Copper(I) Iodide-Promoted Allylation of Allyl- and Vinyl-silanes Assisted by Intramolecular-Coordination

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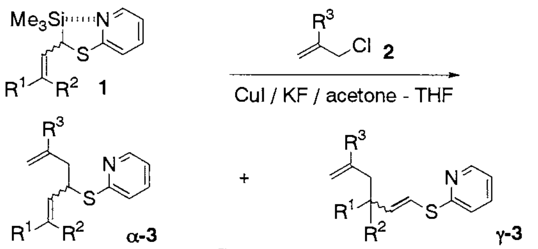
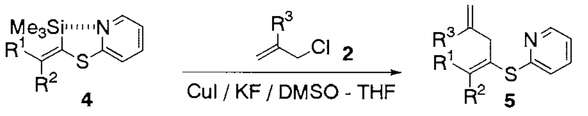
The allylation products, 1-(2-pyridylthio)alk-1,5-dienes, were produced regioselectively when 1-(2-pyridylthio)-1-(trimethylsilyl)alk-2-enes were treated with allylic chlorides in the presence of CuI and KF. The similar reaction of 1-(2-pyridylthio)-1-(trimethylsilyl)alk-1-enes with allylic chlorides produced the 1,4-dienes with complete retention of configuration.

The copper(I) salt promoted reactions of group 14 organometallic compounds are of special interest because of their mild reaction conditions as synthetic methods and undefined reaction mechanism. Although a number of copper(I)-promoted reactions using organotin compounds have been reported,[1] until recently organosilicon compounds have been scarcely employed in such reactions except for the pioneering work by Kumada and his co-workers. They reported that the self-coupling of hypercoordinate vinylsilicates proceeded when being heated in the presence of CuCl.[2] Recently several self- and cross-coupling reactions of organosilicon compounds have been investigated. Urata and Fuchikami reported that the trifluoromethylation of iodobenzene derivatives was achieved by making use of a CF_3SiR_3/KF/CuI system.[3] Lermontov et al. reported the CuCl-promoted phenylation of 1-trimethylsilyl-1-alkynes with triphenylbismuth difluoride in which alkynylcopper(I) was suggested to be an active species.[4] Hosomi and co-worker also showed that the acylation of alkynylsilane proceeded by heating with acyl halides and CuCl in DMI.[5] They confirmed the alkynyl group transfer from silicon to copper by isolation of the intermediary alkynylcopper(I) species. Copper(I) salts also effect the homo-coupling reactions of aryl-, alkenyl-, and alkynyl-substituted chloro- or fluoro-silanes.[6,7] As for the cross-coupling, the reactions of arylsilanes with aryl halides[8] and alkynylsilanes with 1-chloroalkynes[9] have been reported.

In the course of our study on the carbon-carbon bond forming reaction using group 14 organometallics, we found that vinylstannanes react with allylic halides in the presence of CuI.[10] Although the similar reaction of allylstannanes with allylic halides was unsuccessful, the substitution of a 2-pyridylthio group at a position α to tin facilitated the allylation, and 1,5-dienes were produced with high regioselectivity.[11] It is of interest whether such substitution is effective for the allylation of relatively unreactive organosilicon compounds. Then we studied the copper(I) promoted allylation of allyl- and viny-silanes possessing a 2-pyridylthio group (Schemes 1 and 2).



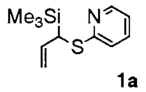
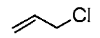
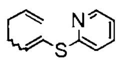
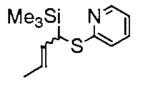
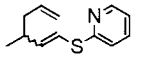
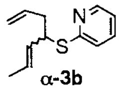
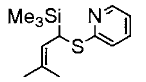
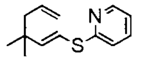
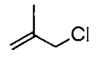
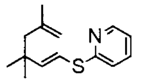
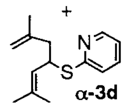
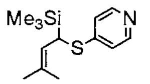
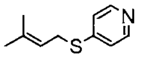
Scheme 1.



Scheme 2.

