

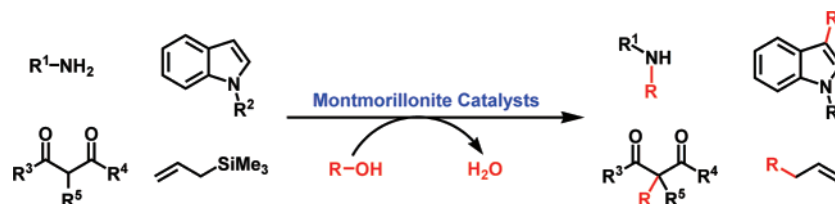
Nucleophilic Substitution Reactions of Alcohols with Use of Montmorillonite Catalysts as Solid Brønsted Acids

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We have developed an environmentally benign synthetic approach to nucleophilic substitution reactions of alcohols that minimizes or eliminates the formation of byproducts, resulting in a highly atom-efficient chemical process. Proton- and metal-exchanged montmorillonites (H- and M^{n+} -mont) were prepared easily by treating Na^+ -mont with an aqueous solution of hydrogen chloride or metal salt, respectively. The H-mont possessed outstanding catalytic activity for nucleophilic substitution reactions of a variety of alcohols with anilines, because the unique acidity of the H-mont catalyst effectively prevents the neutralization by the basic anilines. In addition, amides, indoles, 1,3-dicarbonyl compounds, and allylsilane act as nucleophiles for the H-mont-catalyzed substitutions of alcohols, which allowed efficient formation of various C–N and C–C bonds. The solid H-mont was reusable without any appreciable loss in its catalytic activity and selectivity. Especially, an Al^{3+} -mont showed high catalytic activity for the α -benzylation of 1,3-dicarbonyl compounds with primary alcohols due to cooperative catalysis between a protonic acid site and a Lewis acidic Al^{3+} species in its interlayer spaces.

Introduction

A promising synthetic approach aiming at environmentally benign chemistry minimizes or eliminates the formation of byproducts, to afford high atom-efficient chemical process.¹ Although the use of alcohols instead of halides and acetate compounds as electrophiles is an ideal method because it prevents waste salt formations (Scheme 1), catalytic substitution of the hydroxyl group in alcohols is difficult due to their poor leaving ability, which requires equimolar or greater amounts of reagents. Recently, several homogeneous catalysts, such as $NaAuCl_4$, $InCl_3$, $ZrCl_4$, La, Yb, Sc, and Hf triflate, $B(C_6F_5)_3$, BF_3 , and *p*-toluenesulfonic acid have been used for nucleophilic

substitution reactions of alcohols with amides,² 1,3-dicarbonyl compounds,³ and allylsilanes.^{3d,4} However, these catalysts often are limited by low catalytic activity and selectivity, can be difficult to reuse, and require the use of halogenated solvents.

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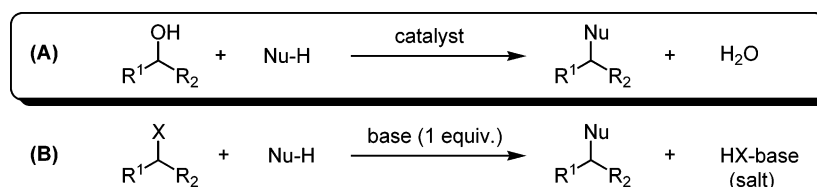
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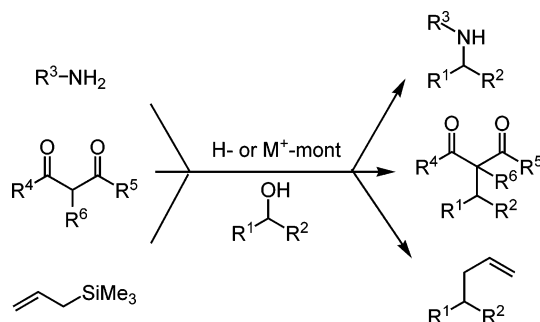
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SCHEME 1. (A) Catalytic Substitution of Alcohols without Salt Formation and (B) Stoichiometric Substitution of Halides



SCHEME 2. Montmorillonites-Catalyzed Substitution of Nitrogen Compounds, 1,3-Dicarbonyls, and Allylsilane



As an alternative strategy for homogeneous acid-catalyzed reactions, we have focused on heterogeneous Brønsted and Lewis acid catalysts based on montmorillonites (monts).^{5,6} Monts are hydrophilic clays with a layered structure and have been investigated as environmentally friendly and reusable catalysts. The ion-exchangeable ability of their interlayer spaces allows the introduction of various metals between the layers. In the course of our studies on the metal-cation-exchanged montmorillonite catalysts (M^{n+} -monts), two types of metal ion species with unique structures within the interlayers of the monts have been defined: a chain-like metal species and monomeric aqua complexes.^{6a,d} These M^{n+} -monts exhibited high catalytic activities for various organic transformations. In addition, we have recently found that a simple proton-exchanged montmorillonite (H-mont) showed excellent catalytic performance for nucleophilic addition of 1,3-dicarbonyls and nitrogen compounds to unactivated alkenes.⁷

Here, we present the nucleophilic substitution of hydroxyl groups in alcohols using proton- and metal-exchanged montmorillonite (H- and M^{n+} -mont) catalysts (Scheme 2), in which a variety of nucleophiles readily reacted with alcohols to form C–N and C–C bonds. These mont catalysts showed high catalytic activities and selectivities, and then were reusable without any appreciable loss of catalytic performance. *This is the first heterogeneous catalyst system for nucleophilic substitution reactions of alcohols with anilines, amides, 1,3-dicarbonyl compounds, and allylsilane.*

Results and Discussion

Preparation and Characterization of Proton- and Metal-Exchanged Montmorillonites. The H-mont was prepared from a sodium-exchanged montmorillonite (Na^+ -mont; Na 2.69%, Al 11.8%, Fe 1.46%, Mg 1.97%), using an aqueous solution of hydrogen chloride. X-ray diffraction (XRD) verified retention of a layered structure. The exchange degree of sodium cations in the H-mont was 98.9%, and the absence of chlorine atom was confirmed by EDX analysis. The specific surface area of the H-mont was $138 \text{ m}^2 \text{ g}^{-1}$ as determined by the BET-plot based on the nitrogen adsorption isotherms. The presence of Brønsted acid sites in the H-mont was confirmed by adsorption of pyridine: the IR spectrum of the H-mont upon pyridine treatment showed a peak at 1543 cm^{-1} due to protonated pyridine (Figure 1), while the treatment of the Na^+ -mont with pyridine gave no peaks at 1543 cm^{-1} .⁸ The IR peaks near 1445 cm^{-1} ascribed to pyridine adsorbed on a Lewis acid site were not observed.⁸ Temperature-programmed desorption of ammonia (NH_3 -TPD) analysis revealed that the quantity and the strength (ΔH)⁹ of acid sites in the H-mont were 0.86 mmol g^{-1} and 111 kJ mol^{-1} ,^{7a} respectively.

