



Unprecedented alkylation of silicon enolates with alcohols via carbenium ion formations catalyzed by tin hydroxide-embedded montmorillonite



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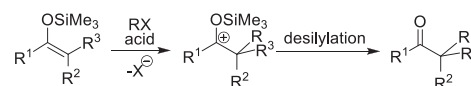
ABSTRACT

The solid acid, tin hydroxide-embedded montmorillonite, catalyzes the unprecedented alkylation of various silicon enolates with primary, secondary and tertiary benzylic alcohols as well as secondary allylic alcohols. The acid catalysis of Sn-Mont was not only higher than that of the other ion-exchanged montmorillonites (M-Mont; M = H, Ti, Fe and Al), but also higher than that of the typical homogeneous acid catalysts such as $\text{BF}_3 \cdot \text{OEt}_2$, TMSOTf and TfOH.

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Alcohols are generally not efficient alkylation reagents due to the poor leaving ability of the hydroxyl group. Therefore, the alcohols are normally transformed into the corresponding more reactive halides, carboxylates, carbonates, sulfonates, etc., and applied to the substitutions with nucleophiles using equimolar amounts of bases, co-producing stoichiometric amounts of waste salts. The direct alkylation with alcohols is an intriguing process, but the concurrent formation of water often confines the alkylation to some specific types of reactions and catalysts.¹

Silicon enolates (silyl enol ethers) are some of the useful nucleophiles which can be easily prepared from the corresponding carbonyl compounds by various methods and have relatively high chemical and thermodynamic stabilities when handling.² In the presence of a stoichiometric or catalytic amount of Lewis acids, tertiary and secondary benzylic halides react as alkylating reagents with silicon enolates to produce α -substituted carbonyl compounds³: The Lewis acid promotes the formation of carbenium ions from the halides, which are subsequently trapped by the silicon enolates to form adduct intermediates. Rapid desilylation of the intermediates then resulted in the formation of the final products (Scheme 1).^{3c} Surprisingly, although Brønsted and Lewis acids,



Scheme 1. Acid-catalyzed alkylation of silicon enolates with alkyl halides.

such as TfOH and $\text{BF}_3 \cdot \text{OEt}_2$, can generate the corresponding carbenium ions directly from alcohols, there have been no reports on the acid catalyzed-one step alkylations of silicon enolates with alcohols.⁴ Because most acid catalysts are water-sensitive and significantly deactivated by water, the alkylation of silicon enolates with alcohols is impeded.⁵

Montmorillonite (Mont) is one of the abundant naturally-occurring clays. It is composed of stacked, negatively charged, aluminosilicate layers with intercalated exchangeable cationic species, mostly sodium ions, between the layers. When the sodium ions in the Mont are substituted by multivalent metal ions or protons, the clays become strongly acidic. Such acidic clays have been utilized in various acid-catalyzed organic reactions. We originally developed tin hydroxide-embedded montmorillonite (Sn-Mont)⁶, and applied it as a solid acid catalyst to various organic transformations of carbonyl compounds and alcohols. As the reactions of carbonyl compounds, we reported the cyanosilylation⁷, the one-pot Strecker synthesis of α -amino nitriles⁸ and the Mukaiyama

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aldol reactions.⁹ We also found that Sn-Mont promoted various reactions of benzylic and allylic alcohols with allyltrimethylsilane¹⁰, 1,3-dicarbonyl compounds¹¹, trialkylsilyl cyanide¹², and trialkylsilanes.¹³ For such S_N1-type reactions of alcohols with typical nucleophiles, it is noteworthy that Sn-Mont plays an essential role as an efficient acid catalyst for not only generating the corresponding carbenium intermediates from benzylic or allylic alcohols but also embracing and stabilizing the unstable carbenium ions, tolerating deactivation by the water molecules produced in the reaction. Therefore, we envisioned that the direct alkylation of silicon enolates with alcohols would be possible using the acidic montmorillonite catalysts.

First, the direct alkylation of trimethylsilyl (TMS) enolates **1a** with benzhydrol **2a** to afford the alkylated product **3aa** was investigated as a model reaction using various heterogeneous and homogeneous acid catalysts according to the manual injection protocol of Ref. 14, and the results are summarized in Table 1.

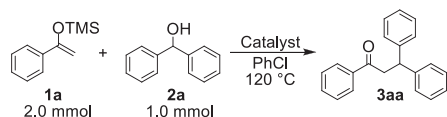
Various ion-exchanged montmorillonites, such as Al-Mont, Fe-Mont, Ti-Mont, Sn-Mont as well as H-Mont, exhibited different catalytic activities.¹⁵ Among the montmorillonite catalysts, Sn-Mont showed the highest catalytic activity (entry 1). On the other hand, Na-Mont, which was pristine, natural montmorillonite, exhibited no catalytic activity (entry 6). The strongly acidic proton-type mor-denite zeolite (H-Mor) also had no catalytic activity. Typical homogeneous acids, such as TfOH, TMSOTf and BF₃·OEt₂, were also examined (entries 8–10). TfOH and BF₃·OEt₂ exhibited a much lower activity than Sn-Mont, while TMSOTf had no activity.

