New Application of Solid Acid to Carbon-Carbon Bond Formation Reactions: Clay Montmorillonite-Catalyzed Aldol Reactions of Silyl Enol Ethers with Aldehydes and Acetals

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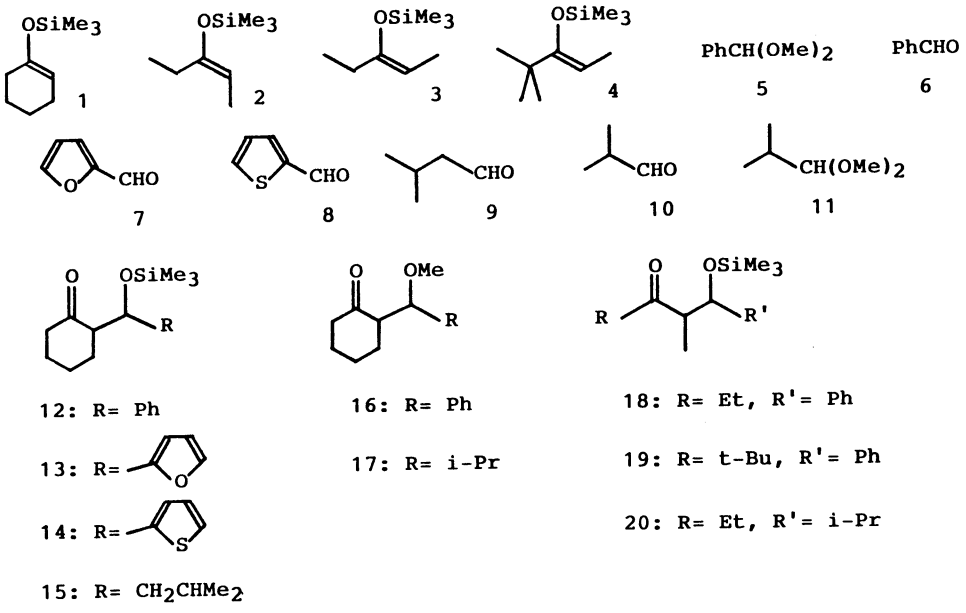
A new attempt of utilizing solid acid to the cross aldol reaction of silyl enol ethers with aldehydes or acetals has been investigated. Among solid acids employed, the reaction is promoted most effectively by a catalytic amount of aluminium ion-exchanged montmorillonite (Al-Mont). Simple diastereoselection is significantly sensitive to the nature of the reaction solvent used in the Al-Mont-catalyzed reaction. When the aluminium ions in Al-Mont were replaced by protons or titanium ions in order to investigate the cation effect, almost the same results were observed on simple diastereoselectivity and diastereofacial selectivity. This fact suggests that the metal cations in montmorillonite do not work as Lewis acid in the present aldol reaction. The acid catalysis of montmorillonite in the present aldol reaction is discussed in comparison with the catalytic behavior of some homogeneous acids.

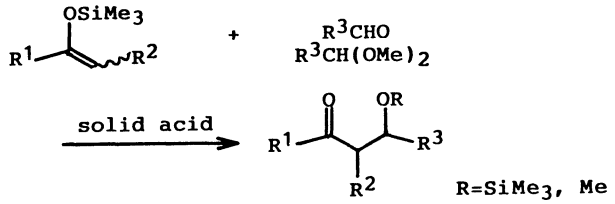
The use of a preformed metal enolate has become a general method for the directed cross aldol reactions.[1] Especially, silyl enol ethers are widely utilized as enolates owing to their isolable properties, and undergo directed aldol reactions with carbonyl compounds in the presence of acidic promoters or by treatment of fluoride ions. As acidic promoters, not only a stoichiometric amount of Lewis acid like $TiCl_4$[2a] but also a catalytic amount of $CF_3SO_3SiMe_3$,[2b] Ph_3CClO_4,[2c] or Me_2AlCl[2d] are used to activate aldehydes or acetals electrophilically. These promoters are soluble in the reaction media, but there is few reports on the aldol reaction using a solid acid as a promoter under heterogeneous conditions.[3]

Recently we demonstrated that the allylation of acetals and carbonyl compounds with allylic silanes was catalyzed by solid acids in a heterogeneous system.[4] Especially clay montmorillonite was found to be the most efficient catalyst among the solid acids of mica, zeolite, silica-alumina, and ion-exchange resin. This experiment is the first example of an inorganic solid acid-catalyzed carbon-carbon bond-formation reaction using organosilicon reagents.[5]

Clay montmorillonite is a layered silicate possessing ion-exchange ability.[6a] Acid property of montmorillonite can be easily altered by replacing interlayered cations in the montmorillonite without any change of the crystalline structure. Although several works using montmorillonite have been done for the acid-catalyzed organic reactions,[6] the application of montmorillonite to C-C bond-formation reactions under mild conditions is quite rare. For example, montmorillonite was reported to promote the Friedel-Crafts type alkylations,[7a] the Diels-Alder reactions,[7b] and the condensation of acetals with alkyl vinyl ethers.[7c]



Our objectives are to utilize inorganic solid acids instead of liquid acids to complete C-C bond-formation reactions and to compare catalysis between heterogeneous and homogeneous acids. A montmorillonite-catalyzed allylation reaction is one of them.[4] We have also showed that aluminium ion-exchanged montmorillonite (Al-Mont) is an effective catalyst for the aldol reactions of silyl enol ethers or silyl ketene acetals with carbonyl compounds or acetals.[8] Here we describe additional examples of the aldol reactions and clarify the catalysis of the montmorillonite.



Results and Discussion

Simple Diastereoselection. The reaction of silyl enol ether **1** with an acetal **5** was examined in the presence of various solid acids and the results are listed in Table 1. The reaction proceeded smoothly with the aid of solids even under heterogeneous conditions to afford the corresponding aldol adducts in good yield (Entries 1—5, 7). Among solid acids, aluminium ion-exchanged montmorillonite (Al-Mont) showed the highest catalytic activity (Entries 1, 2) and good diastereoselectivity for an erythro adduct especially in 1,2-dimethoxyethane (DME) (Entry 2).

Next, the reaction of **1** with an aldehyde **6** was examined with respect to catalytic activity and diastereoselectivity affected both by reaction solvents and by exchangeable cations in the montmorillonite (Table 2, Entries 1—6). Al-Mont showed slightly higher activity than proton- or titanium ion-exchanged montmorillonite (described as H-Mont and Ti-Mont, respectively) (Entries 1, 2, 5, 6). Al-Mont also showed higher diastereoselectivity since the reaction proceeded at lower temperature.