The mont-enwrapped metal cations, Al^{3+} , Fe^{3+} , Ti^{4+} , and Cu^{2+} , were prepared by treating the Na^+ -mont with an aqueous solution of the appropriate metal chloride or nitrate. Among the M^{n+} -monts, the catalytic behavior of the Al^{3+} -mont was particularly useful.¹⁰ From XRD analysis, the layered structure was maintained during the above treatment with a basal spacing of 3.9 \AA . Elemental analysis showed that the degree of exchange of sodium cations in the Al^{3+} -mont was 96.7%; Al atom content increased from 11.8 to 12.9 wt %. The absence of chlorine atom was confirmed by EDX analysis. BET-plot produced a value of $48 \text{ m}^2 \text{ g}^{-1}$ for the surface area of the Al^{3+} -mont. The Al^{3+} -mont possessed both Brønsted and Lewis acid sites: the IR spectrum of the Al^{3+} -mont showed peaks at 1543 cm^{-1} upon treatment with pyridine due to protonated pyridine, while a peak at 1445 cm^{-1} was assigned to pyridine adsorbed on the Lewis acid sites (Figure 1).⁸ NH_3 -TPD revealed that the quantity and the strength (ΔH) of acid sites in the Al^{3+} -mont were 0.75 mmol g^{-1} and 132 kJ mol^{-1} ,¹¹ respectively. The acid strength of the Al^{3+} -mont was large compared to that of the H-mont, which may originate from the Lewis acid site on the Al species in the interlayer. The ^{29}Si MAS NMR spectra of the Al^{3+} -mont indicated the presence of tetrahedron SiO_4 species, assignable

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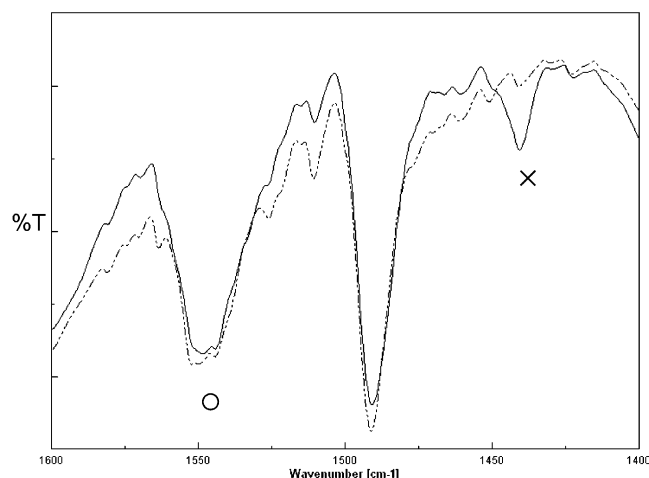


FIGURE 1. The IR spectra of pyridine adsorbed on the Al^{3+} -mont (—) and H-mont (---): (O) pyridinium ion on the mont and (X) pyridine coordinated to Lewis acid site.

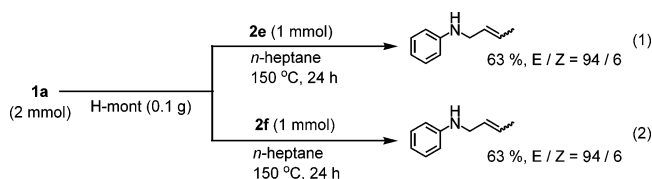
to the montmorillonite structure (chemical shift of δ -94 ppm, Figure 2S, Supporting Information).¹² In addition, a signal assignable to a SiO_4 site connecting two Al sites in the second coordination sphere of the Si—O framework also was observed (-86 ppm, Figure 2S, Supporting Information).¹² These results indicate that the Al species introduced into the mont interlayer by ion exchange are located onto the silicate surface.

Substitution with Nitrogen Compounds. *N*-Allyl and -benzyl anilines are very important synthetic intermediates for a variety of biologically active compounds.¹³ As one of the most common methodologies for the synthesis of *N*-allyl anilines, palladium-catalyzed allylic substitution usually requires large amounts of activators and expensive Pd catalysts.¹⁴ In addition, the use of allylic alcohols as allyl sources¹⁵ has been investigated for environmentally benign syntheses;¹ however, most catalytic systems require allylic halides, acetates, or carbonates due to the poor leaving ability of the hydroxyl groups. Few reports exist on the direct catalytic synthesis of *N*-benzylated anilines from anilines and benzylic alcohols because benzylic species are not suitable for transition-metal-catalyzed reactions based on π -allyl chemistry.¹⁶ In general, anilines are unsuccessful for acid-catalyzed nucleophilic reactions due to their buffering

effect. In 2005, the hydroamination of alkenes with anilines using homogeneous Brønsted acid catalysts was demonstrated by Bergman and co-workers,¹⁷ but Brønsted acid-catalyzed substitution of hydroxyl groups of alcohols with anilines has never been reported.¹⁸ Here, we present the first report on acid-catalyzed nucleophilic substitution reactions of hydroxyl groups of allylic and benzylic alcohols with anilines using the H-mont catalyst.

The H-mont catalyst was used without any pretreatment such as calcinations, which induces decreasing catalytic activity. XRD and TPD analyses revealed the destruction of layered structure and a decrease of the acid amount in the H-mont after calcination. Substitution of a hydroxyl group in 2-cyclohexen-1-ol (**2a**) with aniline (**1a**) was examined with use of heterogeneous and homogeneous acids, as shown in Table 1. The H-mont showed the highest catalytic activity and possessed excellent selectivity toward *N*-(2-cyclohexen-1-yl)aniline (**3a**) together with aromatic-substituted byproducts (**4a** and **5a**) (entry 1). H-beta, H-USY, and Al^{3+} -mont also were effective catalysts for this substitution reaction (entries 2–4), while H-mordenite was less active despite its strong acidity (entry 5). Reaction with H-ZSM-5 zeolite barely proceeded due to its restricted pore size (entry 6). Notably, for homogeneous strong acids, such as H_2SO_4 and *p*-toluenesulfonic acid, neutralization of acids with basic aniline gave inactive salts without the desired *N*-allylated product (entries 7 and 8).

Next, substitution reactions of a variety of allylic alcohols with aniline derivatives were investigated, as shown in Table 2. Electron-withdrawing groups at the para position of anilines enhanced both reaction rate and selectivity toward *N*-allylated products (entries 2–4), while the methoxy of an electron-donating substituent favored an ortho adduct (entry 5). To extend the scope of the allylic alcohols, both aliphatic and aromatic allylic alcohols were examined as potential substrates in the reaction of **1a** (entries 6–9). The substitution of a hydroxyl group of cinnamyl alcohol (**2d**) with **1a** afforded ortho and para adducts (entry 8), while an *N*-allylated product was formed selectively with 4-nitroaniline (**1c**) (entry 9). Notably, the reactions of both 1-methyl-2-propen-1-ol (**2e**) and 1-buten-3-ol (**2f**) with **1a** afforded the same *N*-(2-butenyl)aniline as the major product (eqs 1 and 2).



Because the H-mont catalyst exhibited high catalytic activity in the allylic substitution of alcohols with aniline derivatives, the substitution of a hydroxyl group in benzylic alcohols with anilines also was examined and afforded *N*-benzyl anilines. Results with various benzylic alcohols and anilines are shown in Table 3. Reactions of para-substituted anilines with benzhydrol (**2g**) gave *N*-benzylated products exclusively (entries 2–6).

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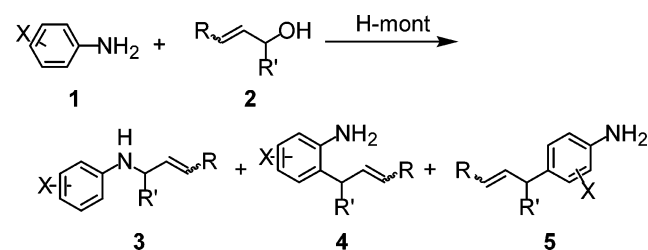
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TABLE 1. Substitution of Alcohol 2a with Aniline 1a with Use of Various Acid Catalysts^a

entry	catalyst	acid amount (mmol/g) ^b	acid strength (kJ/mol) ^b	pore size (Å)	yield (%) ^c	3a:4a:5a ^c
1	H-mont	0.86	111		88	86:10:4
2	H-beta	0.51	126	7.6 × 6.4	80	83:7:10
3	H-USY	0.53	122	7.4 × 7.4	77	75:16:9
4	Al ³⁺ -mont	0.75	132		72	88:8:4
5	H-mordenite	1.07	160	6.5 × 7.0	12	77:10:13
6	H-ZSM-5	0.87	130	5.1 × 5.5	10	91:6:3
7	H ₂ SO ₄ ^d				trace ^e	
8	<i>p</i> -TsOH·H ₂ O ^d				trace ^e	
9	none				n.r.	

