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Heterogeneous Allylsilylation of Aromatic and Aliphatic Alkenes Catalyzed by Proton-Exchanged Montmorillonite

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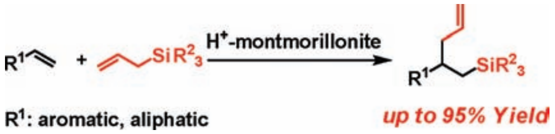
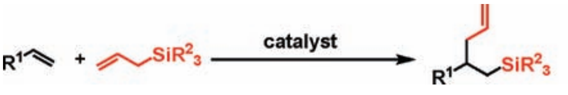
ABSTRACT



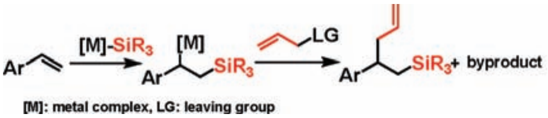
Allylsilylation of an alkene is the only known procedure to install both silyl and allyl groups onto a carbon−carbon double bond directly. Proton-exchanged montmorillonite showed excellent catalytic performances for the allylsilylation of alkenes. For example, the reaction of *p*-chlorostyrene with allyltrimethylsilane proceeded smoothly to afford the corresponding allylsilylated product in 95% yield. We also attempted to isolate the reaction intermediate on the montmorillonite surface to investigate the reaction mechanism.

Allylsilylation of an alkene is the only known procedure to install both silyl and allyl groups onto a carbon−carbon double bond directly (eq 1). Currently, there has been one report of allylsilylation; aluminum chloride-catalyzed reaction of aliphatic alkenes.[1,2] This route is promising because it has been reported to show excellent atom efficiency. However, to install silyl and allyl groups to styrenyl alkenes, stepwise procedures, which generate a large amount of byproducts, are still necessary (eq 2).[3]



(1)

In the $AlCl_3$-catalyzed allylsilylation of alkenes, the key step is acidic activation of allylsilanes to form cationic organosilane intermediates (Scheme 1, step 1). These intermediates then undergo nucleophilic addition of alkenes (step 2). After the C-Si bond formation, nucleophilic addition of an allylsilane to the β-position of the Si atom affords the desired allylsilylated product (step 3).[1]



(2)

In the first step of the reaction, it is important to avoid acidic activation of the alkene to increase the selectivity of the allylsilylated product, because the C−Si bond forms when the alkene acts as a nucleophile and the cationic organosilane acts as an electrophile (Scheme 1, step 2). Acidic activation of alkenes induces alkene oligomerization, especially with styrene derivatives. According to the hard and soft acids and bases (HSAB) principle, soft Lewis acids effectively activate alkenes, which act as soft bases.[4] Therefore, the use of a protonic acid as a hard acid is one means to avoid the

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(1) (a) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M.-Y.; Jung, I. N. *Organometallics* **1995**, *14*, 2361. (b) Jung, I. N.; Yoo, B. R. *Synlett* **1999**, 519.

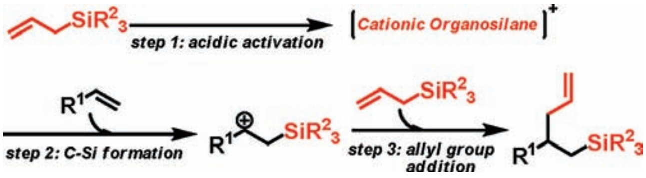
(2) For allylsilylation of alkynes, see: (a) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781. (b) Imamura, K.-i.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5339.

(3) Liepins, V.; Bäckvall, J.-E. *Chem. Commun.* **2001**, 265.

(4) For soft Lewis acid-catalyzed styrene dimerization, see: (a) Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2007**, *26*, 5961. (b) Peng, J.; Li, J.; Qiu, H.; Jiang, J.; Jiang, K.; Mao, J.; Lai, G. *J. Mol. Catal. A: Chem.* **2006**, *255*, 16.

10.1021/ol100228t

Scheme 1. Proposed Reaction Pathway of Allylsilylation of Alkene with Allylsilane

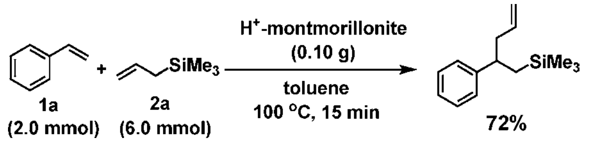


undesired activation of alkenes. Although allylsilane also has a C═C bond, the electrons on the allylsilane are not strongly delocalized due to the electron donating effect of Si atom. Actually, the calculated proton affinity value of allyltrimethylsilane (205.3 kcal/mol)[5] is ∼4 kcal/mol higher than reported proton affinity values of styrene.[6] The protonic acid may favor allylsilanes over the electron-delocalized styrene double bonds. If the active Si species forms from allylsilanes by the acidic activation on protonic acid site,[7] the catalytic allysilylation should be proceeded.