The use of solid acids in liquid-phase organic reactions provides an advantage of a much more simple work-up procedure compared with that of liquid acids. As work up, only filtering a reaction mixture through a Celite pad is required in order to separate a solid catalyst from organic products. Thus the aldol adduct **12** was obtained in the form of trimethylsilyl ether.

Table 1. The Aldol Reaction of **1** with **5**[a]

Entry	Catalyst	Condition Temp/°C (Time/h)	Yield/ %[b]	Threo: Erythro
1	Al-Mont	−78(1), −50(0.2)	84	45:55
2	Al-Mont[b]	−60(0.5), −50(1.5)	93	13:87
3	SiO_2-Al_2O_3	−50(0.3), −30(1)	73	30:70
4	SiO_2-Al_2O_3[b]	−20(6)	79	21:79
5	CaY	0(2)	73	23:77
6	CaY[b]	0(1), 15(70)	0	—
7	Nafion-117[c]	−20(1), 0(1)	69	23:77
8	CF_3SO_3H[d]	−78(0.5)	80	9:91
9	CH_3SO_3H[e]	20(18)	0	—
10	$CF_3SO_3SiMe_3$[f]	−78(0.5)	89	7:93
11	BF_3-OEt_2[g]	−78(0.5)	78	22:78

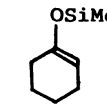
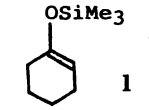
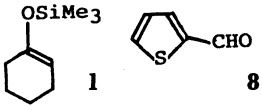
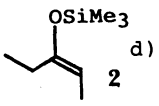
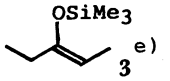
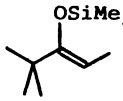
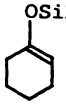
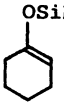
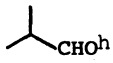
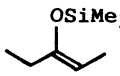
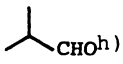
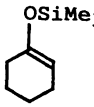
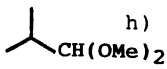
a) **1** (1 mmol), **5** (1 mmol), solid acid (0.2 g), solvent (CH_2Cl_2). b) DME was used as solvent. c) An ion exchange resin which contains 1 mmol·g^{-1} of proton. Nafion 117 (0.1 g) was used. d) 0.01 mmol. e) 0.12 mmol. f) 0.01 mmol. This result is quoted from Ref. 2b. g) 1 mmol.

Table 2. The Aldol Reaction of **1** with **6**[a]

Entry	Catalyst	Solvent	Condition temp/°C (Time/h)	Yield/%	Threo: Erythro
1	H-Mont	$PhCH_3$	−50(2.5), −30(2)	75	68:32
2	Al-Mont	$PhCH_3$	−78(0.5), −50(1)	82	71:29
3	Al-Mont	CH_2Cl_2	−95(2.5)	91	63:37
4	Al-Mont	Et_2O	−50(0.1), −30(1)	82	44:56
5	Al-Mont	DME	−60(6.5)	81	21:79
6	Ti-Mont	DME	−50(0.3), −30(1)	76	28:72
7	SiO_2-Al_2O_3	$PhCH_3$	−30(0.3), −20(0.5)	54	48:52
8	SiO_2-Al_2O_3	CH_2Cl_2	−30(0.5), −10(0.5)	40	50:50
9	SiO_2-Al_2O_3	DME	0(0.3), 25(0.5)	14	32:68
10	CaY	CH_2Cl_2	20(12)	70	51:49
11	CF_3SO_3H[b]	$PhCH_3$	−20(0.2), 25(1)	0	—
12	CF_3SO_3H[c]	CH_2Cl_2	−78(0.5)	74	44:56
13	CF_3SO_3H[d]	DME	−78(0.5), −50(0.5)	58	44:56
14	CH_3SO_3H[b]	CH_2Cl_2	20(18)	0	—
15	$CF_3SO_3SiMe_3$[c]	CH_2Cl_2	−78(0.5)	84	51:49
16	$BF_3 \cdot OEt_2$[e]	$PhCH_3$	−78(0.5)	60	39:61
17	$BF_3 \cdot OEt_2$[e,f]	CH_2Cl_2	−78(1)	80	74:26
18	$BF_3 \cdot OEt_2$[e]	DME	−78(0.5), −40(0.5)	60	50:50

a) **1** (1 mmol), **6** (1 mmol), montmorillonite (0.2 g), SiO_2-Al_2O_3 (0.2 g), CaY (0.5 g). b) 0.1 mmol. c) 0.003 mmol. d) 0.008 mmol. e) 1 mmol. f) This result is quoted from Ref. 2a.

Table 3. The Reactions of Silyl Enol Ethers with Aldehydes or Acetals Catalyzed by Al-Mont[a)]

Entry	Silyl enol ether	Aldehyde or acetal	Solvent	Condition Temp/°C (Time/h)	Yield/%[b)]	Threo: Erythro
1			$PhCH_3$	−78(0.5), −50(1)	82	71:29
2		PhCHO	CH_2Cl_2	−95(2.5)	91	63:37
3	**1**	**6**	DME	−60(6.5)	81	21:79
4			$PhCH_3$	−50(1), −40(1)	58[c)]	41:59
5			CH_2Cl_2	−78(1), −50(1)	85	67:33
6	**1**	**7**	DME	−50(1)	65	20:80
7			$PhCH_3$	−70(1), −40(1.5)	71[c)]	74:26
8			CH_2Cl_2	−78(0.6)	83	62:38
9	**1**	**8**	DME	−50(0.2), −30(1)	56	29:71
10			$PhCH_3$	−60(0.5)	97	76:24
11	d)	PhCHO	CH_2Cl_2	−78(0.5)	93	59:41
12	**2**	**6**	DME	−50(1), −30(1)	76	56:44
13			$PhCH_3$	−70(1), −60(2)	85	63:37
14	e)	PhCHO	CH_2Cl_2	−78(1)	89	53:47
15	**3**	**6**	DME	−50(1), −30(1)	73	50:50
16		PhCHO	CH_2Cl_2	−78(0.3), −60(2)	78	96: 4
17	**4**	**6**	DME	−30(1), 0(1)	40	90:10
18			$PhCH_3$	−50(3), −30(2)	94	49:51
19		$PhCH(OMe)_2$	CH_2Cl_2	−60(0.5), −50(0.2)	84	45:55
20	**1**	**5**	DME	−65(0.5), −50(1.5)	93	13:87
21			$PhCH_3$	−40(1), −30(4)	22[f)]	43:57
22			CH_2Cl_2	−78(0.5), −50(1)	86	62:38
23	**1**	**9**	DME	−30(0.5), −20(1)	29[g)]	43:57
24			$PhCH_3$	−30(2), −20(2)	57	72:28
25	d)		CH_2Cl_2	−65(1), −50(1.5)	69	46:54
26	**2**	**10**	DME	−40(0.5), −20(2)	22[f)]	74:26
27			$PhCH_3$	−30(0.5), −20(2)	68	41:59
28	e)		CH_2Cl_2	−50(1), −30(1)	64	37:63
29	**3**	**10**	DME	−30(0.5), −20(2)	14[f)]	42:58
30			$PhCH_3$	−50(0.5), −30(2)	77	30:70
31			CH_2Cl_2	−50(1), −30(1)	75	30:70
32	**1**	**11**	DME	−55(0.2), −30(1)	55[f)]	25:75

a) Silyl enol ether (1 mmol), aldehyde (1 mmol), and Al-Mont (0.2 g) were used. b) Isolated yield. c) 2 mmol of aldehyde was used. d) E/Z=83/17. e) E/Z=10/90. f) Unidentified by-products were obtained. g) The major by-product was cyclohexanone. h) 1.3 mmol of aldehyde or acetal was used.