In order to uncover the applicability of alcohols, various benzylic and allylic alcohols were tested for the alkylation of **1a**. The results are summarized in Table 2.

In an attempt to perform the alkylation of **1a** using **2b**, a benzhydrol derivative bearing an electron-withdrawing chlorine atom did not yield any desired product (entry 2). The efficiency of the alkylation of **1a** with phenethyl alcohols was closely related to the stability of the carbenium ions derived from the benzylic alcohols: Although an attempt to alkylate **1a** with the pristine phenethyl alcohol **2c** failed (entry 3), the alkylation of **1a** with phenethyl alcohol derivatives bearing an electron-donating substituent, **2c'** or **2c''**, yielded the corresponding products in almost quantitative yields (entries 4 and 5). These results suggest that the reaction should proceed through an S_N1-type mechanism in a fashion similar to that of the acid-catalyzed alkylations of silicon enolates with halides (Scheme 1).

Table 1

Comparison of various acid catalysts for the alkylation of silicon enolate **1a** with an alcohol **2a** as the alkylating reagent.



Entry	Catalyst	Reaction time	Yield of 3aa ^a
1	Sn-Mont ^b	10 min	63%
2	H-Mont ^b	10 min	46%
3	Ti-Mont ^b	20 min	45%
4	Al-Mont ^b	20 min	18%
5	Fe-Mont ^b	20 min	20%
6	Na-Mont ^b	3 h	0%
7	H-Mor ^b	3 h	0%
8	TfOH ^c	10 min	5%
9	BF ₃ ·OEt ₂ ^d	10 min	8%
10	TMSOTf ^c	3 h	0%
11	–	3 h	0%

^a ¹H NMR yield based on mesitylene as the internal standard.

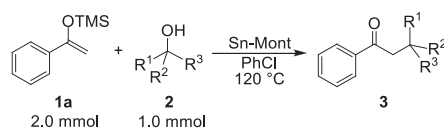
^b 20 mg of catalyst was employed.

^c 5 mol% of the catalyst was employed.

^d 10 mol% of BF₃·OEt₂ was employed.

Table 2

Scope of benzylic and allylic alcohols.^{a,d}



Entry	2	Reaction time	Yield of 3 ^b
1	2a	10 min	63% ^e (77%) ^f
2	2b	1 h	0%
3	2c (R = H)	10 min	0%
4	2c' (R = OMe)	10 min	97%
5	2c'' (R = Me)	10 min	97%
6	2d (R ¹ = R ² = R ³ = H)	10 min	0%
7	2d' (R ¹ = R ² = R ³ = OMe)	10 min	98%
8	2e	10 min	97%
9	2f (R = Me)	10 min	93% ^c
10	2f' (R = Ph)	10 min	97%

^a **1a**: 2.0 mmol, **2**: 1.0 mmol, Sn-Mont: 20 mg, PhCl: 2.0 mL, Temp.: 120 °C.

^b ¹H NMR yield using mesitylene as the internal standard.

^c The total yields of the regioisomeric products.

^d Most of the reactions were performed according to the manual slow-injection procedure.

^e Symmetric ether **4a** and trimethylsilyl ether **5a** were produced as the byproducts in 3% and 23% yields, respectively.

^f The figure in parentheses shows the yield according to the mechanical slow-injection procedure.

The protocol is also applicable for primary benzylic alcohols. Although a simple benzyl alcohol **2d** was not reactive as an alkylating agent (entry 6), the alkylation with a benzylic alcohol bearing three methoxy groups **2d'** successfully proceeded in almost quantitative yield (entry 7), indicating that the relatively stabilized primary carbenium ions are effective alkylating agents in the reaction.

The alkylation of **1a** with tertiary benzylic alcohol **2e** almost quantitatively proceeded (entry 8) even via the formation of a bulky trityl cation.

The alkylation with allylic alcohols was also explored. With the symmetrical allylic alcohol **2f**, the alkylation was successful in almost quantitative yield (entry 10). Using the unsymmetrical allylic alcohol **2f'** gave a regioisomeric mixture of products, the non-rearranged product (3-methyl-1,5-diphenylpent-4-en-1-one) and the rearranged one (1,3-diphenylhex-4-en-1-one), were produced in 58% and 35% yields, respectively (entry 9).

The alkylation of **1a** with benzhydrol **2a** produced not only **3aa** in 63% yield, but a symmetric ether **4a** in 3% and silyl ether

5a in 23% as well as acetophenone, a hydrolyzed product of **1a** as side products (entry 1 of Table 2). Acetophenone was another

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