

AgOAc-Catalyzed Aldehyde Allylation Using Allyldimethyl(2-pyridyl)silane

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(Received July 24, 2002; CL-020608)

Silver salts having relatively strong Ag–O bond were found to promote the allylation of aldehydes with allyldimethyl(2-pyridyl)silane. Catalytic allylation is also possible when AgOAc was employed. A novel cooperative activation of allyl(2-pyridyl)silane has been implicated from several control experiments.

The allylation of carbonyl compounds using allylsilanes is a powerful and important C–C bond-forming reaction.¹ Lewis acid-promoted reaction of allyltrimethylsilanes with aldehydes (Sakurai–Hosomi reaction), where Lewis acids activate carbonyl groups toward allylsilane addition, is amongst the most famous and extensively used in organic synthesis.^{1,2} Alternative to this methodology, Lewis base activation of allylsilanes is also known.³ Hosomi and Sakurai first reported that tetrabutylammonium fluoride (TBAF) could be used as a catalyst for the addition of allyltrimethylsilane to aldehydes and ketones.⁴ After this benchmark achievement, many other Lewis base promoters have been devised mostly using trichloro-, trifluoro-, and trialkoxy(allyl)silanes.^{5–14}

Recently, we have developed dimethyl(2-pyridyl)silyl (2-PyMe₂Si) group as a unique silyl group that bears catalyst- or reagent-directing pyridyl group directly on silicon.¹⁵ We envisaged that this group might open new possibility in allylsilane chemistry especially in Lewis base activation of allylsilane without any electronegative heteroatom on silicon.

Thus, we first searched for appropriate additive for the allylation of benzaldehyde using allyldimethyl(2-pyridyl)silane (**1**) in THF at 60 °C (Table 1).¹⁶ The addition of TBAF resulted in relatively low efficiency (35%). Although KF and TASF (tris(diethylamino)sulfonium difluorotrimethylsilicate)⁵ did not give **3** at all, we found that AgF¹⁷ is a superior additive for this allylation (53%). This drove us for further investigation on silver salts, and we found that the addition of silver oxides (AgO, 35%; Ag₂O, 74%) furnished **3** in moderate to good yields. Interestingly, in contrast to Ag₂O, Ag₂S did not promote the reaction, indicating

Table 1. Effect of additive in the allylation of **2** using **1**

entry	additive	yield (%)	entry	additive	yield (%)
1	none	0	9	AgOAc	76
2	TBAF	35	10	AgOTs	21
3	TASF	0	11	AgOTf	0
4	KF	0	12	AgBF ₄	0
5	AgF	53	13	CuO	0
6	AgO	35	14	Cu ₂ O	41
7	Ag ₂ O	74	15	Au ₂ O ₃	9
8	Ag ₂ S	0			

that Ag–O bond might be a key for activation. Further search on silver salts having Ag–O bond¹⁸ resulted in the discovery of AgOAc¹⁹ as an optimal promoter for this allylation (76%). Other silver salts bearing weaker Ag–O bond or cationic silver atom were found to be ineffective. Other metal oxides such as CuO, Cu₂O, and Au₂O₃ resulted in lower efficiency.

With AgOAc as an optimal promoter, we next investigated the effect of solvent and found that THF (76%) and toluene (59%) are good solvents for this allylation (Table 2). Moreover, the allylation occurred even with a catalytic amount (10 mol%) of AgOAc in THF at 60 °C giving **3** in 66% yield. The use of toluene gave better result under catalytic conditions when the reaction was carried out at 100 °C (85%).

Table 2. Effects of solvent and temperature

entry	AgOAc (equiv)	solvent	temp (°C)	yield (%)
1	1.2	DMF	60	16
2	1.2	N,N-dimethylacetamide	60	25
3	1.2	1,3-dimethylimidazolidinone	60	29
4	1.2	EtOAc	60	29
5	1.2	THF	60	76
6	1.2	dimethoxyethane	60	44
7	1.2	dichloroethane	60	43
8	1.2	toluene	60	59
9	1.2	toluene	100	89
10	0.1	THF	60	66
11	0.1	toluene	100	85

By using these catalytic conditions (10 mol% AgOAc, toluene, 100 °C), the scope and limitations of the present allylation were investigated with various carbonyl compounds (Table 3).²⁰ While the allylation proceeded smoothly with aromatic aldehydes, the allylation was sluggish with α , β -unsaturated aldehydes or totally ineffective with aliphatic

Table 3. AgOAc-catalyzed allylation of carbonyl compounds

entry	carbonyl compound	yield (%)
1	C ₆ H ₅ CHO	85
2	<i>p</i> -CH ₃ C ₆ H ₄ CHO	45
3	<i>p</i> -ClC ₆ H ₄ CHO	59
4	(<i>E</i>)-C ₆ H ₅ CH=CHCHO	19
5	C ₆ H ₅ CH ₂ CH ₂ CHO	0
6	acetophenone	0

aldehydes and ketones.