The diastereoselectivity in the montmorillonite-catalyzed aldol reaction of **1** and **6** was considerably dependent on the nature of solvent.[9)] A threo isomer was preferentially formed in toluene (Table 2, Entries 1, 2), while an erythro isomer was dominant in DME (Table 2, Entries 5, 6).

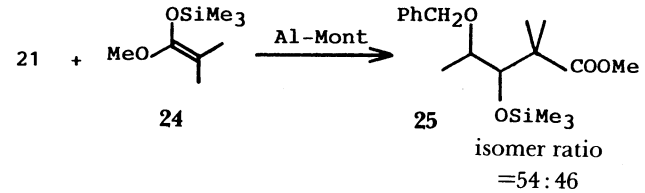
The solvent effect on the diastereoselectivity was also observed with other substrates in Table 3. Generally, when aromatic aldehydes (benzaldehyde, furfural,[10)] 2-thiophenecarbaldehyde) and benzaldehyde dimethyl acetal were used, the ratio of threo to erythro increased in the following order of the solvent except Entry 4: DME < CH_2Cl_2 < $PhCH_3$ (Entries 1—3, 5—20). In the case of an aliphatic aldehyde and its acetal (Entries 21—32), however, the orderly solvent effects were not observed.

The dependence of diastereoselection upon solvents was not specific to the montmorillonite-catalyzed aldol reactions, but also recognized in the reactions promoted by a solid acid of SiO_2-Al_2O_3 (Table 2, Entries 7—9) and a homogeneous liquid acid of $BF_3 \cdot OEt_2$ (Table 2, Entries 16—18) though to a lesser extent. However no common pattern for the solvent effect was observable.

Acid strength of Al-Mont was measured in various solvents by use of Hammett indicators, and the result is listed in Table 4. In CH_2Cl_2 or $PhCH_3$, strongly acidic sites ($H_0 \leqq -8.2$) were detected on Al-Mont.[11] On the other hand, the acid strength of Al-Mont was weakened to $-5.6 < H_0 \leqq -3.0$ in 1,2-dimethoxyethane (DME). DME is relatively basic and thus interacts with the acid sites on montmorillonite to reduce their acid strength. We assume that the diastereoselectivity of the aldol reaction catalyzed by Al-Mont relates with the acid strength of Al-Mont since the interaction between aldehydes (acetals) and acid sites on Al-Mont is depending on the acid strength of the acid sites, and influences the stabilities of transition states of the reaction.

Diastereofacial Selection. In addition to simple diastereoselection, we also investigated diastereofacial selection in Al-Mont-catalyzed aldol reactions.

Reetz and his co-workers found that good asymmetric induction was observed in the Lewis acid-mediated aldol reactions of α- and β-alkoxy aldehydes with silyl enol ethers.[12] The diastereofacial preferences were explained with a chelation model having coordination between the two oxygens of an alkoxy aldehyde and a metal of Lewis acid. We examined whether chelation control is possible for metal cations in montmorillonite. In contrast to $TiCl_4$ which induced exclusively a chelation-controlled product **23a**,[13] various metal ions-exchanged montmorillonites showed only a slight preference for **23a** over **23b** and almost the same ratio of **23a** to **23b** irrespective of a metal cation (Table 5). The reaction of **21** with silyl ketene acetal **24** was also examined, but the diastereoselectivity was low.



24 25

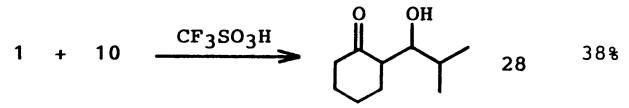
isomer ratio =54:46

These facts suggest that exchangeable ions in montmorillonite do not work as Lewis acid. Moreover, proton-exchanged montmorillonite (H-Mont) showed similar activity and diastereoselectivity to those of Al-Mont (Table 2, Entry 1,2; Table 5). Thus we assume that Brönsted acid sites (protons) generated by the dissociation of hydrated water in Al-Mont[14] actually play an important role in promoting the present aldol reaction.

$$M^{n+}(H_2O) \rightarrow (M\text{-}OH)^{(n-1)+} + H^+$$

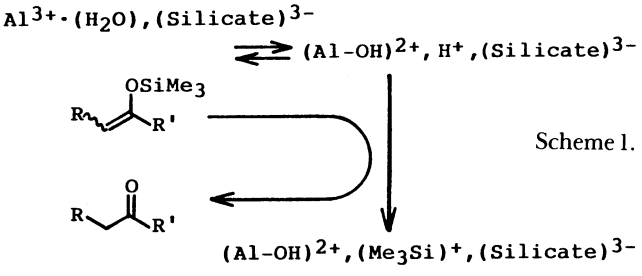
Secondly, we chose an aldehyde **26** to investigate whether Cram's rule is applicable. In analogy with $BF_3 \cdot OEt_2$-mediated reactions of *t*-butyldimethylsilyl enol ether,[15] Al-Mont showed high asymmetric induction in the reaction of **26** with **22** to afford **27a** (a Cram product) selectively (Table 6).

Comparison of Catalysis between Al-Mont and Trifluoromethanesulfonic Acid (CF_3SO_3H). As homogeneous acid catalysts, we chose CF_3SO_3H and its silylated form, trimethylsilyl trifluoromethanesulfonate ($CF_3SO_3SiMe_3$) so as to compare the acid catalysis between heterogeneous and homogeneous acids. $CF_3SO_3SiMe_3$ was reported to be ineffective for the aldol reactions of aldehydes with silyl enol ethers.[2b] In our hands, however, the reaction of **1** with **6** smoothly proceeded even at low temperature in the presence of $CF_3SO_3SiMe_3$ as well as CF_3SO_3H[16] (Table 2, Entries 12, 13, 15). CF_3SO_3H also promoted the reaction of **1** with an aliphatic aldehyde.