Although the CuI promoted reaction of 3-methyl-1-(2-pyridylthio)-1-(trimethylsilyl)but-2-ene (**1c**) with methallyl chloride **2b** in DMSO-THF did not proceed and the starting allylsilane was recovered (82%), the allylation product **3d** was obtained in 68% yield with good regioselectivity (α : γ = 10 : 90) by the combined use of KF. It was confirmed that no allylation product was produced in the absence of CuI. The reaction also proceeded in acetone-THF to afford **3d** in better yield (71%) without formation of

Table 1. Allylation of allylsilanes 1[a]

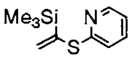
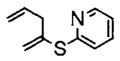
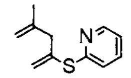
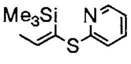
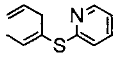
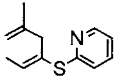
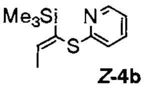
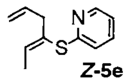
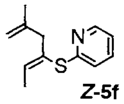
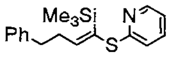
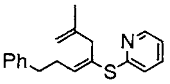
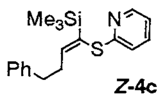
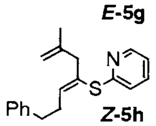
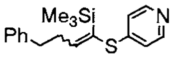
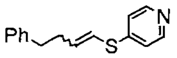
Entry	Allylsilane 1	Allylic Halide 2	Product (Yield / %)
1[b]	 **1a**	 **2a**	 (67) γ-**3a** (*E* : *Z* = 90 : 10)
2[b]	 **1b** (*E* : *Z* = 88 : 12)	**2a**	 (80) γ-**3b** (*E* : *Z* = 30 : 70) +  (1)[c] α-**3b**
3[d]	 **1c**	**2a**	 (58) γ-**3c** (*E* : *Z* = >99 : <1)
4[b,d]	**1c**	 **2b**	 (66) γ-**3d** (*E* : *Z* = >99 : <1) +  (5) α-**3d**
5[d]	 **6**	**2b**	 (80) **8**

[a] All reactions were performed with a similar procedure as described in the text using acetone as a cosolvent. [b] The products were obtained as a mixture of isomers. The yields and ratio of stereoisomers were determined by NMR spectroscopy. [c] The ratio of stereoisomers was not determined. [d] The reaction was quenched after stirring for 30 h.

the adduct with acetone. Using the optimized conditions, the reactions of several allylsilanes **1** with allylic halides were performed (Table 1). All the reactions examined proceeded with high regioselectivity to produce the vinyl sulfides γ-**3** as major isomers.

Next we studied the allylation of vinylsilanes **4** and found that the 1,4-dienes **5** were produced in good yields by the use of an allylic halide-CuI-KF system (Table 2). Contrast to the reaction of allylsilanes **1**, DMSO was a better cosolvent than acetone in these cases (see entry 5).[12] Further it was found that the allylation of vinylsilanes having a β-substituent took place with complete retention of configuration of double bond. The allylation also proceeded in the presence of CuBr though the yield of allylation product decreased (see entry 8). When the reaction of **Z-4c** with **2b** was carried out using a catalytic amount of CuI (0.2 equiv) for 24 h, **Z-5h** was produced in 51% yield and the starting material was recovered (28%).

Table 2. Allylation of vinylsilanes **4**[a]

Entry	Vinylsilane 4	Allylic Halide 2	Product	(Yield / %)
1	 **4a**	**2a**	 **5a**	(83)
2	**4a**	**2b**	 **5b**	(79)
3	 **E-4b**	**2a**	 **E-5c**	(71)
4	**E-4b**	**2b**	 **E-5d**	(78)
5	 **Z-4b**	**2a**	 **Z-5e**	(77, 30[b])
6	 **Z-5f**	**2b**	 **Z-5f**	(80)
7	 **E-4c**	**2b**	 **E-5g**	(74)
8	 **Z-4c**	**2b**	 **Z-5h**	(84, 62,[c] 51[d])
9	 **7**[e]	**2b**	 **9**	(29)[e,f]

[a] All reactions were performed with a similar procedure as described in the text. [b] The reaction was carried out in acetone-THF. [c] The reaction was carried out using CuBr. [d] The reaction was carried out using 0.2 equiv of CuI. The starting material **Z-4c** was recovered (28%). [e] The ratio of stereoisomers was not determined. [f] The starting material **7** was recovered (66%).

