



Direct allylation of α -aryl alcohols with allyltrimethylsilane catalyzed by heterogeneous tin ion-exchanged montmorillonite

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ABSTRACT

The direct allylation of α -aryl alcohols with allyltrimethylsilane efficiently proceeded in the presence of tin ion-exchanged montmorillonite under mild conditions according to the proper addition order of reactants and a catalyst.

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During the past two decades, Lewis acid-catalyzed allylation of carbonyl compounds and acetals with allylic silanes, known as the Sakurai–Hosomi reaction, has been extensively investigated.¹ However, the direct allylation of alcohols as electrophiles received less attention owing to the poor leaving ability of hydroxyl groups in the alcohols. The nucleophilic allylation of alcohols is normally performed through a prior transformation of a hydroxyl group to a good leaving one such as halides, carbonates, phosphonates, and sulfonates.

There have been several precedents on the direct allylation of α -aryl alcohols with allyltrimethylsilane, in which only homogeneous catalysts were employed such as MX_3 ($M = Bi, In; X = Cl, Br$),^{2–5} $B(C_6F_5)_3$,⁶ bis(fluorosulfonyl)imide,⁷ phosphomolybdic acid,⁸ $ZrCl_4$,⁹ and BF_3 .¹⁰ Most of these protocols often require long reaction times, harsh reaction conditions, and tedious workup procedures. Moreover, Lewis acid catalysts such as metal halides are prone to hydrolysis and consequent deactivation, and hence are not reusable. Thus, to overcome these disadvantages, the development of heterogeneous catalyst systems is in high demand. Proton ion-exchanged montmorillonite (H-Mont) as a heterogeneous catalyst was found to be efficient for the direct allylation of α -aryl alcohols with allyltrimethylsilane, but the long reaction times and high reaction temperatures of 60–100 °C were normally required.¹¹

We have been focusing on various metal ion-exchanged montmorillonites as the solid alternatives to homogeneous Brønsted acid catalysts.^{12–17} Montmorillonite, a naturally occurring clay, is composed of stacked, negatively-charged two-dimensional aluminosilicate layers that hold exchangeable cationic species, mostly sodium ions in the interlamellar space.¹⁸ Once multivalent metal cations or protons are substituted for sodium ions in the montmorillonite, the clay becomes acidic and has been utilized in various acid-catalyzed organic reactions.^{12,19} Among the various metal ion-exchanged montmorillonites, tin ion-exchanged montmoril-

lonite (Sn-Mont) was considered the most acidic for the silylation of alcohols.¹² It has also been found that Sn-Mont was an effective acid catalyst for the cyanosilylation of carbonyl compounds,^{15,17,20} the reduction of carbonyl compounds with hydrosilanes,¹⁶ the Michael reaction,¹³ and the one-pot Strecker synthesis of α -amino nitriles.²¹

In continuation of our work to the development of new synthetic organic transformations, we herein report that water-resistant and environmentally benign Sn-Mont, easily prepared from natural Na-Mont,¹⁷ acted as a highly efficient heterogeneous catalyst for the allylation of a wide range of α -aryl alcohols with allyltrimethylsilane in very short reaction times (0.1–0.5 h) at rt. Moreover, it was surprisingly found that the addition order of the reactants and Sn-Mont was definitely critical to the yields and selectivity. The catalyst was easily recovered by filtration and reused without an appreciable loss of activity and selectivity.

Sn-Mont was prepared through the ion-exchange of Na-Mont with an aqueous $SnCl_4$ solution.¹⁷ Elemental analysis of Sn-Mont by inductively coupled plasma (ICP) showed that the tin molar content of the as-prepared Sn-Mont was 1.9 $\mu\text{mol}/\text{mg}$. The nitrogen sorption data showed that the specific surface area greatly increased from 12 $\text{m}^2 \text{g}^{-1}$ of pristine Na-Mont to 280 $\text{m}^2 \text{g}^{-1}$ of Sn-Mont with a porous structure. Transmission electron microscopy (TEM) indicated that Sn-Mont was a nanocomposite of nanoparticles of SnO_2 surrounded by montmorillonite silicate layers. FT-IR spectrum of Sn-Mont after the pyridine adsorption proved that Sn-Mont had Brønsted acidity.²¹