The catalytic behavior of $CF_3SO_3SiMe_3$ and CF_3SO_3H with respect to both the yield and the diastereoselectivity of **12** was found to be almost the same (Table 1, Entries 8, 10; Table 2, Entries 12, 15). CF_3SO_3H is known to be transformed to $CF_3SO_3SiMe_3$ on treatment with a silylating reagent.[17] On the basis of these facts, it seems likely that CF_3SO_3H is silylated by silyl enol ether to generate an active species of $CF_3SO_3SiMe_3$ which is in turn involved in an acid catalysis cycle[2b] of the aldol reaction.

Similarly, in the case of Al-Mont, we speculate that an active species is not a Brönsted acid site (proton) itself but a trimethylsilyl cation species derived from the reaction of Al-Mont and silyl enol ethers.[18]



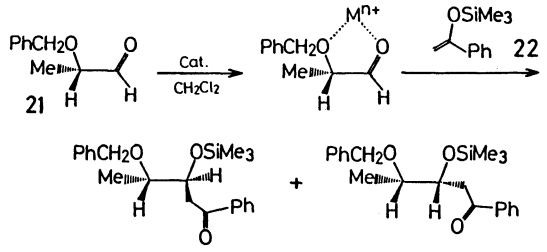
Scheme 1.

Table 4. Acid Strength of Al-Mont in Various Solvents

Indicator (H_0)	AQ (−8.2)	BAP (−5.6)	DCA (−3.0)	Maximum acid strength
$PhCH_3$	+	+	+	$H_0 \leqq -8.2$
CH_2Cl_2	+	+	+	$H_0 \leqq -8.2$
DME	−	−	+	$-5.6 < H_0 \leqq -3.0$

AQ=anthraquinone, BAP=benzylideneacetophenone, DCA=dicinnamylideneacetone.

Table 5. The Aldol Reaction of **21** with **22**

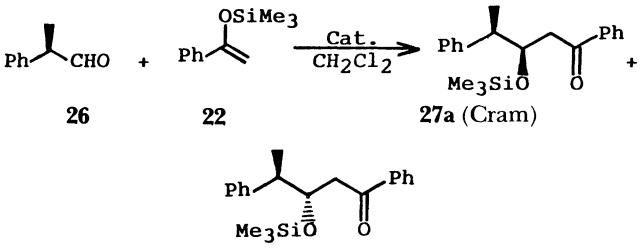


23a (chelation) **23b** (non chelation)

Catalyst	Temp/°C (Time/h)	Yield/%	**23a : 23b**
Al-Mont	−65(1)	36	65 : 35
H-Mont	−50(1)	23	66 : 34
Ti-Mont	−20(1)	31	64 : 36

Reaction conditions: **21** (1 mmol), **22** (1 mmol), montmorillonite (0.2 g), solvent (CH_2Cl_2).

Table 6. The Aldol Reaction of **22** with **26**



26 **22** **27a** (Cram)

27b (anti Cram)

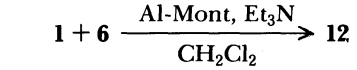
Catalyst	Temp/°C (Time/h)	Yield/%	**27a : 27b**
Al-Mont	−65(1)	65	93 : 7
H-Mont	−50(1)	54	92 : 8

Reaction conditions: **22** (1 mmol), **26** (1 mmol), montmorillonite (0.2 g), solvent (CH_2Cl_2).

Consideration about Acid Strength of Al-Mont. Both Al-Mont and CF_3SO_3H (a super acid[19]) promote the aldol reaction of **1** and **5**, while CH_3SO_3H (a strong acid) is completely ineffective (Table 1, Entry 9; Table 2, Entry 14). Therefore the acid strength of Al-Mont is considered to be stronger than CH_3SO_3H. Moreover, Al-Mont promoted the allylation reaction of 4-*t*-butylcyclohexanone with allyltrimethylsilane (80% yield)[4] but CF_3SO_3H failed.[20] Thus Al-Mont has higher catalytic activity than CF_3SO_3H.

Although acid strength of montmorillonite (dried at 120—130 °C in air) has been estimated to be rather low ($-8.2 < H_0 \leqq -3.0$) by several groups,[14,21] we observed that the sample of Al-Mont which was dried at 25 °C/0.5 Torr (1 Torr=133.322 Pa) for 24 h showed maximum acid strength of $-8.2 < H_0 \leqq -5.6$ in CH_2Cl_2, and the sample which was dried at 120 °C/0.5 Torr for 3 h possessed very strong acid sites of $H_0 \leqq -8.2$ in CH_2Cl_2 (Table 4). Judging from our results concerning the allylation[4] and the aldol reactions, Al-Mont (dried at 120 °C/0.5 Torr for 3 h) is one of the strongest solid acids.

Table 7. Poisoning Experiments[a]



Entry	Et_3N (mol%)[b]	Yield of **12**/%	Threo: Erythro
1	0	93	61 : 39
2	0.05	95	62 : 38
3	0.15	58	64 : 36
4	0.5	1[c]	—
5	4.7	0[c]	—

a) **1** (1 mmol), **6** (1 mmol), Al-Mont (0.2 g), solvent (CH_2Cl_2), −78 °C, 0.5 h. b) Mol% of Et_3N based on **6**. c) Estimated by GC.

The Amount of Active Sites on Montmorillonite for Aldol Reactions. In order to confirm that Al-Mont acts catalytically in promoting the aldol reaction, the number of active site on Al-Mont was estimated by a poisoning experiment. After a part of acid sites on Al-Mont was deactivated by addition of triethylamine, the standard aldol reaction of **1** with **6** was performed, and judged from the change in the yield of **12**. The results are listed in Table 7. Surprisingly, only 0.5 mol% of the amine based on an aldehyde **6** is enough completely to prevent the reaction at −78 °C (Entry 4). It is concluded that a very small amount (less than 0.025 meq/g · Al-Mont) of acid sites on Al-Mont acts as an efficient catalyst in the aldol reaction.

Experimental

Measurement. ^1H NMR spectra were recorded in $CDCl_3$ with a Hitachi R-600 (60 MHz) spectrometer. ^{13}C NMR spectra were measured in $CDCl_3$ with a JEOL FX-60 spectrometer at 15 MHz or a JEOL JNM GX-400 spectrometer at 100 MHz. The chemical shifts (δ) are expressed in parts per million downfield from an internal standard of tetramethylsilane. Infrared spectra were recorded in CCl_4 on a JASCO IRA-2 spectrometer. Analytical gas-liquid chromatography (GC) was done with a Shimadzu GC-8A instrument with a flame ionization detector and nitrogen carrier gas. The following capillary columns were used: OV-1 Bonded, 25 m×0.25 mm; PEG-HT Bonded, 25 m×0.25 mm. The flow rate of carrier gas was 1—2 ml min^{-1} (0.5—1.0 kg cm^{-2}). Preparative thin-layer chromathography (TLC) was done on 20×20 cm glass plates coated with 1 mm thickness of Merck silica gel PF_{254}.