The substitution of 2-pyridylthio group seems to be indispensable for the present reactions because it was confirmed that no allylation product was obtained, and the starting material was recovered (89%) when the phenylthio group substituted allylsilane, 3-methyl-1-phenylthio-1-(trimethylsilyl)but-2-ene, was treated with **2b** under the similar reaction conditions. In order to make clear the role of 2-pyridylthio group, we prepared the allyl- and viny-silanes **6** and **7** having a 4-pyridylthio group and examined their reaction with **2b**. Unlike the 2-pyridylthio group substituted organosilanes, only the protodesilation products **8** and **9** were produced, and the formation of allylation product was not observed in these cases (entry 5, Table 1 and entry 9, Table 2). Since 4-pyridylthio group provides almost the same inductive effect as that of 2-pyridylthio group, these results indicate that the intramolecular-coordination of nitrogen to silicon depicted in schemes facilitates the reactions of **1** and **4** with allylic halides **2**.

Concerning the allylation of organosilicon compounds, the palladium-catalyzed allylation of dimethyl(fluoro)- and difluoro-(methyl)-(1-alkenyl)silanes with allylic carbonates was reported by Hiyama, Hatanaka, and their co-workers. However, they noted that trimethylsilyl derivative was inert under the same reaction conditions.[13] Although Pilcher and DeShong reported the tetrabutylammonium triphenyldifluorosilicate-induced alkylation of allyltrimethylsilane, vinyltrimethylsilane was found to be unreactive under the reaction conditions.[14]

The present allylation is of special interest, for relatively unreactive vinyltrimethylsilanes are activated by the substitution with a 2-pyridylthio group which serves as a ligand. As a consequence they become capable of being allylated under mild reaction conditions.

References and Notes

1 S.-K. Kang, J.-S. Kim, and S.-C. Choi, *J. Org. Chem.*, **62**, 4208 (1997) and references cited therein.

2 J. Yoshida, K. Tamao, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, **1979**, 1141.

3 H. Urata and T. Fuchikami, *Tetrahedron Lett.*, **32**, 91 (1991).

4 S. A. Lermontov, I. M. Rakov, N. S. Zefirov, and P. J. Stang, *Tetrahedron Lett.*, **37**, 4051 (1996).

5 H. Ito, K. Arimoto, H. Sensui, and A. Hosomi, *Tetrahedron Lett.*, **38**, 3977 (1997).

6 S. Kang, T.-H. Kim, and S.-J. Pyun, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 797.

7 K. Ikegashira, Y. Nishihara, A. Mori, and T. Hiyama, *Chem. Commun.*, **1997**, 1039.

8 H. Ito, H. Sensui, K. Arimoto, K. Miura, and A. Hosomi, *Chem. Lett.*, **1997**, 639.

9 Y. Nishihara, K. Ikegashira, A. Mori, and T. Hiyama, *Tetrahedron Lett.*, **39**, 4075 (1998).

10 T. Takeda, K. Matsunaga, Y. Kabasawa, and T. Fujiwara, *Chem. Lett.*, **1995**, 771.

11 T. Takeda, K. Matsunaga, T. Uruga, M. Takakura, and T. Fujiwara, *Tetrahedron Lett.*, **38**, 2879 (1997).

12 The typical experimental procedure is as follows: To a flask charged with KF (52 mg, 0.9 mmol) and CuI (63 mg, 0.33 mmol) was added a DMSO (0.9 ml) solution of allyl chloride **2a** (25 mg, 0.33 mmol) and a THF (0.9 ml) solution of 1-[(2-pyridylthio)]-1-(trimethylsilyl)ethene (**4a**) (63 mg, 0.3 mmol) successively at room temperature. After being stirred for 24 h, the reaction was quenched with 3.5% NH_3 aqueous solution, and organic materials were extracted with ether. The organic layer was dried (Na_2SO_4) and condensed. The residue was purified by silica-gel PTLC (hexane : AcOEt = 9 : 1) to give 2-(2-pyridylthio)pent-1,4-diene (**5a**) (44 mg, 83%).

13 H. Matsuhashi, S. Asai, K. Hirabayashi, Y. Hatanaka, A. Mori, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **70**, 1943 (1997).

14 A. S. Pilcher and P. DeShong, *J. Org. Chem.*, **61**, 6901 (1996).