmethane (4c): Bp 150 °C (bath temperature)/20 Torr; IR (CCl_4) 2910 and 1455 cm^{-1} (CH_2); ^1H NMR ($CDCl_3$) $\delta=3.97$ (s, 2H, CH_2), 7.22 (s, 10H, C_6H_5).

4,4'Dimethoxydiphenylmethane (6): Mp 49.0—50.0 °C; IR (CCl_4) 1464 cm^{-1} (CH_2); ^1H NMR ($CDCl_3$) $\delta=3.77$ (s, 6H, CH_3O), 3.86 (s, 2H, CH_2), 6.82 (d, 4H, $J=8.8$ Hz, $C\underline{H}COCH_3$), 7.09 (d, 4H, $J=8.8$ Hz, $C\underline{H}CCH_2$); ^{13}C NMR ($CDCl_3$) $\delta=39.97$, 55.15, 113.91, 129.85, 133.85, 158.10.

Benzyl Methyl Ether (8): Bp 80 °C (bath temperature)/20 Torr; IR (CCl_4) 1452 (CH_2), 1100 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) $\delta=3.37$ (s, 3H, CH_3), 4.45 (s, 2H, CH_2), 7.73 (s, 5H, C_6H_5).

Triethoxy(heptyloxy)silane (12a): Bp 110 °C (bath temperature)/0.3 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=0.88$ (t, 3H, $J=6.8$ Hz, CH_3), 1.24 (t, 9H, $J=7.0$ Hz, $C\underline{H}_3CH_2O$), 1.20—1.40 (br, 8H, $(CH_2)_4$), 1.58 (m, 2H, $C\underline{H}_2CH_2O$), 3.77 (t, 2H, $J=6.6$ Hz, CH_2), 3.85 (q, 6H, $J=7.0$ Hz, $CH_3C\underline{H}_2O$); ^{13}C NMR ($CDCl_3$) $\delta=13.88$, 17.93, 22.44, 25.45, 28.88, 31.69, 32.20, 59.09, 63.49. Found: C, 55.88; H, 11.01%. Calcd for $C_{13}H_{30}O_4Si$: C, 56.07; H, 10.86%.

Benzyloxy(triethoxy)silane (12b): Bp 150 °C (bath temperature)/0.5 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=1.23$ (t, 9H, $J=7.0$ Hz, $C\underline{H}_3CH_2O$), 3.85 (q, 6H, $J=7.0$ Hz, $CH_3C\underline{H}_2O$), 4.88 (s, 2H, $C_6H_5C\underline{H}_2O$), 7.25—7.40 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) $\delta=17.90$, 59.22, 65.19, 126.79, 127.37, 128.38, 140.33. Found: C, 57.99; H, 8.00%. Calcd for $C_{13}H_{22}O_4Si$: C, 57.74; H, 8.20%.

Triethoxy(1-methylheptyloxy)silane (12c): Bp 100 °C (bath temperature)/0.2 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=0.87$ (t, 3H, $J=6.2$ Hz, $C\underline{H}_3CH_2$), 1.19 (d, 3H, $J=6.2$ Hz, $C\underline{H}_3CH$), 1.23 (t, 9H, $J=7.0$ Hz, $C\underline{H}_3CH_2O$), 1.20—1.35 (br, 10H, $(CH_2)_5$), 3.84 (q, 6H, $J=7.0$ Hz, $CH_3C\underline{H}_2O$), 3.92—4.08 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) $\delta=13.90$, 17.94, 22.47, 23.06, 25.39, 29.14, 31.73, 39.08, 59.02, 69.64. Found: C, 57.58; H, 11.02%. Calcd for $C_{14}H_{32}O_4Si$: C, 57.49; H, 11.03%.

Cyclohexyloxy(triethoxy)silane (12d): Bp 70 °C (bath temperature)/0.2 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=1.23$ (t, 9H, $J=6.8$ Hz, $C\underline{H}_3CH_2O$), 1.0—2.0 (br, 10H, $(CH_2)_5$), 3.85 (br, 1H, CH), 3.85 (q, 6H, $J=6.8$ Hz, $CH_3C\underline{H}_2O$). Found: C, 54.72; H, 10.04%. Calcd for $C_{12}H_{26}O_4Si$: C, 54.92; H, 9.99%.