Although the allylation protocol described herein is somewhat lower in efficacy and narrower in scope compared with other allylation methods at this stage, the discovery of a new class of promoter may be interesting for exploring a new mode of activation in allylsilane chemistry¹ especially for the activation of triorgano(allyl)silanes, which is relatively unexplored in Lewis base activation.²¹

Based on our finding that some silver salts having relatively strong Ag–O bond can function as promoters for allylation using allyl(2-pyridyl)silane, we are currently assuming that the oxygen atom in those silver salts is acting as a Lewis basic donor for silicon atom, whereas the silver atom is acting as a Lewis acidic acceptor for pyridyl group and brings the Lewis basic oxygen atom proximate to silicon (Figure 1). Such simultaneous and cooperative interactions should result in the activation of **1** toward allylation. Although, at this stage, this is speculative with no direct evidence, some control experiments are in line with this presumption: (i) silver salts with weak Ag–O bond or without Ag–O bond exhibit low or no promoting effect; and (ii) displacement of pyridyl group with phenyl or methyl group in **1** caused no allylation in the presence of AgOAc (eq 1).

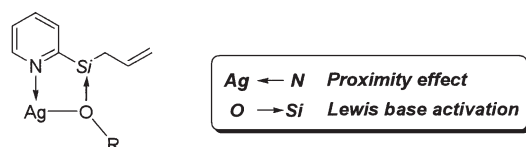
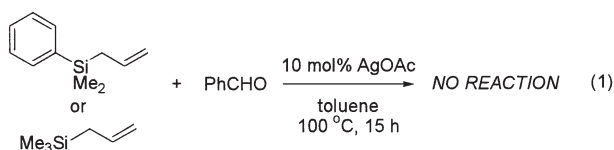


Figure 1. A plausible activation mode of **1** with silver salts.



In summary, some silver salts having relatively strong Ag–O bond were found to promote the allylation of aldehydes with allyldimethyl(2-pyridyl)silane. This procedure should not only be used as a removal protocol in our recently demonstrating removable directing group strategy¹⁵ and phase tag strategy²² using 2-PyMe₂Si group, but also open new possibility in allylsilane chemistry.

