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SOLID ACID-CATALYZED ALLYLATION OF ACETALS AND CARBONYL COMPOUNDS WITH ALLYLIC SILANES

Motomitsu KAWAI, Makoto ONAKA,* and Yusuke IZUMI
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

Acetals and carbonyl compounds are allylated with allylic silanes in good yields in the presence of a catalytic amount of clay montmorillonite.

The addition of allylic silanes to electrophiles is one of the most useful C-C bond formation reactions.[1)] Reactions of allylic silanes with carbonyl compounds are promoted by a stoichiometric amount of Lewis acids such as $TiCl_4$,[2)] $BF_3 \cdot OEt_2$,[2)] and $AlCl_3$[3)] or by a catalytic amount of $^nBu_4NF$[4)] and Ph_2BOTf.[5)] In the case of acetals as electrophiles, a catalytic amount of Me_3SiOTf,[6)] Me_3SiI,[7)] and Ph_3CClO_4[5)] is also used as a promoter. All of the promoters mentioned above operate in a homogeneous system. We have found that the allylation of acetals, aldehydes, and ketones with allylic silanes can be catalyzed by solid acids in a heterogeneous system. This new method is characterized by rapid promotion of the reactions and easy separation of the acid catalyst from the organic products.

Table 1 shows the results of the reaction of octanal dimethyl acetal (1) with allyltrimethylsilane (2a) in the presence of various solid acids. By using aluminium cation or proton exchanged montmorillonite (Al-Mont, H-Mont, Mont-K10) homoallyl ether (3) was obtained in high yield and no by-products were observed (Entries 2,3,4). Montmorillonites are known to be thermally less stable than zeolites and silica-alumina.[8)] Thus the drying conditions of the montmorillonites greatly affected the yield of 3.[9)]

Some examples of various reactants are listed in Table 2. The reaction of prenylsilane (2b) took place regioselectively at the γ-carbon in a similar manner to the previously reported results[1)] (Entry 2). It should be noted that Al-Mont and Mont-K10 can also catalyze the reaction of aldehydes and ketones with 2a, while Me_3SiOTf, Me_3SiI, and Ph_3CClO_4 did not catalyze the reactions.[5-7)] 4-t-Butylcyclohexanone and its acetal were predominantly allylated from the equatorial direction.[10)]

As a work-up procedure, only filtration of the reaction mixture is enough for separation of the acid catalyst. As the treatment with water is unnecessary, the present method converts aldehydes and ketones to the corresponding homoallyl silyl ethers.

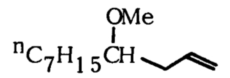
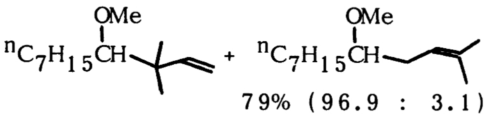
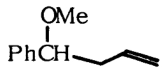
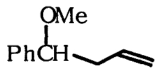
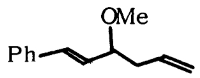
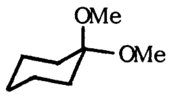
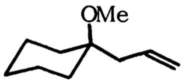
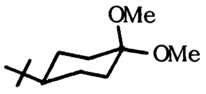
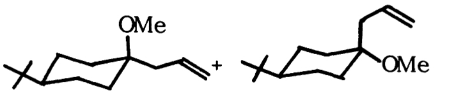
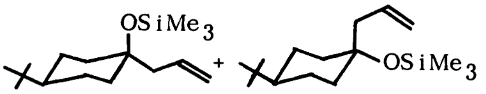
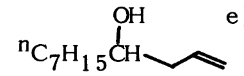
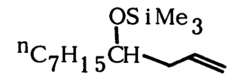
$$\underset{\underline{1}}{{}^{n}C_7H_{15}CH(OMe)_2} \quad + \quad \underset{\underline{2a}}{CH_2{=}CHCH_2SiMe_3} \quad \longrightarrow \quad \underset{\underline{3}}{{}^{n}C_7H_{15}CH(OMe)CH_2CH{=}CH_2}$$

Table 1. The reaction of octanal dimethyl acetal (1) with allyltrimethylsilane catalyzed by solid acid[a)]

Entry	Solid acid	Drying method of solid acid[b)]	Conditions Temp/°C	Time/h	Mol%[c)] of homoallyl ether	Mol%[c)] of unreacted acetal
1	Na-Mont[d)]	A	0	0.5	0	86
2	Al-Mont[e)]	A	0	0.5	95	1
3	H-Mont[f)]	A	0	0.5	87	11
4	Mont-K10[g)]	A	0	0.5	85	14
5	Na-TSM[h)]	A	0	0.5	0	86
6	Al-TSM[i)]	A	0	0.5	48	44
7	HY[j)]	B	25	2	43	30
8	CaY[k)]	B	25	2	30	30
9	Silica-Alumina[l)]	B	25	2	58	16
10	γ-Alumina[m)]	B	25	2	0	89
11	Amberlyst-15[n)]	C	25	2	47	44
12	Nafion-117[o)]	-	25	2	51	33