^a 1a (2 mmol), 2a (1 mmol), catalyst (0.1 g), *n*-heptane (2 mL), 80 °C, 24 h. ^b Determined by NH₃-TPD. ^c Combined yield, determined by GC. ^d 0.1 mmol. ^e Inactive salt was formed by the neutralization of acid with 1a.

TABLE 2. Substitution of Allylic Alcohols with Anilines with Use of the H-mont Catalyst^a

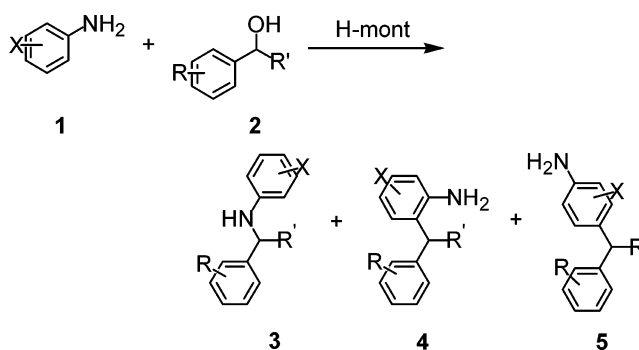
entry	aniline	alcohol	<i>t</i> (h)/ <i>T</i> (°C)	yield (%) ^b	3:4:5
1	1a	2a	24/80	88	86:10:4
2	4-Cl 1b	2a	2/80	95 (76 ^c)	95:5:0
3 ^d	4-NO ₂ 1c	2a	1/80	81 ^c	100:0:0
4	3,5-CF ₃ 1d	2a	2/80	75	100:0:0
5	4-OMe 1e	2a	24/150	59 ^c	7:93:0
6	1a	2b	24/40	70	92:4:4
7 ^e	1a	2c	24/150	29	100:0:0
8	1a	2d	3/150	73 ^f	0:65:35
9 ^d	1c	2d	1/100	78 ^{c,f}	100:0:0

^a Aniline (2 mmol), alcohol (1 mmol), H-mont (0.1 g), *n*-heptane (2 mL), 24 h. ^b Determined by GC. ^c Isolated yield. ^d 1,4-Dioxane (2 mL) was used as a solvent. ^e Aniline (1 mmol), alcohol (2 mmol). ^f Only (*E*)-product was detected.

Similar to the above allylic substitution reaction, an electron-withdrawing group at the para position of anilines enhanced their reactivity (entries 2 and 3). Other secondary alcohols of 1-phenylethanol (**2f**) and 1-(2-naphthyl)ethanol (**2n**) functioned as good substrates (entries 8–11). This is the first report of successful direct *N*-benzylation of anilines with alcohols. In the reactions of both allylic and benzylic alcohols with **1a**, para- and ortho-alkylated products were formed (Table 2, entries 1, 6, and 8; Table 3, entries 1, 8, and 10). These aromatic allylated and benzylated products became the major product at longer reaction times and higher temperatures, which indicates that *N*-adducts undergo a Hofmann–Martius rearrangement.^{17,19,20}

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(20) After reaction of **2a** with **1a** under the reaction conditions of Table 1, entry 1 (88% combined yield, *N*:ortho:para adducts = 86:10:4), further treatment of the reaction mixture at 150 °C for 24 h afforded a 59% yield of the ortho adduct as a major product (75% combined yield, *N*:ortho:para = 9:79:12).

TABLE 3. Substitution of Benzylic Alcohols with Anilines with Use of the H-mont Catalyst^a

entry	aniline	alcohol	<i>t</i> (h)/ <i>T</i> (°C)	isolated yield (%)	3:4:5 ^b
1	1a	2g	1/150	96	51:0:49
2	1b	2g	3/120	83	100:0:0
3	1c	2g	1/100	97	100:0:0
4	1c	2g	1/100	98 ^c	100:0:0
5	4-Me 1f	2g	7/150	66	100:0:0
6	1e	2g	30/150	39	100:0:0
7	1c	2h	1/100	93	100:0:0
8	1a	2l	15/125	93 ^b	54:28:18
9	1c	2l	1/100	77	100:0:0
10	1a	2n	30/100	99 ^b	82:9:9
11	1c	2n	1/100	93	100:0:0

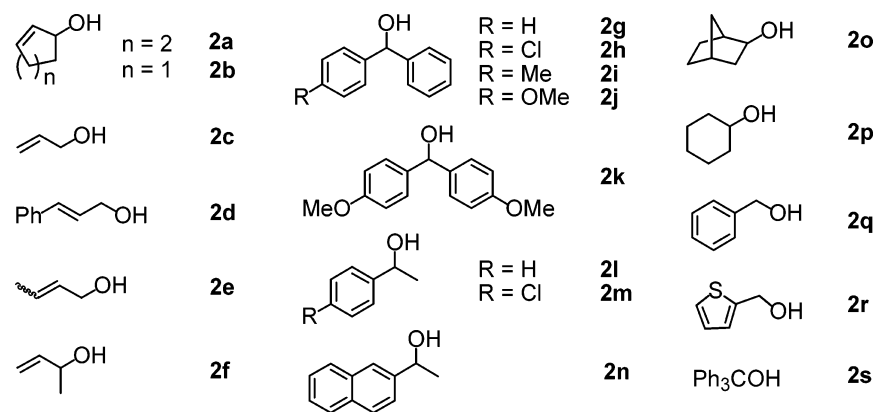
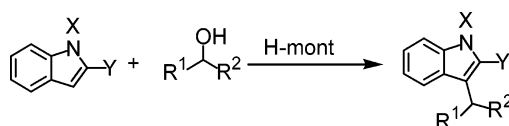
^a Aniline (2 mmol), alcohol (1 mmol), 1,4-dioxane (2 mL), H-mont (0.1 g). ^b Determined by GC. ^c Third reuse experiment.

The use of indoles instead of anilines gave 3-benzylated and -allylated indoles in this H-mont catalyst system with alcohols (Table 4). Both indole (**6a**) and *N*-methylindole (**6b**) readily reacted with **2g**, affording the corresponding 3-benzylated indoles. An allylic alcohol of **2a** also was a good electrophile. No *N*-alkylated product was detected for any of these indoles.