Because it has been already shown that the addition order of reactants had a great influence on the cyanation of α -aryl alcohols with cyanotrimethylsilane in the presence of solid Brønsted acid catalysts,²² the addition order was initially examined in the reaction of benzhydrol (**1a**) with allyltrimethylsilane (ATMS) in CH_2Cl_2 in the presence of Sn-Mont (20 mg, 3.8 mol %), as shown in Figure 1.²⁴

When Method A in which ATMS was added to a suspended mixture of **1a** and Sn-Mont was adopted at rt, the desired **2a** was

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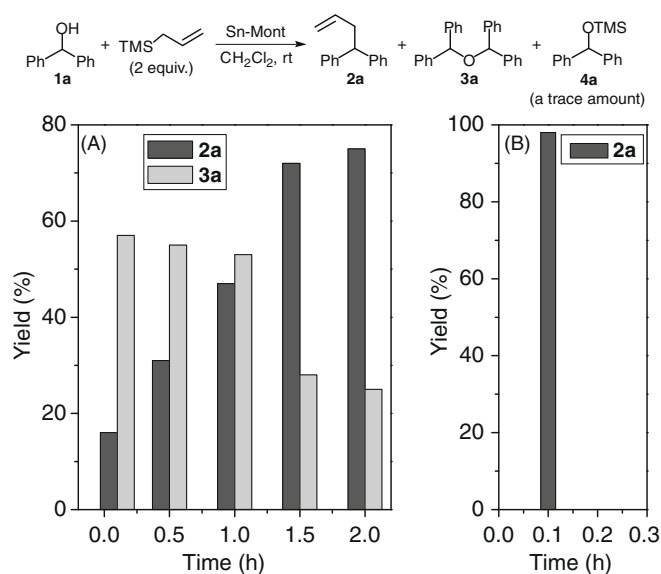


Figure 1. The effects of the addition orders of reactants and a catalyst on the yields of the allylated product **2a** and ether **3a** for the reaction of benzhydrol **1a** and allyltrimethylsilane catalyzed by Sn-Mont at rt. Reaction conditions: Sn-Mont (20 mg, 3.8 mol %), **1a** (1 mmol), allyltrimethylsilane (2 mmol), CH₂Cl₂ (2 mL), rt. (A) Method A; (B) Method B.

obtained in only 16% yield, together with a large amount of **3a** (57%) in 0.1 h, as indicated in Figure 1A. By-product **3a** gradually changed into **2a**, and a moderate yield (75%) of **2a** was gained with remaining **3a** (24%) when the reaction time was extended to 2 h. It is evident that the formation of side product **3a** reduced the yield of **2a**.

In order to suppress the intermolecular condensation of **1a** to **3a** by the acid catalysis of Sn-Mont, another addition procedure called Method B was employed, in which a CH₂Cl₂ solution of **1a** was slowly added to a suspended mixture of Sn-Mont and ATMS. Following this method, to our surprise, the reaction became very fast and completed in only 0.1 h at rt as shown in Figure 1B. The yield of **2a** was dramatically improved to 98% without the formation of **3a**. In both Methods A and B, only trace amounts of **4a** were found based on ¹H NMR and GC.

It is noteworthy that the turn-over frequency (TOF) of the reaction of **1a** with ATMS catalyzed by Sn-Mont is as high as 258 h⁻¹; this value is far greater than the preceding ones for the same reaction using various homogeneous catalysts such as BiCl₃ 36.8 h⁻¹,² Brønsted acid, bis (fluorosulfonyl)imide HN(SO₂F)₂ 115 h⁻¹,⁷ InCl₃ 6.7 h⁻¹,⁴ InBr₃ 34 h⁻¹,⁵ and ZrCl₄ 196 h⁻¹.⁹ The activity of Sn-Mont for the allylation of **1a** is also far superior to that of the commercially available Amberlyst-15. And the reaction rate (490 mmol h⁻¹ g_{cat}⁻¹) based on the weight of Sn-Mont was far higher than those (Method A, 1.5 mmol h⁻¹ g_{cat}⁻¹; Method B, 34.5 mmol h⁻¹ g_{cat}⁻¹) for Amberlyst-15.²⁵ Moreover in our case the Sn-Mont catalyst was easily separable from the reaction mixture by a simple filtration. Although H-Mont was reported to be efficient for the same reaction, but heating at 60 or 100 °C was required,¹¹ and the reaction rate of 48 mmol h⁻¹ g_{cat}⁻¹ based on the weight of H-Mont was also far lower than that of 490 mmol h⁻¹ g_{cat}⁻¹ of Sn-Mont which promoted the reaction even at ambient temperature.