References and Notes

- H. Sakurai, *Pure Appl. Chem.*, **54**, 1 (1982); A. Hosomi, *Acc. Chem. Res.*, **21**, 200 (1988); I. Fleming, J. Dunoguès, and R. Smithers, *Org. React.*, **37**, 57 (1989).
- A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, **1976**, 1295.
- H. Sakurai, *Synlett*, **1989**, 1; C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, *Chem. Rev.*, **93**, 1371 (1993).
- A. Hosomi, A. Shirahata, and H. Sakurai, *Tetrahedron Lett.*, **1978**, 3043.
- TASF and *t*-BuOK for CF₂=CHCH₂SiMe₂Ph: T. Hiyama, M. Obayashi, and M. Sawahata, *Tetrahedron Lett.*, **24**, 4113 (1983).
- CsF for CH₂=CHCH(NR₂)SiMe₃: R. J. P. Corriu, V. Huynh, and J. J. E. Moreau, *J. Organomet. Chem.*, **259**, 283 (1983).
- Pentacoordinate allylsilicate: G. Cerveau, C. Chuit, R. J. P. Corriu, and C. Reye, *J. Organomet. Chem.*, **328**, C17 (1987); M. Kira, K. Sato, and H. Sakurai, *J. Am. Chem. Soc.*, **110**, 4599 (1988); A. Hosomi, S. Kohra, K. Ogata, T. Yanagi, and Y. Tominaga, *J. Org. Chem.*, **55**, 2415 (1990).
- Formamides and phosphoramides for CH₂=CHCH₂SiCl₃: S. Kobayashi and K. Nishio, *J. Org. Chem.*, **59**, 6620 (1994).
- Ureas for CH₂=CHCH₂SiCl₃: I. Chataigner, U. Piarulli, and C. Gennari, *Tetrahedron Lett.*, **40**, 3633 (1999).
- Chiral formamides for CH₂=CHCH₂SiCl₃: K. Iseki, S. Mizuno, Y. Kuroki, and Y. Kobayashi, *Tetrahedron*, **55**, 977 (1999).
- Chiral phosphoramides for CH₂=CHCH₂SiCl₃: S. E. Denmark, D. M. Coe, N. E. Pratt, and B. D. Griedel, *J. Org. Chem.*, **59**, 6161 (1994); K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto, and Y. Kobayashi, *Tetrahedron*, **53**, 3513 (1997); J. Hellwig, T. Belser, and J. F. K. Müller, *Tetrahedron Lett.*, **42**, 5417 (2001); S. E. Denmark and J. Fu, *J. Am. Chem. Soc.*, **123**, 9488 (2001).
- Chiral amines for CH₂=CHCH₂SiCl₃: R. M. Angell, A. G. M. Barrett, D. C. Braddock, S. Swallow, and B. D. Vickery, *Chem. Commun.*, **1997**, 919.
- Chiral amine *N*-oxides for CH₂=CHCH₂SiCl₃: M. Nakajima, M. Saito, M. Shiro, and S. Hashimoto, *J. Am. Chem. Soc.*, **120**, 6419 (1998); A. V. Malkov, M. Orsini, D. Pernazza, K. W. Muir, V. Langer, P. Meghani, and P. Kočovský, *Org. Lett.*, **4**, 1047 (2002); T. Shimada, A. Kina, S. Ikeda, and T. Hayashi, *Org. Lett.*, **4**, 2799 (2002).
- Very recently Shibasaki has developed an efficient catalytic allylation using allyltrimethoxysilane. S. Yamasaki, K. Fujii, R. Wada, M. Kanai, and M. Shibasaki, *J. Am. Chem. Soc.*, **124**, 6536 (2002).
- K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, and J. Yoshida, *J. Am. Chem. Soc.*, **122**, 12013 (2000); K. Itami, K. Mitsudo, and J. Yoshida, *Angew. Chem., Int. Ed.*, **40**, 2337 (2001); K. Itami, T. Nokami, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 5600 (2001); K. Itami, T. Koike, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 6957 (2001); K. Itami, T. Kamei, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 8773 (2001); K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei, and J. Yoshida, *J. Am. Chem. Soc.*, **123**, 11577 (2001); K. Itami, K. Mitsudo, T. Nokami, T. Kamei, T. Koike, and J. Yoshida, *J. Organomet. Chem.*, **653**, 105 (2002).
- Lewis acid methodology may not be efficient for allyl(2-pyridyl)silane because pyridyl-to-metal coordination could compete with carbonyl activation. In such circumstance, excess Lewis acid may be required. K. Itami, T. Nokami, and J. Yoshida, *Adv. Synth. Catal.*, **344**, 441 (2002).
- Yamamoto has reported that *p*-Tol-BINAP·AgF complex is a good chiral catalyst for aldehyde allylation using allyltrimethoxysilanes. A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, and H. Yamamoto, *Angew. Chem., Int. Ed.*, **38**, 3701 (1999).
- AgOTf was found to be beneficial as an additive in Ph₃PO-promoted aldehyde allylation using CH₂=CHCH₂SiCl₃. J. D. Short, S. Attenoux, and D. J. Berrisford, *Tetrahedron Lett.*, **38**, 2351 (1997).
- Zn/AgOAc-promoted aldehyde allylation: T. Ishihara, S. Miwata-shi, M. Kuroboshi, and K. Utimoto, *Tetrahedron Lett.*, **32**, 1069 (1991); AgOAc-promoted ring enlargement of silacyclobutane: K. Matsumoto, K. Miura, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **32**, 6383 (1991).
- Typical procedure: A suspension of benzaldehyde (1.0 mmol), **1** (1.2 mmol), and AgOAc (0.1 mmol) in toluene (2 mL) was stirred at 100 °C for 15 h under argon. After being cooled to room temperature, 5% HF aq CH₃CN (4 mL) was added to the reaction mixture. Extractive work-up and subsequent silica gel chromatography afforded 1-phenyl-3-buten-1-ol (**3**) (0.85 mmol, 85%).
- N. Asao, A. Shibato, Y. Itagaki, F. Jourda, and K. Maruoka, *Tetrahedron Lett.*, **39**, 3177 (1998); Z. Wang, P. Kisanga, and J. G. Verkade, *J. Org. Chem.*, **64**, 6459 (1999).
- J. Yoshida, K. Itami, K. Mitsudo, and S. Suga, *Tetrahedron Lett.*, **40**, 3403 (1999); J. Yoshida and K. Itami, *Yuki Gosei Kagaku Kyokaiishi*, **59**, 1086 (2001).