N-Benzylation and allylation of various amide compounds also were examined in the presence of the H-mont catalyst, as summarized in Table 5. For example, the reaction of *p*-toluenesulfonamide (**7a**) with **2g** proceeded smoothly to afford a 94% isolated yield of *N*-(diphenylmethyl)-*p*-toluenesulfona-

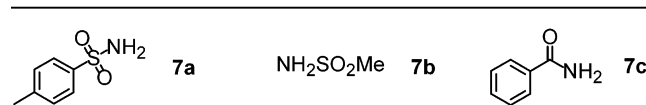
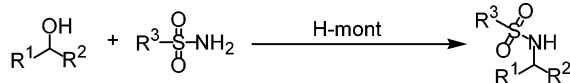
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CHART 1

TABLE 4. Substitution of Alcohol with Indoles with Use of the H-mont Catalysts^a

entry	indole	alcohol	isolated yield (%)
1	X = Y = H (6a)	2g	99
2	X = Me, Y = H (6b)	2g	90
3	X = H, Y = Me (6c)	2g	70
4	6a	2l	77
5	6a	2a	66

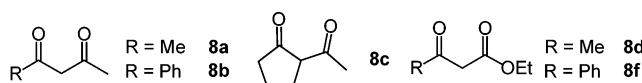
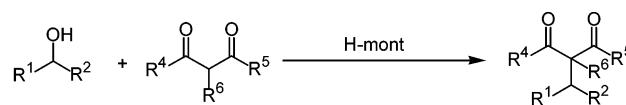
^a Indole (2 mmol), alcohol (1 mmol), *n*-heptane (2 mL), H-mont (0.1 g), 100 °C, 12 h.

TABLE 5. *N*-Benzylation and Allylation of Amides by Treatment with Alcohols with Use of the H-mont^a

entry	amide	alcohol	isolated yield (%) ^b
1	7a	2g	94
2	7a	2g	95 ^c
3	7a	2h	97
4	7a	2l	60
5 ^d	7a	2a	50 ^e
6 ^f	7a	2o	97
7 ^g	7a	2p	39 ^e
8	7b	2g	87
9 ^g	7c	2g	90

^a Alcohol (1.0 mmol), amide (1.5 mmol), H-mont (0.1 g), 1,4-dioxane (2 mL), 100 °C, 2 h. ^b Based on the alcohol. ^c Third reuse experiment. ^d Amide (5 mmol) was used. Alcohol was added in portions. ^e GC yield. ^f Alcohol (1.5 mmol), **1b** (1 mmol). Yield was based on **1b**. ^g 20 h.

amide (entry 1). Notably, the reaction of **2a** with **7a** gave *N*-cyclohex-2-enyl-*p*-toluenesulfonamide (entry 5), which is usually synthesized through a tedious multistep procedures.²¹ Reactions of aliphatic alcohols, such as *exo*-2-norborneol (**2o**) and cyclohexanol (**2p**), also proceeded (entries 6 and 7). Furthermore, inactive aliphatic sulfonamide and carboxamide, methanesulfonamide (**7b**), and benzamide (**7c**) were found to

TABLE 6. α -Benzylation and Allylation of Various 1,3-Dicarbonyl Compounds with Alcohols with Use of the H-mont Catalyst^a

entry	1,3-dicarbonyl	alcohol	<i>T</i> (°C)	isolated yield (%) ^b
1	8a	2l	100	90
2	8a	2l	100	91 ^c
3	8a	2m	150	80
4 ^d	8a	2n	150	72
5	8a	2g	100	91
6	8a	2a	90	80 ^e
7 ^f	8b	2l	100	86 ^g
8 ^d	8c	2l	150	86 ^g
9	8d	2l	100	88 ^g
10	8f	2l	100	51 ^g
11	8d	2a	90	48 ^g

^a Alcohol (1 mmol), 1,3-dicarbonyl compound (1.5 mmol), catalyst (0.15 g), *n*-heptane (2 mL), 1 h, 100 °C. ^b Based on alcohol. ^c Fifth reuse experiment. ^d 0.5 h. ^e GC yield. ^f 1,3-Dicarbonyl (1 mmol). ^g 1:1 diastereoisomers were formed (¹H NMR).

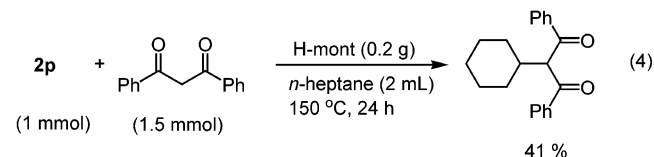
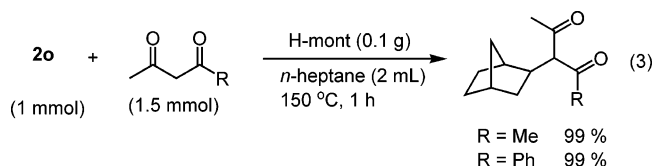
be excellent nucleophiles (entries 8 and 9). In these H-mont-catalyzed *N*-C bond formations with anilines and amide compounds, the used solid catalysts were recovered easily from the reaction mixture and could be reused at least three times without any appreciable loss of its activities and selectivities (Table 3, entry 4; Table 5, entry 2).

Substitution with 1,3-Dicarbonyls. The α -benzylation and allylation of 1,3-dicarbonyl compounds are common procedures in organic synthesis. The traditional method for benzylation of 1,3-dicarbonyls is a stoichiometric reaction with benzyl halides in the presence of an equimolar amount of strong bases.²² The high catalytic activity of solid Brønsted acids for the above substitutions using nitrogen compounds encouraged us to explore the nucleophilic substitution of hydroxyl groups in benzylic and allylic alcohols with 1,3-dicarbonyl compounds, which afforded α -benzylated and allylated 1,3-dicarbonyls.

The reactions of various 1,3-dicarbonyl compounds with secondary alcohols are summarized in Table 6. The α -benzyl-

(22) (a) Ranu, B. C.; Bhar, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 365. (b) Arumugam, S.; McLeod, D.; Verkade, J. G. *J. Org. Chem.* **1998**, 63, 3677.

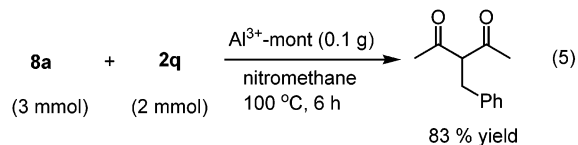
ation of acetylacetone (**8a**) with **2l** proceeded in the presence of the H-mont catalyst to give a 90% yield of 3-(1-phenylethyl)-2,4-pentanedione (entry 1). Catalytic activity of the Al^{3+} -mont was slightly lower than that of the H-mont. For other zeolite catalysts, such as H-beta, H-mordenite, and H-ZSM-5, the above substitution reaction scarcely occurred. Sterically hindered alcohols of **2n** and **2g** also reacted to afford the corresponding diones in 72% and 91% yields, respectively (entries 4 and 5). Notably, not only aliphatic, aromatic, and cyclic 1,3-diketones, but also 1,3-ketoesters, underwent benzylation reaction with **2l** to give the excellent yields of the desired products (entries 1 and 7–10). Furthermore, an allylic alcohol of **2a** could act as a good substrate (entries 6 and 11).²³ This H-mont catalyst system also was applicable to aliphatic alcohols: reaction of **2o** with 1,3-diketones readily proceeded to afford quantitative yields of the corresponding products (eq 3), while **2p** possessed



low reactivity in the substitution reaction (eq 4). In the substitution reaction of alcohols with 1,3-dicarbonyls, only benzylic and allylic alcohols have been used.³ The substitutions of aliphatic alcohols were achieved as the first example with the H-mont catalyst. Unfortunately, reaction with diethyl malonate as a 1,3-diester, which has a high pK_a value of the α -proton, did not occur. It should be noted that after the substitution reaction of **2l** with **8a**, the used H-mont catalyst was separated easily from the reaction mixture, and the spent catalyst could be reused at least five times without an appreciable loss of its activity and selectivity (entry 2). Initial reaction rates did not change significantly during these recycling experiments. To confirm whether the substitution of alcohols occurred on the solid surface, the H-mont catalyst was removed by filtration after ca. 50% conversion of alcohol. ICP analysis of the filtrate of the H-mont-catalyzed reaction showed 0.03% leaching of Al and Fe species; however, further treatment of the filtrate under the identical reaction conditions did not afford any product. These results strongly suggest that the substitution reactions of alcohols proceeded on the solid mont catalyst.