Herein, allylsilylation of alkenes with allylsilanes was examined using protonic acids. Among the protonic acids evaluated, proton-exchanged montmorillonite (H^+-montmorillonite)[8] was found to be an excellent catalyst for allylsilylation of both aromatic and aliphatic alkenes. In addition, we investigated the chemical reactivities of Si species on montmorillonite surface for mechanistic considerations.

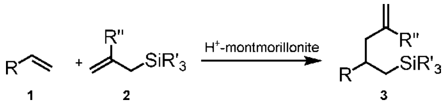
Scheme 2 shows the results of allylsilylation of styrene (**1a**) with allyltrimethylsilane (**2a**) using H^+-montmorillonite.

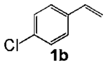
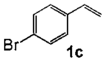
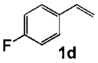
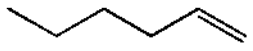
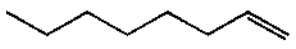
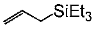
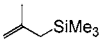
Scheme 2. Allylsilylation of Styrene (**1a**) with Allyltrimethylsilane (**2a**) using H^+-Montmorillonite



The desired allylsilylated product was obtained in 72% yield in the presence of H^+-montmorillonite. The scope of substrate in the H^+-montmorillonite-catalyzed allylsilylation is shown in Table 1. The allylsilylation occurred with *p*-chlorostyrene (**1b**) to give the corresponding product in 95% yield. The heterogeneous H^+-montmorillonite could be removed from the reaction mixture by simple filtration, and reused at least 3 times with retention of the high catalytic performance (89% yield for third reaction). Other *p*-substituted styrenes, such as *p*-bromo, and *p*-fuluoro styrenes, with **2a** also proceeded smoothly to afford the corresponding allylsilylated products in 87 and 91% yields, respectively. This is the first reports of the allylsilylation of styrene derivatives with allylsilane. Styrenes with electron-donating groups, such as *p*-methoxystyrene, did not work well as substrates. H^+-montmorillonite promotes allylsilylation of aliphatic alkenes with **2a** in good to excellent yields. In addition to **2a**, allyltriethylsilane and methallyltrimethylsilane were also found to be good allylsilylating reagents.

Table 1. Allylsilylation of Alkenes (**1**) with Allylsilanes (**2**) using H^+-Montmorillonite Catalyst[a]



alkene (**1**)	allylsilane (**2**)	time (min)	convn of **1** (%)[b]	yield of **3** (%)[b]
 **1b**	**2a**	120	99	95
 **1c**	**2a**	30	96	87[c]
 **1d**	**2a**	60	98	91
 **1e**	**2a**	60	97[d]	88[e]
 **1f**	**2a**	60	99[d]	55[e]
1b	 **2b**	30	99	61
1b	 **2c**	30	99	86

[a] Reaction conditions: **1** (1.0 mmol), **2** (3.0 mmol), H^+-montmorillonite (0.10 g), toluene (1 mL), 100 °C. Around 15% of **2a** was dimerized to form [2-(2-propenyl)-1,3-propanediyl]-bis(trimethylsilane). For aliphatic alkenes, **1** (3.0 mmol) and **2** (1.0 mmol) were used. [b] Determined by GC using internal standard technique. Calibration curve was made by use of isolated products. Yield was based on alkene **1**. [c] At 80 °C. [d] Conversion of allylsilane **2a** was shown. [e] Reaction carried out at 60 °C. Yield was based on allylsilane **2a**.

Catalytic activity of other heterogeneous and homogeneous protonic acids was evaluated in the reaction of **1b** with **2a**. The product yield using commercially available montK10 (7.2%) was lower than that for the H^+-montmorillonite. Proton-exchanged zeolites, such as ZSM-5 and mordenite, were less active (<1%) due to restricted pore size. The product yield was very low with strong acids, Amberlyst, Nafion, trifilic acid, *p*-toluenesulfonic acid, and H_2SO_4. Reported acid strength of H^+-montmorillonite ($\Delta H = 111$ kJ mol^{-1})[8] is lower than those of other zeolites (122−160 kJ mol^{-1}). It can be expected that suitable acid strength is necessary for the allylsilylation.[8] The product did not form

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(5) The proton affinity was calculated using AM1 method, see: Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.