Secondly, to investigate the scope and limitations of the present catalytic protocol with Sn-Mont following the optimal addition order (Method B), various alcohols were examined and the results are summarized in Table 1.²⁶ Most reactions gave the desired products with good to excellent yields in the presence of Sn-Mont (20 mg; 3.8 mol %) in very short reaction times (0.1–0.5 h). Benz-

hydrol (**1a**) and its derivatives **1b–d** which have electron-withdrawing or electron-donating substituents on the aromatic rings were effectively allylated at rt (entries 1–4). No product was produced without the catalyst (entry 5).

A secondary alcohol, 1-phenylethanol (**1e**), yielded the corresponding alkene **2e** in moderate yield (61%), which might be due to the formation of polystyrene as a side product (Table 1, entry 7).¹⁰ The direct allylation of **1e** with ATMS failed by the use of bis(fluorosulfonyl)imide,⁷ phosphomolybdic acid,⁸ and ZrCl₄.⁹ BF₃ gave a poor yield (22%) of the desired products with a large amount of side products.¹⁰ The introduction of an electron-donating group at the *para*-position of **1e** resulted in higher yields: 75% for **1f** in entry 8 and 98% for **1g** in entry 9. Similarly, 1-(4'-Me or MeO-substituted phenyl)propanols (**1h–i**) afforded a middle yield of 81% (entry 10) and a high yield of 94% (entry 11), respectively. An acid-sensitive substrate (**1j**) was also applicable for the present heterogeneous catalytic system and the desired allylated product (**2j**) was gained in 73% yield (entry 12). Other 1-arylethanol derivatives (**1k–m**) reacted with ATMS to produce the allylated products in middle to good yields (entries 13–15). Unfortunately, primary alcohols such as benzyl alcohol and a simple aliphatic alcohol like decan-3-ol were not suitable for the Sn-Mont-catalyzed reactions and no desired products were obtained. Reactions of allylic alcohols **1n** and **1o** also gave good yields (entries 16–17). To our delight, two sterically hindered alcohols **1p** and **1q** were also proper substrates for giving the corresponding allylated products in excellent yields at rt (entries 18–19).

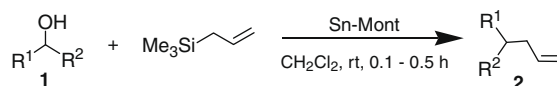
In order to confirm that the observed catalysis is truly caused by the solid Sn-Mont rather than the Sn species leaching into the solution, the following experiments were performed: The allylation of **1a** with ATMS was carried out at rt as shown in entry 1 of Table 1. After the complete consumption of **1a**, Sn-Mont was removed from the reaction mixture by filtration. Another substrate **1d** and ATMS were then added to the filtrate at rt. Even in 1 h, no **2d** was produced, indicating that the solution phase did not include any catalytically active species. Moreover, Sn-Mont is superior to homogeneous catalysts in the way that Sn-Mont can be easily separated from the reaction mixture and be reused without an appreciable loss of activity and selectivity (Table 1, entry 6).

Sn-Mont is a nanoporous material with strong Brønsted acidity.²¹ Thus, the most probable reaction pathway in the allylation of alcohols with allyltrimethylsilane should involve a carbocation intermediate dehydrated by the Brønsted acidity of Sn-Mont, followed by the direct attack with allyltrimethylsilane to form the allylated products.¹¹ In fact, during the allylation of **1a** with ATMS, the ether (**3a**) and a trace amount of diphenylmethyl trimethylsilyl ether (**4a**) were observed, together with the allylated product **2a**. Thus, **3a** and **4a** are probable intermediates which further react with ATMS to afford **2e**.