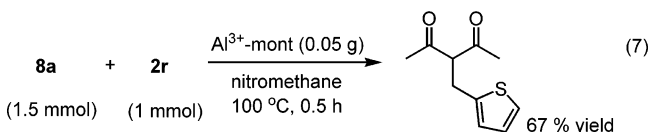
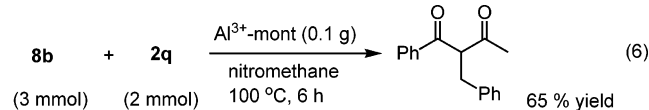
To extend the scope of the alcohols used in the H-mont-catalyzed nucleophilic addition of 1,3-dicarbonyl compounds, a primary alcohol, benzyl alcohol (**2q**), was investigated as a potential substrate. However, the H-mont-catalyzed reaction of **2q** with **8a** showed low selectivity toward production of the desired α -benzylated acetylacetone (**9a**), accompanied by a large amount of dibenzyl ether (**10a**) under the standard conditions employed for secondary alcohols (*n*-heptane, 100 °C). For development of an effective heterogeneous catalyst system, the α -benzylation reaction of **8a** with **2q** as a model substrate was

conducted (Table 1S, Supporting Information). The selectivity to **9a** could be improved by using the Al^{3+} -mont catalyst instead of the H-mont in nitromethane solvent, to afford the desired product (yield: 51%). Yield and selectivity increased significantly by stepwise addition of **2q** (83%) (eq 5). Use of other



solvents, such as *n*-heptane (24%) and 1,4-dioxane (trace), resulted in decrease of the product selectivity: no reaction occurred with DMF and THF as solvents. Using Fe^{3+} (42%)-, Ti^{4+} (33%)-, Cu^{2+} (22%)-, and H^+ (43%)-exchanged montmorillonites resulted in lower yields than that of the Al^{3+} -mont. Commercially available zeolites, such as H-beta (17%), H-USY (trace), H-mordenite (trace), and H-ZSM-5 (trace), were less active for this benzylation reaction. Furthermore, the homogeneous H_2SO_4 -catalyzed reaction did not result in high yield (39%).

Notably, this Al^{3+} -mont catalyst system was applicable to other 1,3-dicarbonyls and primary alcohols. The reaction of benzoylacetone (**8b**) with **2q** proceeded readily to give a 65% yield of α -benzylated benzoylacetone (eq 6). A heteroaromatic alcohol of 2-thiophenemethanol (**2r**) also reacted to afford the corresponding α -substituted acetylacetone in good yield (eq 7). This catalytic α -alkylation of 1,3-dicarbonyl compounds with primary aromatic and heteroaromatic alcohols has not been demonstrated before.



Allylation with Allylsilane. Although nucleophilic allylation of carbonyl compounds and acetals with allylsilanes is well-known as the Sakurai–Hosomi reaction,²⁴ a transformation that uses alcohols as electrophiles has been rarely investigated. Protocols for this reaction usually require stoichiometric amounts of reagents, and few examples on catalytic allylation of alcohols with allylsilanes have been reported.⁴ For the development of a “green” allylation procedure, herein, we applied this montmorillonite catalyst system for the heterogeneous allylation reaction of alcohols with allyltrimethylsilane.

The H-mont showed high catalytic activity for direct substitution of a hydroxyl group in **2g** with allyltrimethylsilane (**11a**) to afford allyldiphenylmethane (**12a**) in 96% yield (Table 2S, Supporting Information). The Al^{3+} -mont (74%) and mont K10 (72%) also were effective catalysts. The reaction scarcely occurred in the presence of other solid acids, such as $\text{SO}_4^{2-}/\text{ZrO}_2$, H-USY, H-mordenite, H-ZSM-5, or the precursor Na^+ -

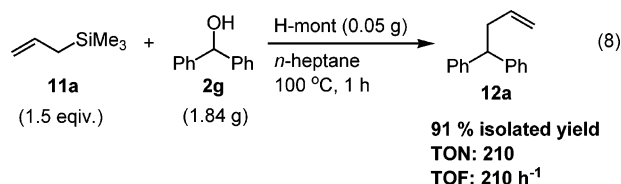
(23) Allylation of 1,3-dicarbonyls with allyl alcohols is usually catalyzed by Pd catalysts, see ref 13.

(24) (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (b) Sakurai, H. *Pure Appl. Chem.* **1989**, *57*, 1759. (c) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (d) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (e) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.

mont. Interestingly, homogeneous acids of H₂SO₄ and *p*-toluenesulfonic acid gave bis(diphenylmethyl) ether (**10b**) as the main product without the desired **12a**.

Allylation of various alcohols with **11a** is shown in Table 7. The reaction of both electron-donating and -withdrawing groups at the para position of benzhydrol proceeded readily, affording the corresponding allylated products in excellent yields (entries 1–4). For reaction of 4,4'-dimethoxy benzhydrol (**2k**), 1,4-dioxane was a better solvent than *n*-heptane because of the greater solubility of **2k** (entry 5). Several 1-arylethanol derivatives reacted with **11a** to afford good to moderate yields of the allylated products (entries 6–8). Notably, reaction of an allylic alcohol of **2a** also proceeded readily to give an 88% yield of the 1,5-diene derivative (entry 9), which is an important precursor for various heterocyclic compounds.²⁵ During these allylations, isomerization of the olefinic double bonds of the products did not occur. Treatment of the recovered H-mont with aqueous hydrogen chloride allowed regeneration of a high catalytic activity: an 87% yield of **12a** was obtained in the recycling experiment. The desired products were not formed selectively when other silyl nucleophiles such as propargyl- and alkenylsilanes were used, due to side reactions (i.e., oligomerization and hydration of the silanes). The reaction of triphenylmethanol (**2s**) did not proceed efficiently (entry 10) and the reaction of the primary alcohol **2q** with **12a** afforded benzyl-oxytrimethylsilane without formation of an allylation product.

The high performance of the H-mont-catalyzed reaction was highlighted by the reaction of 10 mmol of **2g** with 1.5 equiv of **11a**, which proceeded successfully in the presence of 0.05 g of the H-mont (eq 8). After the reaction, the used catalyst was



separated easily from the reaction mixture by a simple filtration, and distillation of the filtrate at 200 °C under 15 mmHg gave the desired product **12a** (1.90 g; 91% isolated yield). In this reaction, the turnover number (TON) and turnover frequency (TOF) based on acid site of the H-mont reached 210 and 210 h⁻¹, respectively. These values were higher than those reported for other catalyst systems, such as ZrCl₄ (TON and TOF, 49 and 196 h⁻¹),^{4f} InCl₃ (20, 6.7 h⁻¹),^{4e} B(C₆F₅)₃ (16),^{4d,26} and HN(SO₂F)₂ (9.6, 1.9 h⁻¹).^{4b}

Reaction Pathways for the Mont-Catalyzed Nucleophilic Substitutions. (I) Nitrogen Compounds. The addition of pyridine significantly decreased the catalytic activity of the H-mont. Upon treatment with pyridine, the IR spectrum of the H-mont showed a new peak at 1543 cm⁻¹ due to a protonated pyridine. Reactions of **2e** and **2f** with **1a** both produced the same product, *N*-(2-butenyl)aniline (eqs 1 and 2). These results suggest that the active species for the nucleophilic substitution reaction is a Brønsted acid site, and a plausible reaction path involving a carbocation intermediate is illustrated in Scheme 3 and proceeds as follows: (i) protonation of an alcohol by H⁺ site and formation of an allyl or benzyl cation intermediate, (ii) attack of a nitrogen nucleophile, followed by (iii) elimination