Solvents and Reagents. Dichloromethane was distilled from P_2O_5 and stored over Molecular Sieves 3A. Toluene was dried over Molecular Sieves 3A. 1,2-Dimethoxyethane (DME) and ether were distilled from $LiAlH_4$ prior to use. Triethylamine, $CF_3SO_3SiMe_3$, and pyridine were distilled from CaH_2. $BF_3 \cdot OEt_2$, 4-*t*-butylcyclohexanone, and Hammett indicators [anthraquinone (AQ), benzylideneacetophenone (BAP), and dicinnamylideneacetone (DCA)] were purchased and used without further purification. Silyl enol ethers, **1**,[22] **2** (*E* : *Z*=87 : 13),[23] **3** (*E* : *Z*=10 : 90),[24] **4** (*Z* isomer

only),[23] and **22**[22] were prepared according to the literature and the isomeric ratio of these substrates was determined by GC. Silyl ketene acetal **24** was prepared according to the literature.[25] Aldehydes **6**—**10**, **26** and CF_3SO_3H were commercially available and distilled before use. Aldehyde **21** was prepared according to the literature.[26] Acetals **5** and **11** were prepared by a conventional procedure.

Preparation of Ion-Exchanged Montmorillonites. The montmorillonite used in this study was purified Na^+ ion-exchanged montmorillonite, "Kunipia F" (cation-exchange capacity=1.19 meq. g^{-1}) supplied by Kunimine Industries Co. Aluminium ion exchange was effected by the addition of the powdered sodium ion-exchanged montmorillonite (Na-Mont, 100 g) to an aqueous solution (800 ml) of $Al(NO_3)_3 \cdot 9H_2O$ (150 g, 0.4 mol) with vigorous stirring at rt for 2 h. The resultant suspension was filtered on a Büchner funnel by suction. The clay was collected, suspended again in deionized water (500 ml) with stirring at rt for 1 h, filtered on a suction funnel, and washed with deionized water (200 ml). The clay collected was again suspended in a mixture of deionized water (200 ml) and methanol (200 ml) with stirring at rt for 1 h and filtered. This procedure was repeated twice. The washed clay was predried at 20 °C/1 Torr for 6 h, and the agglomerated clay was then ground and passed through a 60 mesh screen. The resultant powdery clay was dried at 20 °C/0.5 Torr for 24 h, and stored in a desiccator over anhydrous silica gel until use.

Similarly titanium ion exchange was conducted using 10 g of Na-Mont and aqueous $TiCl_3$ and the grinding of the Ti-excanged montmorillonite was performed under nitrogen atmosphere. Proton exchange was done using 5 g of Na-Mont and 100 ml of 1 mol dm^{-3} HCl.

Other Solid Acids. SiO_2-Al_2O_3 is a reference catalyst provided by Catalysis Society of Japan: JRC-SAL-2 (Al_2O_3 content: 13.75%). Zeolite CaY (the content of cations: Ca^{2+} 45%, Na^+ 55%) was prepared by treatment of NaY (Shokubai Kasei Co.: ZCP-50) with aqueous $CaCl_2$.[27] SiO_2-Al_2O_3 and CaY was predried at 400 °C in air for 3 h, stored in a desiccator, and then dried over flames at ca. 350 °C/0.5 Torr for 10 min or dried over an electric furnace at 400 °C/0.5 Torr for 3 h (Table 2, Entries 7—9) in a reaction vessel prior to use.

Nafion-117 [a perfluorinated resin of sulfonic acid (1 meq. g^{-1}, Du Pont)] was immersed in dry methanol overnight, washed with dry methanol, dried at 25 °C and 0.5 Torr for 30 min, and used for the reaction of **1** with **5**.

General Procedure for Clay Montmorillonite-Catalyzed Aldol Reactions of Silyl Enol Ethers with Aldehydes and Acetals. Montmorillonite (0.2 g) in a 20 ml round-bottomed flask was dried at 120 °C and 0.5 Torr for 3 h in an oil bath, and cooled under nitrogen. A solution of an aldehyde or an acetal (1 mmol) in a solvent (3 ml) was added. After the mixture being stirred for 1 min, a solution of silyl enol ether (1 mmol) in a solvent (1 ml) was added at −78 °C. The temperature was raised, the mixture was stirred under the conditions listed in tables. As work-up, cold ether (−50 °C, 5 ml) was added, the montmorillonite was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield aldol products.

General Procedure for Liquid Acid Promoter-Mediated Reactions (Table 1, Entries 8—11). To a stirred solution of **1** (1 mmol) and **5** (1 mmol) in CH_2Cl_2 (3 ml) was added an appropriate amount of an acid promoter in CH_2Cl_2 (1 ml) under a nitrogen atmosphere at −78 °C. After the mixture being stirred, aqueous $NaHCO_3$ was added, the resulting mixture was extracted with ether. An organic layer was dried over Na_2SO_4, and distilled on a Kugelrohr apparatus to yield **16**.

General Procedure for CF_3SO_3H and $CF_3SO_3SiMe_3$-Mediated Reactions of Aldehydes with Nucleophiles. To a stirred solution of an aldehyde (1 mmol) and a nucleophile (1 mmol) in CH_2Cl_2 (3 ml) was added an acid promoter (0.003 mmol) in CH_2Cl_2 (1 ml) under a nitrogen atmosphere at −78 °C. When the reaction was slow, the temperature was raised and/or the acid promoter was supplemented. The mixture was quenched with a few drops of pyridine, diluted with ether, and poured into an aqueous $NaHCO_3$ solution, and then the organic solvent was evaporated. Organic products were extracted with ether. The extract was washed with water and dried over Na_2SO_4, and products were purified by distillation or by TLC.

$BF_3 \cdot OEt_2$-Mediated Reaction of 1 and 6 (Table 2, Entries 16—18). To a stirred solution of **6** (1 mmol) in a solvent (2 ml) at −78 °C was added a solution (1 ml) of $BF_3 \cdot OEt_2$ (1 mmol) under a nitrogen atmosphere. Then **1** (1 mmol) in a solvent (1 ml) was added. After the mixture being stirred under conditions listed in Table 2, the reaction was quenched by injecting aqueous $NaHCO_3$. The mixture was warmed to room temperature and the mixture was extracted with ether. The organic layer was dried over Na_2SO_4 and the solvent was removed. The crude product was treated with *N*-(trimethylsilyl)imidazole (1 mmol) and one drop of chlorotrimethylsilane in ether for 0.5 h at room temperature. The reaction mixture was washed with water and the organic layer was dried over Na_2SO_4. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield **12**.