Triethoxy(1-phenylethoxy)silane (12e): Bp 120 °C (bath temperature)/0.3 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=1.18$ (t, 9H, $J=6.8$ Hz, $C\underline{H}_3CH_2O$), 1.50 (d, 3H, $J=6.4$ Hz, CH_3), 3.78 (q, 6H, $J=6.8$ Hz, $CH_3C\underline{H}_2O$), 5.12 (q, 1H, $J=6.4$ Hz, CH), 7.20—7.42 (m, 5H, C_6H_5). Found: C, 58.86; H, 8.63%. Calcd for $C_{14}H_{24}O_4Si$: C, 59.12; H, 8.51%.

Benzhydrol: Product **12f** was desilylated to benzhydrol, followed by distillation. Bp 130 °C (bath temperature)/0.5 Torr; IR (CCl_4) 3600 and 3450 cm^{-1} (OH); ^1H NMR ($CDCl_3$) $\delta=2.40$ (s, 1H, OH), 5.75 (s, 1H, CH), 7.29 (s, 10H, C_6H_5).

Triethoxy(hexyloxy)silane (12h'): Bp 70 °C (bath temperature)/0.5 Torr; IR (CCl_4) 1100 and 1080 cm^{-1} (Si–O–C); ^1H NMR ($CDCl_3$) $\delta=0.89$ (t, 3H, $J=6.8$ Hz, CH_3), 1.24 (t, 9H, $J=7.0$ Hz, $C\underline{H}_3CH_2O$), 1.20—1.40 (br, 6H, $(CH_2)_3$), 1.59 (m, 2H, $C\underline{H}_2CH_2O$), 3.77 (t, 2H, $J=6.6$ Hz, CH_2OSi), 3.85 (q, 6H, $J=7.0$ Hz, $CH_3C\underline{H}_2O$); ^{13}C NMR ($CDCl_3$) $\delta=13.84$, 17.93, 22.46, 25.17, 31.43, 32.16, 59.09, 63.50. Found: C, 54.35; H, 10.84%. Calcd for $C_{12}H_{28}O_4Si$: C, 54.51; H, 10.67%.

Triethoxy(3-phenyl-2-propenyloxy)silane (12i): Bp 150 °C (bath temperature)/0.3 Torr; IR (CCl_4) 1600

(C=C), 1100 and 1080 cm^{-1} (Si–O–C); ^{1}H NMR ($CDCl_3$) δ=1.25 (t, 9H, J=7.0 Hz, $C\underline{H}_3CH_2O$), 3.88 (q, 6H, J=7.0 Hz, $CH_3C\underline{H}_2O$), 4.49 (dd, 2H, J=5.4, 1.6 Hz, CH_2), 6.32 (dt, 1H, J=15.8, 5.4 Hz, $C_6H_5CH=C\underline{H}$), 6.63 (dt, 1H, J=15.8, 1.6 Hz, $C_6H_5C\underline{H}=CH$), 7.20—7.42 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ=17.95, 59.25, 63.99, 126.57, 127.62, 128.02, 128.66, 130.55.

Triethoxy(1-methyl-3-phenyl-2-propenyloxy)silane (12j): Bp 150 °C (bath temperature)/0.5 Torr; IR (CCl_4) 1600 (C=C), 1100 and 1080 cm^{-1} (Si–O–C); ^{1}H NMR ($CDCl_3$) δ=1.24 (t, 9H, J=7.0 Hz, $C\underline{H}_3CH_2O$), 1.39 (d, 3H, J=6.4 Hz, CH_3COSi), 3.86 (q, 6H, J=7.0 Hz, $CH_3C\underline{H}_2O$), 4.66—4.78 (m, 1H, CHOSi), 6.25 (dd, 1H, J=6.0, 16.0 Hz, $C_6H_5CH=C\underline{H}$), 6.57 (d, 1H, J=16.0 Hz, $C_6H_5C\underline{H}=CH$), 7.20—7.45 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ=17.92, 23.88, 59.13, 70.02, 126.53, 127.52, 128.64, 128.83, 133.34. Found: C, 62.03; H, 8.21%. Calcd for $C_{16}H_{26}O_4Si$: C, 61.91; H, 8.44%.

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