TABLE 7. Allylation of Various Alcohols with **11a** with Use of the H-mont Catalyst^a

entry	alcohol	<i>t</i> (h)	isolated yield (%) ^b
1	2g	1	96
2	2h	1	86
3	2i	1	98
4 ^c	2j	1	97
5 ^{d,e}	2k	1	96
6 ^c	2l	2	66
7 ^d	2m	2	54
8 ^c	2n	2	58
9 ^d	2a	1	88 ^f
10	2s	1	trace

^a Alcohol (1 mmol), **9a** (1.5 mmol), H-mont (0.02 g), *n*-heptane (2 mL), 60 °C. ^b Based on alcohol. ^c **9a** (2 mmol). ^d **9a** (3 mmol). ^e 1,4-Dioxane (2 mL) was used as a solvent. ^f GC yield.

of a proton to give the allylated or benzylated product. In general, the proton of an ammonium cation shows higher acidity than that of the componential neutral nitrogen compound,²⁷ therefore, proton elimination from the amine may occur smoothly after the formation of the ammonium cation intermediate. Anilines with an electron-withdrawing group showed higher reactivity than anilines with an electron-donating group, and the reaction rate decreased with the increase of the aniline concentration (see Figure 4S, Supporting Information). These results indicate that an alcohol protonation might be depressed by interaction between the acid site in the H-mont and a basic aniline. Solid acid catalysts with weak acidity (ΔH) such as the H-mont ($\Delta H = 111$ kJ mol⁻¹) exhibited higher activity in substitution reactions compared to H-mordenite having strong acid sites ($\Delta H = 160$ kJ mol⁻¹). A suitable strength of the Brønsted acid sites is required for the efficient substitution reaction of alcohols, and prevents the neutralization by the basic aniline,²⁸ when compared with other heterogeneous and homogeneous strong acids. Furthermore, for the reactions of neutral nitrogen compounds, amides and indoles, the two-dimensional silicate sheets of the H-mont provide wide spaces for the catalytic reaction, and effectively act as the macro counter anions to decrease their anion coordination ability toward the H⁺ site,¹⁷ leading to high activity for generation of the allyl and benzyl cation intermediates.^{6d}

(II) 1,3-Dicarbonyl Compounds. Upon treatment of the H-mont with **8a**, both the keto and enol forms of **8a** were detected (Figure 2),^{7a} therefore, a proposed reaction path might involve the dual activation of alcohols and 1,3-dicarbonyls as shown in Scheme 4A: (i) formation of a carbocation intermediate from an alcohol and coordination of a 1,3-dicarbonyl onto neighboring H⁺ sites,²⁹ (ii) formation of an activated enol intermediate, and (iii) nucleophilic attack of the enol. Presumably, concentrated protonic acid sites in the interlayer space would provide higher activity of the H-mont.³⁰

(27) For example, the pK_a value of protonated aniline (3.6) is much lower than that of aniline (30.6); see: Fu, Y.; Li, R.-Q.; Liu, R.; Guo, Q.-X. *J. Am. Chem. Soc.* **2004**, *126*, 814.

(28) In the reaction of neutral nitrogen nucleophile of amides, this deactivation of H⁺ site might not occur.

(29) Enolization of ketone is promoted by Brønsted acid, see ref 5a and: Han, X.; Wang, X.; Pei, T.; Widenhoefer, R. A. *Chem. Eur. J.* **2004**, *10*, 6333.

(25) J. Kurth, M.; Rodriguez, M. J. *Tetrahedron*, **1989**, *45*, 6963.

(26) Reaction time was not reported.

SCHEME 3. A Proposed Reaction Pathway for Substitution of Alcohols with Anilines

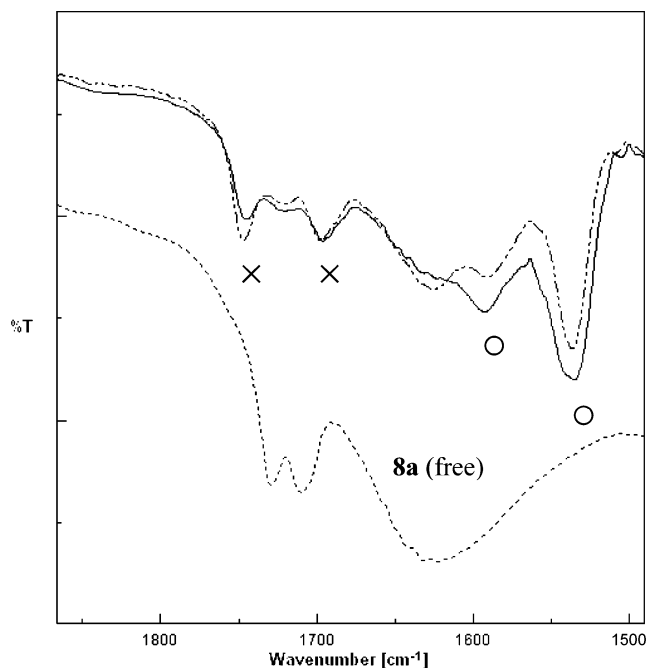
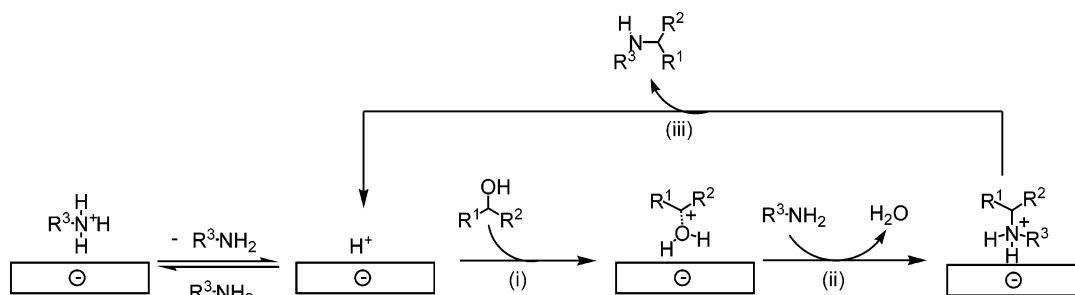


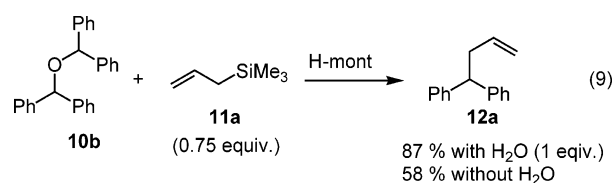
FIGURE 2. The IR spectra of **8a** adsorbed on the Al^{3+} -mont (—) and H-mont (---): enol (○) and keto (×) form of adsorbed **8a**.