Poisoning Experiments of Al-Mont with Triethylamine. Al- Mont (0.2 g) in a 20 ml round-bottomed flask was dried at 120 °C and 0.5 Torr for 3 h in an oil bath, cooled to −78 °C under nitrogen, and dipped with CH_2Cl_2 (1 ml). Then a solution of triethylamine (0.0005—0.047 mmol) in CH_2Cl_2 (1 ml) was added. After the mixture was stirred for 10 min, a solution of **6** (1 mmol) in CH_2Cl_2 (1 ml) was added. After 5 min, a solution of **1** (1 mmol) in CH_2Cl_2 (1 ml) was added dropwise over 0.5 min and the mixture was stirred for 30 min at −78 °C and cold ether (5 ml) was added. Al-Mont was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield **12**.

Measurement of Acid Strength of Al-Mont.[21] Al-Mont (0.05 g) was dried at 120 °C and 0.5 Torr for 3 h. This sample was immersed in a solvent (1 ml). Then a few drops of a 0.1 wt% benzene solution of a Hammett indicator was added and the color of the indicator on the sample was judged with naked eyes.

Stereochemistry of Products. The assignment of relative configuration (threo or erythro) of the aldol products derived from **12**—**15** was made with ^1H NMR analysis of the $J_{threo} > J_{erythro}$ relationship[1b,28] and ^{13}C NMR analysis based on the upfield chemical shifts of the carbinol carbon and the methine carbon in the erythro isomer compared with those in the threo isomer.[29] Othe products were identified according to the literatures.[2a,2b,13,15,23,29,30] Diastereomer ratios were determined by GC except for **18**.

2-[Phenyl(trimethylsiloxy)methyl]cyclohexanone (12).[2a]

A mixture of diastereomers (threo : erythro=3 : 1): bp 140 °C (bath temp)/0.3 Torr; ^{1}H NMR ($CDCl_3$) δ=0.01 and 0.05 (two s, 3 : 1 ratio, 9H, CH_3Si), 1.3—2.6 (br, 9H, aliphatic CH), 5.10 (d, J=7.9 Hz, CHO, threo), 5.38 (d, J=3.9 Hz, CHO, erythro), and 7.28 (s, 5H, C_6H_5); IR (CCl_4) 1713 cm^{-1} (C=O); GC (OV-1, 25 m, 180 °C, 0.5 kg cm^{-2}) t_R 12.8 min (threo), 13.2 min (erythro).

2-(Phenylhydroxymethyl)cyclohexanone. A mixture of diastereomers obtained from **12** by hydrolysis: ^{1}H NMR ($CDCl_3$) δ=1.2—2.7 (br, 9H, aliphatic CH), 4.78 (d, J=8.7 Hz, CHO, threo), 5.37 (d, J=2.3 Hz, CHO, erythro), and 7.30 (s, 5H, C_6H_5), ^{13}C NMR ($CDCl_3$) δ=57.0 and 57.2 (1 : 3 ratio, O=C<u>C</u>H), 70.3 and 74.4 (1 : 3 ratio, CHO); IR (CCl_4) 1700 (C=O) and 3560 cm^{-1} (OH).

2-[(2-Furyl)trimethylsiloxymethyl]cyclohexanone (13). A mixture of diastereomers (threo : erythro=1 : 4): bp 140 °C (bath temp)/0.3 Torr; ^{1}H NMR ($CDCl_3$) δ=0.01 and 0.04 (two s, 1 : 4 ratio, 9H, CH_3Si), 1.4—3.1 (br, 9H, aliphatic CH), 5.14 (d, J=8.2 Hz, CHO, threo), 5.28 (d, J=6.0 Hz, CHO, erythro), 6.3 (m, 2H, CH=C), and 7.4 (m, 1H, C=CH-O); IR (CCl_4) 1714 cm^{-1} (C=O); GC (PEG-HT, 150 °C, 1.0 kg cm^{-2}; t_R 6.8 min (erythro), 7.4 min (threo).

2-[(2-Furyl)hydroxymethyl]cyclohexanone. Obtained from **13** by hydrolysis. ^{13}C NMR ($CDCl_3$) δ=54.5 and 54.9 (4 : 1 ratio, O=C<u>C</u>H), 66.4 and 68.0 (4 : 1 ratio, CHO). Each diastereoisomer was separated by preparative TLC (3 : 1 ether-hexane, developed 2 times). **A Threo Isomer:** R_f 0.42; ^{1}H NMR ($CDCl_3$) δ=1.4—3.2 (br, 9H, aliphatic CH), 3.9 (br, 1H, OH), 4.85 (d, J=8.2 Hz, CHO), 6.30 (m, 2H, CH=C), and 7.38 (m, 1H, C=CH-O); IR (CCl_4) 1702 (C=O) and 3560 cm^{-1} (OH). Found: C, 67.72; H, 7.27%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.23%. **An Erythro Isomer:** R_f 0.48; ^{1}H NMR ($CDCl_3$) δ=1.4—3.2 (br, 10H, aliphatic CH and OH), 5.24 (d, J=3.0 Hz, 1H, CHO), 6.30, (m, 2H, CH=C) and 7.33 (m, 1H, C=CHO); IR (CCl_4) 1968 (C=O) and 3580 cm^{-1} (OH).

2-[(2-Thienyl)trimethylsiloxymethyl]cyclohexanone (14). A mixture of diastereomers (threo : erythro=3 : 1): bp 150 °C (bath temp)/0.5 Torr; ^{1}H NMR ($CDCl_3$) δ=0.01 and 0.04 (two s, 3 : 1 ratio, 9H, CH_3Si), 1.4—2.6 (br, 9H, aliphatic CH), 5.39 (d, J=6.8 Hz, CHO, threo), 5.55 (d, J=4.8 Hz, CHO, erythro), 6.9 (m, 2H, CH=C), and 7.2 (m, 1H, C=CHS); IR (CCl_4) 1708 cm^{-1}(C=O); GC (OV-1, 170 °C, 1.0 kg cm^{-2}) t_R 9.1 min (threo), 9.6 min (erythro).

2-[(2-Thienyl)hydroxymethyl]cyclohexanone. A mixture of diastereomers obtained from **14** by hydrolysis: ^{1}H NMR ($CDCl_3$) δ=1.4—2.9 (br, 9H, aliphatic CH), 3.8 (br, 1H, OH), 5.07 (d, J=8.3 Hz, CHO, threo), 5.53 (d, J=3.0 Hz, CHO, erythro), 7.0 (m, 2H, CH=C), and 7.3 (m, 1H, C=CHS); ^{13}C NMR ($CDCl_3$) δ=57.2 and 57.8 (1 : 3 ratio, O=C<u>C</u>H), 68.2 and 70.6 (1 : 3 ratio); IR (CCl_4) 1702 (C=O) and 3560 cm^{-1} (OH). Found: C, 62.81; H, 6.83%. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71%.