(6) Kafafi, S. A.; Meot-Ner, M.; Liebman, J. F. *Struct. Chem.* **1989**, *1*, 101.

(7) Onaka and co-workers proposed the formation of cationic silanes at Brönsted acid sites, see: (a) Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016. (b) Wang, J.; Masui, Y.; Watanabe, K.; Onaka, M. *Adv. Synth. Catal.* **2009**, *351*, 553.

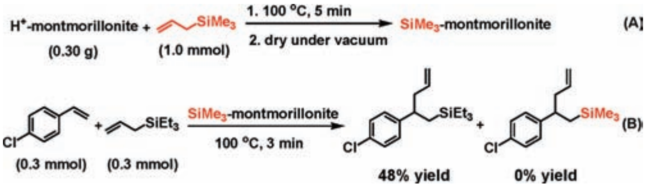
(8) (a) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605. (b) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006.

when using sodium-exchanged montmorillonite. This result shows H^+ on the montmorillonite surface acts as catalytically active site.

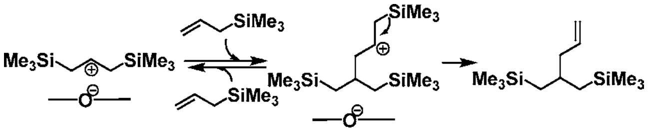
To estimate the H^+-montmorillonite-catalyzed reaction pathway, we examined the reaction of cyclohexene with **2a**. The ^1H NMR study revealed the formation of allylsilylated product with exclusively trans allyl and silyl groups. There were no other major products converted from cyclohexene. This result suggests stepwise addition of silyl and allyl groups of the allylsilane to alkenes.[1]

Jung and co-workers proposed two reaction mechanisms for the $AlCl_3$-catalyzed allylsilylation of alkenes.[1] The main difference between the two mechanisms involves the structure of the cationic silane intermediate: (i) trimethylsilyl cation (Si^+Me_3)[1b] and (ii) 1,3-disilylpropyl cation ($SiCH_2C^+HCH_2Si$).[1a] We attempted to isolate the silyl species on the montmorillonite surface in an effort to examine its reactivity. After the treatment of H^+-montmorillonite with **2a**, the obtained solid was washed with solvent, dried under vacuum, and subjected to solid-state NMR analyses (Supporting Information). NMR results revealed the formation of only trimethylsiloxy species ($Me_3Si{-}O{-}Si$(surface)) on the montmorillonite (Scheme 3A).[9] The reaction of **1b** with allyltri*ethyl*silane was then carried out using the treated montmorillonite ($SiMe_3$-montmorillonite). If the trimethylsiloxy species is an active cationic intermediate, the allylsilylated product is expected to contain a trimethylsilyl ($SiMe_3$) group. However, the reaction afforded an allylsilylated product only bearing a triethylsilyl ($SiEt_3$) group (Scheme 3B). This suggests that the surface $SiMe_3$ is not an active species in the allylsilylation of alkenes.[10]

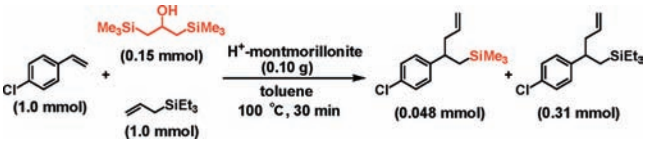
Scheme 3. (A) Formation of $SiMe_3$ Species on Montmorillonite Surface and (B) Allylsilylation using the $SiMe_3$-Montmorillonite



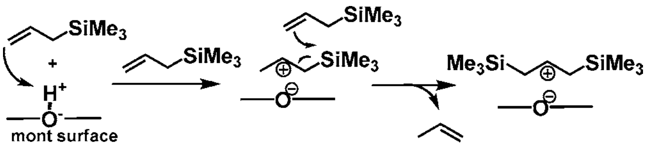
Scheme 4. Estimated Pathway for Dimerization of **2a** on Montmorillonite Surface