Both Al^{3+} - and H-mont-catalyzed reactions of **8a** with the ether **10a** afforded low yields, ca. 30%, of the benzylated product **9a** for 6 h at 100 °C in the presence of water, in sharp contrast to the reaction of **8a** with **10b**.³¹ These results indicate that the main reaction path might be direct α -alkylation of a 1,3-dicarbonyl compound with a primary alcohol, which does not occur via an ether intermediate. Upon treatment with pyridine, the IR spectrum of the Al^{3+} -mont showed peaks due to a protonated pyridine and to pyridine adsorbed on the Lewis acid site. After the treatment of the Al^{3+} -mont with **8a**, IR absorptions assignable to both keto and enol forms of **8a** also were detected (Figure 2).³²

Since the peaks due to enol form were stronger relative to those of the H-mont, the Al site in the Al^{3+} -mont interlayer is effective at producing the active enol of **8a**. A proposed reaction

pathway might involve the dual activation of alcohols and 1,3-dicarbonyls by the H^+ and Al^{3+} site, respectively (Scheme 4B): a 1,3-dicarbonyl coordinates onto the Lewis acidic Al site, giving an activated enol intermediate that readily attacks a protonated alcohol. Li and co-workers also reported activation of both 1,3-dicarbonyls and alkenes using $\text{Ga}(\text{TfO})_3$ and TfOH for the addition reaction.^{33,34} Since primary alcohols, such as benzyl alcohol, easily undergo ether formation under acidic conditions relative to secondary alcohols, the selective formation of C–C coupling products requires stepwise addition of primary alcohols into the reaction mixture, accompanied by activation of the 1,3-dicarbonyl compounds. Effective activation of 1,3-dicarbonyls by Lewis acidic Al sites would depress formation of the ether, which promotes higher selectivity toward the benzylation product compared to other catalysts.

(III) Allylsilane. Among various solid acids, reactions with only mont clays with a layered structure achieved high yields of **12a** (Table 2S, Supporting Information). The low activity of zeolites, such as H-USY, H-mordenite, and H-ZSM-5, is due to their restricted small pore size that does not accommodate the relatively large molecular size of the alcohol **2g**. The addition of pyridine significantly decreased the catalytic activity of the H-mont, similar to that in the above reactions of nitrogen compounds. An ether of **10b** was observed during allylation of **2g** with **11a** with use of the H-mont. These results indicate that the active species for these nucleophilic additions seems to be a Brønsted acid site, and a plausible reaction path involving a carbocation intermediate is illustrated as Scheme 5 and could proceed as follows: (i) protonation of an alcohol by the H^+ site to give a carbocation intermediate, (ii) reversible formation of an ether, (iii) attack of an allylsilane followed by (iv) formation of an allylated product, and (v) regeneration of the H^+ active site by hydration.³⁵ The reaction of **10b** with **11a** in the presence of water afforded the allylation product **12a** in excellent yield, while a slow reaction rate was observed in the absence of water (eq 9). Water can promote the hydration step (v), then the strong hydrophilic ability of the H-mont interlayers provides the high activity for the allylation reaction, compared with those of homogeneous acids (see Table 2S, Supporting Information).

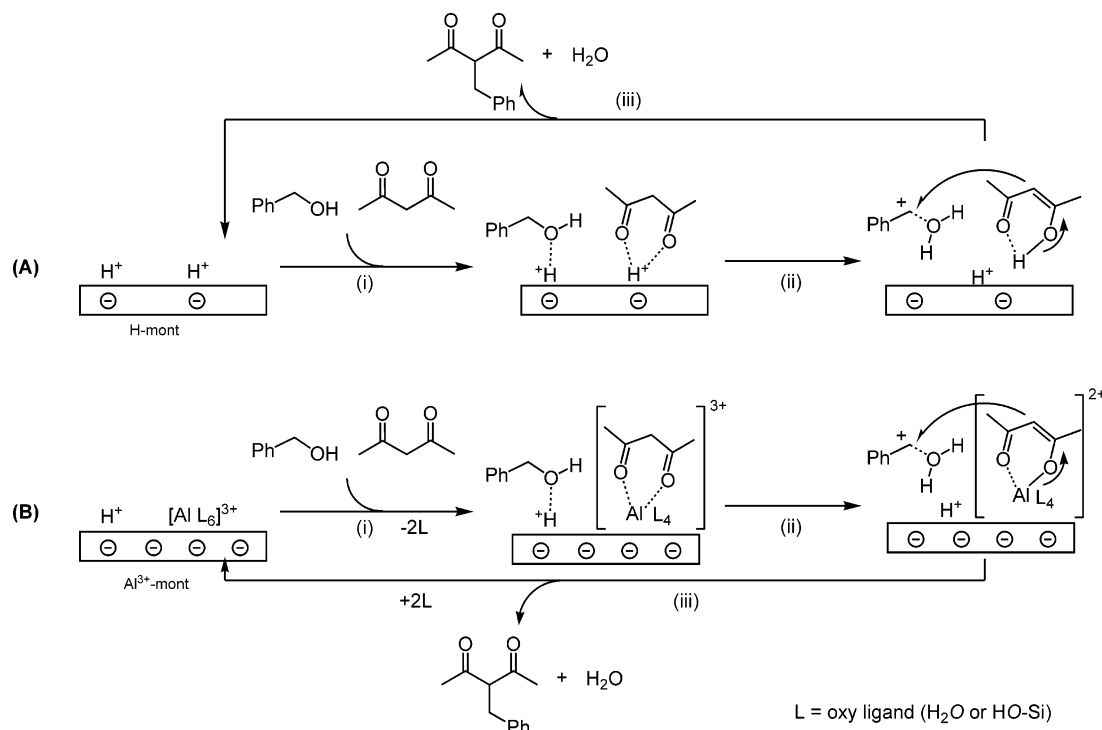


(30) The concentration of the acid sites on the H-mont surface (6.3×10^{-3} mmol/m²) is much larger than that on zeolite catalysts such as H-beta (0.95×10^{-3} mmol/m²) and H-USY (0.75×10^{-3} mmol/m²). These values were calculated as follows: (concentration of acid site [mmol/m²]) = (amount of acid site [mmol/g])/(specific surface area [m²/g]).

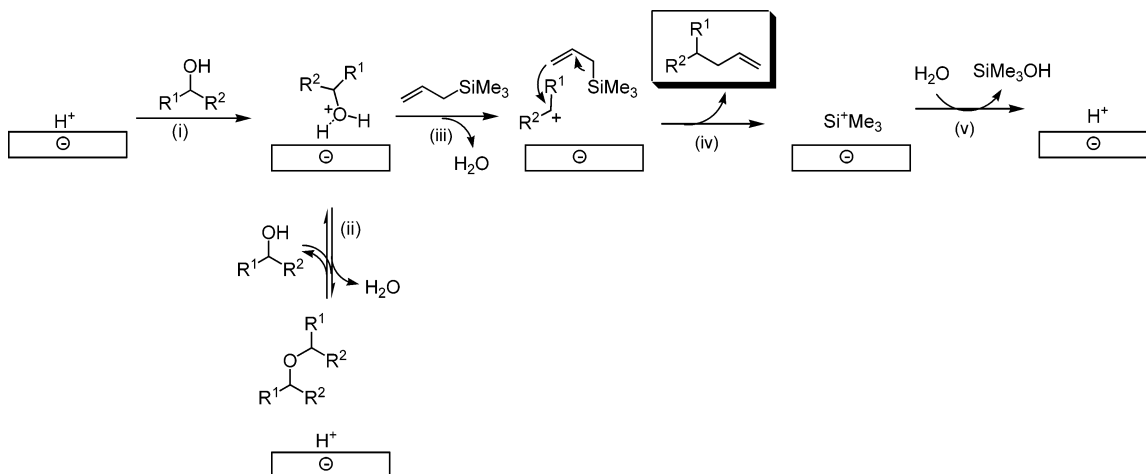
(31) The H-mont-catalyzed reaction of **8a** with ether **10b** from the secondary alcohol of **2g** afforded quantitative yield of the α -benzhydryl acetylacetone.