2-(3-Methyl-1-trimethylsiloxybutyl)cyclohexanone (15). bp 130 °C (bath temp)/0.5 Torr; GC (PEG-HT, 120 °C, 0.5 kg cm^{-2}) t_R 10.8 min (erythro), 11.1 min (threo). Each diastereoisomer was separated by preparative TLC (15 : 1 hexane-ether, developed 5 times). **A Threo Isomer:** R_f 0.59; ^{1}H NMR ($CDCl_3$) δ=0.12 (s, 9H, CH_3Si), 0.94 (d, J=6.0 Hz, 6H, CHC<u>H</u>$_3$), 1.2—2.5 (br, 9H, aliphatic CH), and 4.15—4.45 (m, 1H, CHO); IR (CCl_4) 1712 cm^{-1} (C=O). **An Erythro Isomer:** R_f 0.63; ^{1}H NMR ($CDCl_3$) δ=0.12 (s, 9H, CH_3Si), 0.92 (d, J=6.0 Hz, 6H, CHC<u>H</u>$_3$), 1.2—2.5 (br, 9H, aliphatic CH), and 4.20—4.50 (m, 1H, CHO); IR(CCl_4) 1712 cm^{-1} (C=O).

2-(1-Hydroxy-3-methylbutyl)cyclohexanone. Obtained from **15** by hydrolysis. A mixture of diastereomers (threo : erythro=3 : 2): ^{13}C NMR; δ=55.4 and 56.7 (2 : 3 ratio, O=C<u>C</u>H), 67.0 and 69.8 (2 : 3 ratio, CHO). Found: C, 71.71; H, 10.83%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%. **A Threo Isomer:** ^{1}H NMR ($CDCl_3$) δ=0.90 and 0.92 (two d, J=6.1, 6.1 Hz, 6H, CH_3), 1.2—2.5 (br, 13H, aliphatic CH), 3.79 (ddd, J=9.0, 7.0, 4.5 Hz, 1H, CHO), and 4.6 (s, 1H, OH); IR (CCl_4) 1708 cm^{-1} (C=O). **An Erythro Isomer:** ^{1}H NMR ($CDCl_3$) δ=0.92 (d, J=6.0 Hz, 6H, CH_3), 1.2—2.5 (br, 14H, aliphatic CH and OH), 4.21 (ddd, J=9.0, 3.6, 2.7 Hz, 1H, CHO), and 4.6 (s, 1H, OH); IR (CCl_4) 1708 cm^{-1} (C=O).

2-(Methoxyphenylmethyl)cyclohexanone (16).[2b] A mixture of diastereomers (threo : erythro=1 : 6): bp 145 °C (bath temp)/0.8 Torr; ^{1}H NMR ($CDCl_3$) δ=1.4—2.6 (br, 9H, aliphatic CH), 3.20 and 3.27 (two s, 1 : 6 ratio, 3H, OCH_3), 4.56 (d, J=8.6 Hz, CHO, threo), 4.79 (d, J=4.1 Hz, CHO, erythro), and 7.30 (s, 5H, C_6H_5); IR (CCl_4) 1712 cm^{-1} (C=O); GC (OV-1, 180 °C, 0.5 kg cm^{-2}) t_R 9.9 min (erythro), 10.2 min (threo).

2-(1-Methoxy-2-methylpropyl)cyclohexanone (17).[2b] bp 110 °C (bath temp)/2 Torr; GC PEG-HT (110 °C, 1.0 kg cm^{-2}) t_R 6.4 min (erythro), 8.5 min (threo). Each diastereoisomer was separated by preparative TLC (5 : 1 hexane-ether, developed 2 times). **A Threo Isomer:** R_f 0.42; ^{1}H NMR ($CDCl_3$) δ=0.91 and 0.94 (two d, J=6.7, 6.7 Hz, 6H, CH_3), 1.4—2.6 (br, 10H, aliphatic CH), 3.3—3.5 (m, 1H, CHO), and 3.43 (s, 3H, OCH_3); IR (CCl_4) 1712 cm^{-1} (C=O). **An Erythro Isomer:** R_f 0.58; ^{1}H NMR ($CDCl_3$) δ=0.88 and 0.93 (two d, J=6.5, 6.5 Hz, 6H, CH_3), 1.4—2.6 (br, 10H, aliphatic CH), 3.43 (s, 3H, OCH_3), and 3.4—3.6 (m, 1H, CHO); IR (CCl_4) 1708 cm^{-1} (C=O).

2-Methyl-1-phenyl-1-trimethylsiloxy-3-pentanone (18). A mixture of diastereomers (threo : erythro=3.2 : 1): bp 110 °C/0.4 Torr; ^{1}H NMR ($CDCl_3$) δ=−0.08 and 0.02 (two s, 3.2 : 1 ratio, 9H, CH_3Si), 0.73 (d, J=8.0 Hz, 3H, CHC<u>H</u>$_3$), 1.08 (t, J=8.9, Hz, 3H, CH_2C<u>H</u>$_3$), 1.9—3.2 (m, 3H, CH and CH_2), 4.65 (d, J=9.3 Hz, CHO, threo), 4.81 (d, J=8.0 Hz, CHO, erythro), 7.24 and 7.29 (two s, 5H, C_6H_5); IR (CCl_4) 1714 cm^{-1} (C=O). These diastereomers were inseparable by GC. The isomer ratio was determined by NMR.

1-Hydroxy-2-methyl-1-phenyl-3-pentanone.[30] Obtained from **18** by hydrolysis: ^{1}H NMR ($CDCl_3$) δ=0.8—1.2 (m, 6H, CH_3), 2.3—3.0 (m, 3H, C<u>H</u>$_2$COC<u>H</u>), 3.1 (br, 1H, OH), 4.73 (dd, J=8.3, 2.7 Hz, CHO, threo), 5.00 (d, J=4.8 Hz, CHO, erythro), and 7.31 (s, 5H, C_6H_5); IR (CCl_4) 1712 (C=O) and 3500 cm^{-1} (OH).