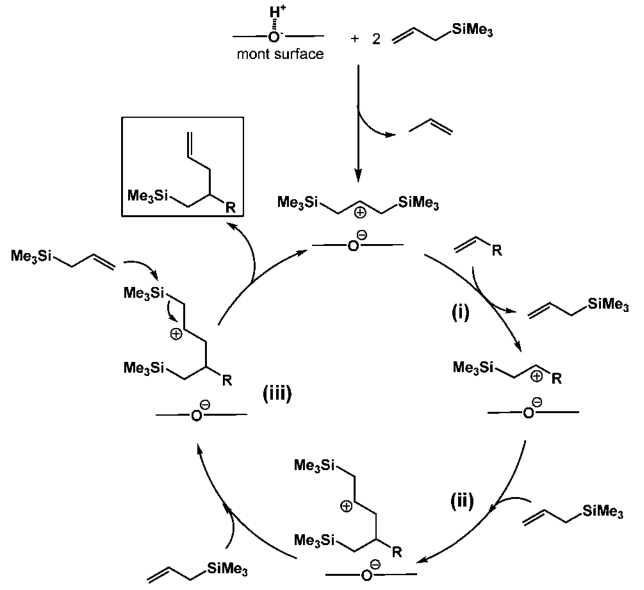
Scheme 5. Allylsilylation of **1b** with Allyltriethylsilane in the Presence of 1,3-Disilylpropan-2-ol



Scheme 6. Possible Formation Pathway of 1,3-Disilylpropyl Cation from **2a** and H^+-Montmorillonite



Scheme 7. Proposed Reaction Mechanism of H^+-Montmorillonite-Catalyzed Allylsilylation



During the treatment of H^+-montmorillonite with **2a**, a dimerization of **2a** took place. The dimerized product was thought to be obtained from the reaction of the 1,3-disilylpropyl cation with **2a** (Scheme 4). To confirm the participation of the 1,3-disilylpropyl cation in the catalytic allylsilylation of alkenes, reaction of **1b** with allyltri*ethyl*silane was examined in the presence of 1,3-di(trimethylsilyl)propan-2-ol, a precursor to the 1,3-disilylpropyl cation.

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[9] Signals at −0.057 ppm (^{13}C NMR) and −13.68 ppm (^{29}Si NMR) were observed. These signals are assignable to Me_3Si-O-Si(surface) species, see Supporting Information. See also: (a) Haukka, S.; Root, A. *J. Phys. Chem.* **1994**, *98*, 1695. (b) Derouet, D.; Thuc, C. N. H. *J. Appl. Polym. Sci.* **2008**, *109*, 2113.

[10] ^{29}Si NMR shift of cationic trimethylsilyl species ($MeSi^+$) were generally appeared at down field (30−40 ppm) compared with methoxysilyl species (∼14 ppm), see: Iley, J.; Bassindale, A. R.; Patel, P. *J. Chem. Soc., Perkin Trans.* **1984**, 77. This fact explains the inactivity of the Me_3Si species on montmorillonite surface.

After the reaction, formation of allylsilylated product with $SiMe_3$ was observed (Scheme 5). These results suggest that the 1,3-disilylpropyl cation forms from allylsilane on the montmorillonite surface and acts as a reaction intermediate. The possible pathway of formation of the 1,3-disilylpropyl cation from **2a** and H^+- montmorillonite is shown in Scheme 6. Formation of propylene by reaction of allylsilane with H^+-montmorillonite also supports this pathway. The 1,3-disilylpropyl cation might be easily decomposed to **2a** and the inactive $SiMe_3$ species, which can be detected by the solid-state NMR analyses.[11]

The catalytic cycle for the allylsilylation of alkenes using H^+-montmorillonite is proposed, as shown in Scheme 7; (i) nucleophilic attack of an alkene to disilyl cation to form allylsilane and a secondary carbocation intermediate stabilized by the silyl group at the β-position, (ii) nucleophilic attack of an allylsilane to the intermediate to form a new C−C bond, and (iii) formation of allylsilylated product and disilyl cation by nucleophilic addition of another allylsilane.

In summary, proton-exchanged montmorillonite was found to be an excellent catalyst for the allylsilylation of aromatic and aliphatic alkenes. The corresponding allylsilylated products were obtained in up to 95% yield. The formation of a disilyl cationic intermediate on the montmorillonite surface was proposed in the catalytic cycle. Investigations of a detailed reaction mechanism and spectroscopic analysis of the active intermediate are currently underway.

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Supporting Information Available: Proton affinity calculation, experimental procedures, product characterizations, and solid-state NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Because of the highly reusability of H^+-montmorillonite, the inactive $SiMe_3$ species may form during solid-state NMR measurment or pretreatment for the NMR analysis.