Here we independently examined whether or not these two side products (**3a** and **4a**) would be further transformed into **2a**. Firstly, **3a** was in advance prepared in a 71% isolated yield by simply mixing Sn-Mont and **1a** in CH₂Cl₂ as shown in Eq. 1. Secondly, the reaction of **3a** with ATMS afforded **2a**, but in a poor yield of 20% even after 6 h (Eq. 2). Moreover, another side product **4a**, prepared

Table 1
Allylation of various alcohols with allyltrimethylsilane using Sn-Mont^{a,b}



Entry	Alcohol 1	R	Product 2	Yield ^c (%)	
1		H	1a	2a	95
2		Cl	1b	2b	92
3		Me	1c	2c	96
4		OMe	1d	2d	98
5 ^d	1a			2a	0
6 ^e	1a			2a	96
7		H	1e	2e	61
8		Me	1f	2f	75
9		OMe	1g	2g	98
10		Me	1h	2h	81
11		OMe	1i	2i	94
12			1j	2j	73
13 ^f			1k	2k	71
14 ^f		H	1l	2l	66
15 ^f		OMe	1m	2m	85
16			1n	2n	93
17			1o	2o	72
18 ^f			1p	2p	89
19 ^{f,g}			1q	2q	91

^a Alcohol (1 mmol), allyltrimethylsilane (2 mmol), Sn-Mont (20 mg, 3.8 mol %), dichloromethane (2 mL), rt.

^b Method B was employed.

^c Isolated yields.

^d The reaction was performed without catalyst.

^e With the recovered catalyst.

^f Alcohol (0.5 mmol).

^g 1.5 h.

according to the literature,²³ efficiently reacted with ATMS in a good yield of 84% (Eq. 3). Thus, it was concluded that in the allylation of **1a**, **3a** and **4a** were both intermediates which further reacted with ATMS to give **2a**. Since the reaction of **3a** with ATMS is very slow, the production of **2a** should be avoided by optimizing the addition order of the reactants and the catalyst.

In summary, we have demonstrated the direct allylation of *sec*-benzylic or *sec*-allylic alcohols with allyltrimethylsilane in the presence of a catalytic amount of heterogeneous acid, Sn-Mont by employing the proper addition order of the reactants and the catalyst under mild conditions. Sn-Mont provided the high activity for the allylation compared with those of the previously reported homogeneous catalysts. In all cases, the desired allylated products were obtained from a wide range of the alcohols in middle to

excellent yields. Furthermore, the catalyst could be reused without any loss of activity and selectivity.

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References and notes

- Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1–22; Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200–206; Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31–47.
- De, S. K.; Gibbs, R. A. *Tetrahedron Lett.* **2005**, *46*, 8345–8350.
- Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2006**, *71*, 8516–8522.

4. Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414–1416.
5. Kim, S. H.; Shin, C.; Pae, A. N.; Koh, H. Y.; Chang, M. H.; Chung, B. Y.; Cho, Y. S. *Synthesis-Stuttgart* **2004**, 1581–1584.
6. Rubin, M.; Gevorgyan, V. *Org. Lett.* **2001**, *3*, 2705–2707.
7. Kaur, G.; Kaushik, M.; Trehan, S. *Tetrahedron Lett.* **1997**, *38*, 2521–2524.
8. Kadam, S. T.; Lee, H.; Kim, S. S. *Appl. Organomet. Chem.* **2009**, *24*, 67–70.
9. Sharma, G. V. M.; Reddy, K. L.; Lakshmi, P. S.; Ravi, R.; Kunwar, A. C. *J. Org. Chem.* **2006**, *71*, 3967–3969.
10. Cella, J. A. *J. Org. Chem.* **1982**, *47*, 2125–2130.
11. Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006–6015.
12. Onaka, M.; Hosokawa, Y.; Higuchi, K.; Izumi, Y. *Tetrahedron Lett.* **1993**, *34*, 1171–1172.
13. Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2157–2164.
14. Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1237–1245; Onaka, M.; Ohno, R.; Kawai, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2689–2691.
15. Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016–2032.
16. Onaka, M.; Higuchi, K.; Nanami, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2638–2645.
17. Wang, J. C.; Masui, Y.; Watanabe, K.; Onaka, M. *Adv. Synth. Catal.* **2009**, *351*, 553–557.
18. Pinnavaia, T. J. *Science* **1983**, *220*, 365–371; Laszlo, P. *Science* **1987**, *235*, 1473–1477.
19. Kaneda, K. *Synlett* **2007**, 999–1015; Kaneda, K.; Ebitani, K.; Mizugaki, T.; Mori, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 981–1016.
20. Izumi, Y.; Onaka, M. *J. Mol. Catal.* **1992**, *74*, 35–42.
21. Wang, J. C.; Masui, Y.; Onaka, M. *Eur. J. Org. Chem.* **2010**, 1763–1771.
22. Wang, J. C.; Masui, Y.; Onaka, M. Submitted for publication.
23. Zareyee, D.; Karimi, B. *Tetrahedron Lett.* **2007**, *48*, 1277–1280; Azizi, N.; Yousefi, R.; Saidi, M. R. *J. Organomet. Chem.* **2006**, *691*, 817–820.
24. Two different addition orders of the reactants and the catalyst were investigated for the allylation of alcohols with allyltrimethylsilane as follows: Method A: Into a flask were placed Sn-Mont (20 mg, 3.8 mol %), alcohol (1 mmol), and CH₂Cl₂ (2 mL). The obtained solution was vigorously stirred and then allyltrimethylsilane (2 mmol) was added. After stirred for a time interval at rt, the solution was analyzed by GC. Method B: Into a flask were added Sn-Mont (20 mg, 3.8 mol %), CH₂Cl₂ (0.5 mL), and allyltrimethylsilane (2 mmol). Under stirring vigorously, alcohol (1 mmol) dissolved in CH₂Cl₂ (1.5 mL) was then introduced to the above reaction system dropwise (about 5 s per drop) using a syringe. After the completion of the reaction checked by GC, the catalyst was removed by filtration and the solvent was evaporated to give the crude product. Further purification was carried out with silica chromatography.
25. We performed the direct allylation of **1a** (1 mmol) with allyltrimethylsilane (2 mmol) in CH₂Cl₂ (2 mL) catalyzed by Amberlyst-15 (20 mg) at rt. In 1 h, the yields of the desired product are 3% for Method A and 69% for Method B, respectively.
26. The spectral data of the selected alkenes: 4-(4-methylphenyl)-4-phenyl-1-butene (**2c**), ¹H NMR (500 MHz, CDCl₃) δ 7.42–7.10 (m, 9H), 5.79 (dd, *J* = 6.7, 10.4, 17.1, 1H), 5.06 (ddd, *J* = 5.5, 9.5, 37.8, 2H), 4.04 (t, *J* = 7.9, 1H), 2.87 (dd, *J* = 6.7, 7.9, 2H), 2.36 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.8, 141.5, 137.0, 135.7, 129.1, 128.4, 127.9, 127.8, 126.1, 116.2, 50.8, 39.9, 20.9. HRMS calcd for C₁₇H₁₈ 222.1409, found 222.1423. 4-(4-Methoxyphenyl)-1-pentene (**2g**), ¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, *J* = 8.5, 2H), 6.84 (d, *J* = 8.5, 2H), 5.77–5.63 (m, 1H), 5.04–4.88 (m, 2H), 3.79 (s, 3H), 2.80–2.69 (m, 1H), 2.40–2.21 (m, 2H), 1.23 (d, *J* = 6.7, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.8, 139.2, 137.4, 127.9, 115.8, 113.7, 55.2, 42.8, 38.9, 21.7. HRMS calcd for C₁₂H₁₆O 176.1201, found 176.1203. 4-(4-Methoxyphenyl)-1-hexene (**2i**), ¹H NMR (500 MHz, CDCl₃) δ 7.10–7.03 (m, 2H), 6.88–6.81 (m, 2H), 5.75–5.57 (m, 1H), 5.06–4.83 (m, 2H), 3.78 (s, 3H), 2.46 (ddd, *J* = 5.8, 8.5, 11.6, 1H), 2.40–2.24 (m, 2H), 1.77–1.65 (m, 1H), 1.51 (tdd, *J* = 6.1, 10.7, 14.6, 1H), 0.76 (t, *J* = 7.3, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.8, 137.4, 137.3, 128.6, 115.6, 113.6, 55.1, 46.7, 41.0, 28.9, 11.9. HRMS calcd for C₁₃H₁₈O 190.1358, found 190.1364.