a) 1 : 1 mmol, 2a : 1 mmol, Solid acid : 0.2 g, CH_2Cl_2 : 4 ml. b) A : Pre-dried at 25 °C/0.5 Torr for 16 h and stored in a desicator, and then dried at 120 °C/0.5 Torr for 3 h in a reaction vessel. B : Pre-dried at 400 °C in air for 3 h and stored in a desicator, and then dried at 350 °C/0.5 Torr for 10 min in a reaction vessel. C : Washed with MeOH and dried at 25 °C/0.5 Torr. c) Determined by GLC using an internal standard. d) Purified Montmorillonite "Kunipia F" (Kunimine Industries Co.). e) Aluminium cation exchanged "Kunipia F."[11)] f) Proton exchanged "Kunipia F."[12)] g) Commercial acid catalyst, Montmorillonite "K10" (Süd Chemie A.G.). h) Fluoro tetrasilisic mica (Topy Industries Co.). i) Aluminium cation exchanged Na-TSM. j) Proton exchanged Y type zeolite. k) Calcium cation exchanged Y type zeolite. l) A reference catalyst from the Catalysis Society of Japan : JRC-SAL-2 (Al_2O_3 13.75%). m) Woelm-200-neutral, activity super I. n) Ion exchange resin (4.9 mequiv./g, Rhom & Haas). o) Ion exchange resin (1 mequiv./g, Du Pont). 0.1 g of Nafion-117 was used.

Table 2. The reaction of acetals or carbonyl compounds catalyzed by solid acids$^{a)}$

Entry	Acetal or carbonyl compound	Allylic silane	Solid acid (Amount/g)	Reaction conditions Temp/°C (Time/h)	Products/Yield$^{b)}$
1	${}^{n}C_7H_{15}CH(OMe)_2$	2a	Mont-K10 (0.2)	0 (0.5)	 90%
2	${}^{n}C_7H_{15}CH(OMe)_2$	2b$^{c)}$	Mont-K10 (0.2)	0 (0.5), and 25 (12)	 79% (96.9 : 3.1)
3	$PhCH(OMe)_2$	2a	Mont-K10 (0.2)	0 (0.5)	 84%
4	$PhCH(OMe)_2$	2a	Al-Mont (0.2)	0 (0.5)	 95%
5	$PhCH{=}CHCH(OMe)_2$	2a	Mont-K10 (0.02)	-78 (0.5), 0 (0.5), and 25 (0.5)	 80%
6		2a	Mont-K10 (0.2)	0 (0.5)	 73%
7		2a	Mont-K10 (0.2)	0 (0.5)	 88% (95 : 5)
8		2a	Al-Mont (0.2)	-30 (0.1), and -15 (3)	 80% (87 : 13)
9	${}^{n}C_7H_{15}CHO$	2a$^{d)}$	Mont-K10 (0.05)	-78 (0.5), 0 (0.5), and 25 (0.5)	 e) 63%
10	${}^{n}C_7H_{15}CHO$	2a$^{d)}$	Al-Mont (0.1)	-30 (0.5) and -12 (4)	 57%

(continued)

a) Acetal or carbonyl compound (1 mmol), Allyltrimethylsilane (1.3 mmol), Solid acid (0.2 g), CH_2Cl_2 (4 ml).
b) Isolated yield after distillation.
c) 2 mmol of prenylsilane, which was contaminated with 4.5% of 1,1-dimethyl-2-propenyltrimethylsilane ($CH_2=CHCMe_2SiMe_3$), was used.
d) 2.5 mmol of allyltrimethylsilane was used.
e) A product after hydrolysis.

A typical experimental procedure is described for the reaction of octanal dimethyl acetal with allyltrimethylsilane (Entry 1 in Table 2) : A suspension of Mont-K10 (0.2 g, dried by the method A in Table 1) in CH_2Cl_2 (2 ml) was cooled at 0 ^{o}C under nitrogen atmosphere, and a mixture of octanal dimethyl acetal (1.0 mmol) and allyltrimethylsilane (1.3 mmol) in CH_2Cl_2 (2 ml) was added. The mixture was stirred for 0.5 h and then ether was added. The solid acid was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled. 4-Methoxy-1-undecene (3) was obtained in 90% yield.

The aldol reactions of silyl enol ethers with aldehydes were also catalyzed by solid acids.

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References

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6) T. Tsunoda, M. Suzuki, and R. Noyori, Tetrahedron Lett., 1980, 71.
7) H. Sakurai, K. Sasaki, and A. Hosomi, Tetrahedron Lett., 1981, 745.
8) On heat treatment at 300 ^{o}C, H- and Al- montmorillonites lose the bulk of the cation exchange capacity, see Ref. 12.
9) Without drying treatment, Mont-K10 afforded 3 in 23% yield under the reaction conditions in Table 1.
10) Stereo-selective allylation of 4-t-butylcyclohexanone was performed with trialkylallyltins : Y. Naruta, S. Ushida, and K. Maruyama, Chem. Lett., 1979, 919. In the case of 4-t-butylcyclohexanone dimethyl acetal and allyltrimethylsilane, see Ref. 6.
11) Aluminium ion exchange was performed by Ballantine's method : J. A. Ballantine, J. H. Purnell, M. Rayanakorn, and K. J. Williams, J. Mol. Catal., 30, 373 (1985).
12) Proton exchange was performed by Coleman's method : A. G. Mathers, S. B. Weed, and N. T. Coleman, "Clays and Clay Minerals," ed by W. O. Milligan, Natl. Acad. Sci., Natl. Research Council, Washington, (1955), Publ. 395, p. 403.

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