(32) Alexander, S. M.; Bibby, D. M.; Howe, R. F.; Meinhold, R. H. *Zeolite* **1993**, *13*, 441.

SCHEME 4. Proposed Reaction Pathways for Substitution of Alcohols with 1,3-Dicarbonyl Compounds via Dual Activation by (A) Brønsted Acid–Brønsted Acid (H-mont) and (B) Brønsted Acid–Lewis Acid (Al³⁺-mont)



SCHEME 5. A Proposed Reaction Pathway for Allylation of Alcohols with Allylsilane



Conclusions

The Brønsted acid-catalyzed substitution reactions of the hydroxyl groups of allylic and benzylic alcohols with basic aniline nucleophiles were demonstrated for the first time. Interestingly, the H⁺ site in the H-mont was not neutralized by the basic nucleophiles because of their weak acid strength. Furthermore, nucleophilic substitution of alcohols with amides, indoles, 1,3-dicarbonyl compounds, and allylsilane also was

shown. Use of alcohols instead of halides, acetates, and carbonates as alkylating reagents eliminated waste byproducts because it led only to the formation of water. This H-mont as a heterogeneous catalyst realized easy separation of the catalyst from the reaction mixture and was recycled without an appreciable loss of activity and selectivity. For the substitution reaction of primary alcohols with 1,3-dicarbonyl compounds, the Al³⁺-exchanged montmorillonite showed high product selectivity derived from cooperative catalysis of the Lewis and Brønsted acid sites. The unique acid properties of the monts with delocalized counter anions of two-dimensional silicate sheets will allow the development of methods for a variety of organic transformations.

Experimental Section

General. ¹H and ¹³C NMR spectra were obtained on a JEOL GSX-270 or a JNM-AL400 spectrometer at 270 or 400 MHz in

(33) Nguyen, R.-V.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 17184.
 (34) For activation of 1,3-dicarbonyls by Lewis acidic metal centers, see: (a) Sasai, H.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1994**, *116*, 1571. (b) Christoffers, J. *Eur. J. Org. Chem.* **1998**, 1259. (c) Mori, K.; Oshiba, M.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2005**, *46*, 4283. (d) Mori, K.; Oshiba, M.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *New J. Chem.* **2006**, *30*, 44.
 (35) Formation of triisopropylsilanol was detected by GC-MS analysis together with **12a** in the reaction of **2g** and triisopropylallylsilane.

CDCl₃ with TMS as an internal standard. Solid state ²⁹Si MAS NMR spectra (MAS rate = 6 kHz) were recorded with a Chemagnetics CMX-300 spectrometer operating at 59.7 MHz. Repetition time was 20 s (²⁹Si). Polydimethylsilane (²⁹Si: -34.2 ppm) was used as an external standard for the calibration of chemical shifts. Infrared spectra were obtained with a JASCO FTIR-410. Analytical GLC and GLC-mass were performed by using a Shimadzu GC-8A PF with a flame ionization detector equipped with KOCL 3000T, Silicon SE-30, and OV-17 columns, and a Shimadzu GCMS QP5000 equipped with ULBON HR-1 column. Powder X-ray diffraction patterns were recorded with a Philips X'Pert-MPD with Cu K α radiation. NH₃-TPD of the samples was conducted in a flow-type fixed bed reactor with a Japan BEL TPD-77 instrument. BET surface area of the catalysts was determined by N₂ adsorption-desorption measurements with a BELSORP 18PLUS-SP analyzer. The identities of products were confirmed by comparison with reported IR, MS, and ¹H and ¹³C NMR data.

Preparation of the H-mont Catalyst. A mixture of parent Na⁺-mont (3.0 g) and 200 mL of aqueous HCl (1.1 wt %) was stirred at 90 °C for 24 h. The slurry obtained was filtered and washed with 1 L of distilled water to remove chlorine, followed by drying at 110 °C in air to afford the H-mont as a whitish gray powder. Elemental analysis: Na, 0.03; Al, 10.1; Fe, 1.34; Mg, 1.73.

Preparation of the Al³⁺-mont Catalyst. A mixture of parent Na⁺-mont (4.2 g) and 200 mL of aqueous AlCl₃·6H₂O (3.3 × 10⁻² M) was stirred at 50 °C for 24 h. The slurry obtained was filtered and washed with 1 L of distilled water, followed by drying at 110 °C in air to afford the Al³⁺-mont as a whitish gray powder. Elemental analysis: Na, 0.06; Al, 12.9; Fe, 1.50; Mg, 2.04.

A Typical H-mont-Catalyzed Substitution Reaction of Alcohols with Anilines. H-mont (0.1 g), *n*-heptane (2 mL), **1a** (1 mmol), and **2a** (2 mmol) were placed into a reactor. The resulting mixture was stirred vigorously at 80 °C. After 24 h, the catalyst was separated by filtration and GC analysis of the filtrate showed an 88% combined yield of allylated products, *N*-(2-cyclohexen-1-yl)-aniline (**3a**), 2-(2-cyclohexen-1-yl)aniline (**4a**), and 4-(2-cyclohexen-1-yl)aniline (**5a**). GC analysis revealed a product ratio of 86:10:4. The filtrate was evaporated and the crude product purified by column chromatography with use of silica (*n*-hexane/ethyl acetate = 9:1) to afford pure products.

A Typical H-mont-Catalyzed Addition Reaction of 1,3-Dicarbonyl Compounds to Alcohols. Into a pressure tube were placed H-mont (0.15 g), *n*-heptane (2 mL), **8a** (1.5 mmol), and **2f** (1.0 mmol). The resulting mixture was stirred vigorously at 100 °C. After 1 h, the catalyst was separated by filtration. Then, the filtrate was evaporated and the crude product was purified by column chromatography with use of silica (*n*-hexane/ethyl acetate = 9:1) to afford pure 3-(1-phenylethyl)-2,4-pentanedione in 90% isolated yield. The recovered catalyst was washed with ethyl acetate and dried under vacuum before the reuse experiment.

A Typical Al³⁺-mont-Catalyzed Addition Reaction of 1,3-Dicarbonyl Compounds to Primary Alcohols. Into a reactor were

placed Al³⁺-mont (0.1 g), nitromethane (2 mL), and **8a** (3 mmol). The resulting mixture was stirred vigorously at 60 °C. Then, **2q** (2 mmol) was added dropwise into the reaction mixture over 5.5 h. After 30 min, the catalyst was separated by filtration and GC analysis of the filtrate showed an 83% yield of 3-(phenylmethyl)-2,4-pentanedione.

A Typical H-mont-Catalyzed Allylation Reaction of Alcohols with Allylsilane. Into a reactor were placed H-mont (0.02 g), *n*-heptane (2 mL), **11a** (1.5 mmol), and **2g** (1.0 mmol). The resulting mixture was stirred vigorously at 60 °C. After 1 h, the catalyst was separated by filtration and GC analysis of the filtrate showed a 96% yield of 1,1-diphenyl-3-butene. The recovered H-mont was washed with ethyl acetate and dried under vacuum, followed by treatment of the catalyst with aqueous HCl (1.1 wt %) for 10 h at room temperature. The HCl-treated catalyst was dried under vacuum before the reuse experiment.

IR Measurement of Pyridine-Adsorbed mont Catalysts. Into a reactor were placed mont catalyst (0.1 g) and pyridine (1 mmol). The resulting mixture was stirred at room temperature for 3 h. After the adsorption of pyridine, the excess pyridine was removed by evacuating the samples at 150 °C for 12 h. The IR spectra of the strongly adsorbed pyridine were obtained with use of self-supporting wafers containing 12 mg of the sample.

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Supporting Information Available: Details of experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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