2,4,4-Trimethyl-1-phenyl-1-trimethylsiloxy-3-pentanone (19).[23] **A Threo Isomer:** bp 135 °C (bath temp)/0.3 Torr; ^{1}H NMR ($CDCl_3$) δ=−0.13 (s, 9H, CH_3Si), 0.73 (d, 3H, J=7.0 Hz, CHC<u>H</u>$_3$), 1.20 (s, 9H, *t*-Bu), 3.2 (m, 1H, C<u>H</u>CH$_3$), 4.71 (d, 1H, J=9.8 Hz, CHO), and 7.29 (s, 5H, C_6H_5); IR (CCl_4) 1703 cm^{-1}; GC (OV-1, 160 °C , 0.85 kg cm^{-2}) t_R 8.9 min (erythro), 9.3 min (threo). An authentic sample of an erythro isomer was prepared according to the literature.[23]

4,6-Dimethyl-5-trimethylsiloxy-3-heptanone (20). A mixture of diastereomers (threo : erythro=3 : 1): bp 125 °C (bath temp)/15 Torr; ^{1}H NMR ($CDCl_3$) δ=0.02 and 0.06 (two s, 3 : 1 ratio, 9H, CH_3Si), 0.8—1.2 (m, 12H, CH_3), 1.6 (m, 1H, $CHMe_2$), 2.3—2.9 (m, 3H, C<u>H</u>$_2$COC<u>H</u>), and 3.6—3.9 (m, 1H, CHO); IR (CCl_4) 1713 cm^{-1} (C=O); GC (PEG-HT, 80 °C, 1.0 kg cm^{-2}) t_R 5.1 min (threo), 6.0 min (erythro).

5-Hydroxy-4,6-dimethyl-3-heptanone.[29] Obtained from **20** by hydrolysis. A mixture of diastereomers (threo : eryth-

ro=3 : 1): ^{1}H NMR ($CDCl_3$) δ=0.8—1.2 (m, 12H, CH_3), 1.7 (m, 1H, $CHMe_2$), 2.3—2.9 (m, 3H, $C\underline{H}_2COC\underline{H}$), 2.6 (s, 1H, OH) and 3.3—3.6 (m, 1H, CHO); IR (CCl_4) 1697 (C=O), and 3520 cm^{-1} (OH); ^{13}C NMR ($CDCl_3$) δ=47.5 and 48.3 (1 : 3 ratio, O=CCH), 76.4 and 78.4 (1 : 3 ratio, CHO).

4-Benzyloxy-1-phenyl-3-trimethylsiloxy-1-pentanone (23). A mixture of diastereomers (**23a** : **23b**=2 : 1) purified by TLC. ^{1}H NMR ($CDCl_3$) δ=0.05 and 0.08 (two s, 2 : 1 ratio, 9H, CH_3Si), 1.27 (d, J=6.0 Hz, 3H, CH_3), 3.20 (d, 2H, J=6.2 Hz, CH_2CO), 3.6 (m, 1H, CHOSi), 4.4 (m, 1H, $C\underline{H}OCH_2Ph$), 4.6 (m, 2H, CH_2Ph), 7.3 (s, 5H, $CH_2C_6\underline{H}_5$), and 7.4—8.1 (m, 5H, C_6H_5CO); IR (CCl_4) 1692 cm^{-1} (C=O); GC (OV-1, 220 °C, 1.0 kg cm^{-2}) t_R 10.1 min (**23a**), 10.4 min (**23b**). An authentic sample of **23a** was prepared using a $TiCl_4$-mediated reaction.[13]

Methyl 4-Benzyloxy-2,2-dimethyl-3-trimethylsiloxypentanoate (25). A solution of **21** (1 mmol) and **24** (1 mmol) in CH_2Cl_2 (4 ml) was treated with Al-Mont (0.2 g) at 25 °C for 1 h to afford **25** in 62% yield. A mixture of diastereomers (isomer ratio =54 : 46): bp 180 °C (bath temp)/0.5 Torr; ^{1}H NMR ($CDCl_3$) δ=0.12 and 0.16 (two s, 1 : 1 ratio, 9H, CH_3Si), 1.1—1.3 (m, 9H, CCH_3), 3.39 and 3.60 (two s, 1 : 1 ratio, 3H, CH_3O), 3.3—3.6 (m, 1H, $CH_3C\underline{H}O$), 3.96 and 4.00 (two d, 1 : 1 ratio, J=5.2, 6.0 Hz, 1H, CHOSi), 4.44 and 4.47 (two d, 1 : 1 ratio, J=5.1, 4.7 Hz, 2H, $PhCH_2$), and 7.31 (s, 5H, C_6H_5); IR (CCl_4) 1730 cm^{-1} (C=O); GC (OV-1, 180 °C, 1.0 kg cm^{-2}) t_R 10.7 min, 11.2 min.

1,4-Diphenyl-3-trimethylsiloxy-1-pentanone (27). A mixture of diastereomers purified by TLC: ^{1}H NMR ($CDCl_3$) δ=−0.08 (s, 9H, CH_3Si), 1.33 (d, J=7.0 Hz, 3H, CH_3), 2.7—3.2 (m, 3H, CH_2 and PhCH), 4.56 (ddd, J=7.3, 6.6, 4.0 Hz, 1H, CH), 7.27 (s, 5H, $C_6\underline{H}_5CH$), and 7.3—8.0 (m, 5H, C_6H_5CO); IR (CCl_4) 1686 cm^{-1} (C=O); GC (OV-1, 180 °C, 1.0 kg cm^{-2}) t_R 24.9 min (**27b**), 25.6 min (**27a**). An authentic sample of **27a** was prepared from **21** and acetophenone by use of LDA.[15]

2-(1-Hydroxy-2-methylpropyl)cyclohexanone (28).[2a] A solution of **1** (1 mmol) and **10** (1.5 mmol) in CH_2Cl_2 (4 ml) was treated with CF_3SO_3H (0.02 mmol) at −30 °C for 0.5 h. Hydrolysis of the silylated aldol product with 1 mol dm^{-3} HCl gave **28** in 38% yield. A mixture of diastereomers (isomer ratio =57 : 43): ^{1}H NMR ($CDCl_3$) δ=0.7—1.0 (m, 6H, CH_3), 1.3—2.6 (m, 10H, aliphatic CH and OH), and 3.2—3.8 (m, 1H, CHO); IR (CCl_4) 1712 (C=O) and 3500 cm^{-1} (OH); GC (OV-1, 110 °C, 0.8 kg cm^{-2}) t_R 12.0, 12.3 min.

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9) The diastereoselectivity of the reaction was independent of the amount of Al-Mont used. The dependence of diastereoselectivity on solvent has not been reported in the aldol reaction using silyl enol ether.

10) Furfural (**7**) is so labile under acidic conditions that the reaction of **1** with **7** gave a complex mixture by use of $TiCl_4$. A $BF_3 \cdot OEt_2$-mediated reaction in CH_2Cl_2 gave lower yield of the aldol product (64%, threo : erythro=40 : 60) than an Al-Mont-mediated reaction in CH_2Cl_2.

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