February, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 607—608 (1984)*

Catalytic Conversion of Allylic Esters to Corresponding Allylic Silanes with Hexamethyldisilane and Palladium(0) or Rhodium(I) Complexes

Hisao URATA, Hiroharu SUZUKI,* Yoshihiko MORO-OKA,* and Tsuneo IKAWA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227

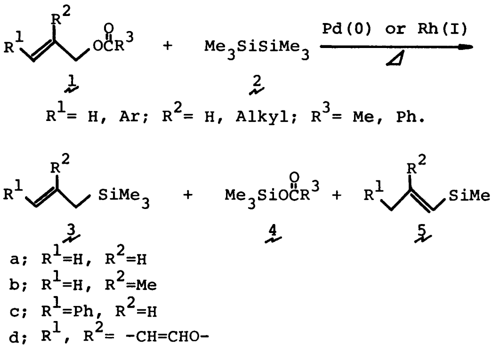
(Received June 20, 1983)

Synopsis. Treatment of allylic esters ($R^1CH{=}CR^2CH_2OCOR^3$: R^1=H, Ar; R^2=H, alkyl; and R^3=Me, Ph) with hexamethyldisilane in the presence of catalytic amounts of PdL_4 (L=PPh_3 or $P(OPh)_3$) or $RhCl(PPh_3)_3$ gives the corresponding allylic silanes in the excellent yield.

Synthetic utility of disilanes ($Cl_nMe_{6-n}Si_2$: n=0—6) have recently been developed. Monosilylation[1] and disilylaion ("double silylation")[2] of many classes of organic substrates have been achieved *via* the cleavage of Si–Si bond catalyzed by transition metal complexes. Disilane can also be used in the Pd(0)-catalyzed reductive dehalogenation of α-halogenated carbonyl and cyano compounds.[3] We report herein a simple preparative method of allylic silances, **3**, from allylic esters, **1**, and hexamethyldisilane, **2**, by using PdL_4 (L=PPh_3 or $P(OPh)_3$) or $RhCl(PPh_3)_3$ as catalyst.

Results and Discussion

Treatment of allylic acetates or benzoates, **1**, with hexamethyldisilane, **2**, in the presence of catalytic amounts of Pd(0) or Rh(I) complex at 140—160 °C in sealed tube gave the corresponding allylic silanes, **3** (Eq. 1). Trimethylsilyl acetate[4] or benzoate,[5] **4**, was also formed in this reaction. The products were separated by column chromatography on silica gel and were identified and quantified by means of ^{1}H-NMR and GLC. Gaseous by-products were also identified and quantified by use of GLC. The results of the Pd(0) and Rh(I)-catalyzed conversion of allylic esters to allylic silanes are summarized in Table 1.

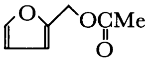


(1)

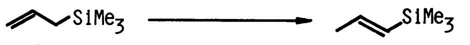
As shown in Table 1, β-methallyl acetate, β-methallyl benzoate, cinnamyl acetate, and furfuryl acetate were efficiently converted to the corresponding allylic silanes. Trimethylsilyl group was regioselectively introduced into the α-position of cinnamyl group to give (*E*)-cinnamyltrimethylsilane,[6] **3c** (entries 12 and 13).

Tetrakis(triphenylphosphite)palladium(0) effectively catalyzed the reaction of allyl acetate or benzoate with hexamethyldisilane to give allyltrimethylsilane,[6] **3a**, in an excellent yield whereas tetrakis(triphenylphosphine)palladium(0) and chlorotris(triphenylphosphine)rhodium(I) caused side reaction to afford propylene and (*E*)-1-propenyltrimethylsilane,[7] **5**, the double bond migration product of **3a**. The isomerization of allyltrimethylsilane, **3a**, to (*E*)-1-propenyltrimethylsilane, **5**, was examined under the various

TABLE 1. CONVERSION OF ALLYLIC ESTERS TO ALLYLIC SILANES CATALYZED BY Pd(0) OR Rh(I) COMPLEXES

Entry	Allylic ester(**1**)			Cat[1)]	[Cat]	Temp	Time	Yield/%		
	R^1	R^2	R^3		[**1**]	°C	h	**3**	**4**	**5**
1[2)]	H	H	Me	A	1/204	180	2	**a**; 48	100	48
2				B	1/90	160	4	**a**;100	100	0
3[2)]				C	1/106	160	24	**a**; 19	69	10
4[2)]	H	H	Ph	A	1/73	160	3	**a**; 41	100	41
5				B	1/71	160	3	**a**; 82	84	0
6	H	Me	Me	A	1/101	150	10	**b**;100[3)]	100	0
7				B	1/65	160	3	**b**;100	100	0
8				C	1/98	160	24	**b**; 31	31	0
9	H	Me	Ph	A	1/81	160	5	**b**; 75	99	0
10				B	1/98	160	24	**b**; 66	84	0
11[4)]				C	1/80	160	5	**b**; 33	100	0
12	Ph	H	Me	A	1/91	160	10	**c**; 79	95	0
13				B	1/90	160	10	**c**; 60	50	0
14[5)]				C	1/77	160	10	**c**; 42	42	0
15		 OCMe		A	1/83	140	2	**d**; 37[6)]	—	0

1) A: $Pd(PPh_3)_4$, B: $Pd[P(OPh)_3]_4$, C: $RhCl(PPh_3)_3$. 2) Propylene was detected as a by-product. 3) Ref. 11. 4) 2,5-Dimethyl-1,5-hexadiene was obtained in a 17% yield. 5) β-Methylstyrene was obtained in a 40% yield. 6) Furfuryltrimethylsilane was obtained. Ref. 12.



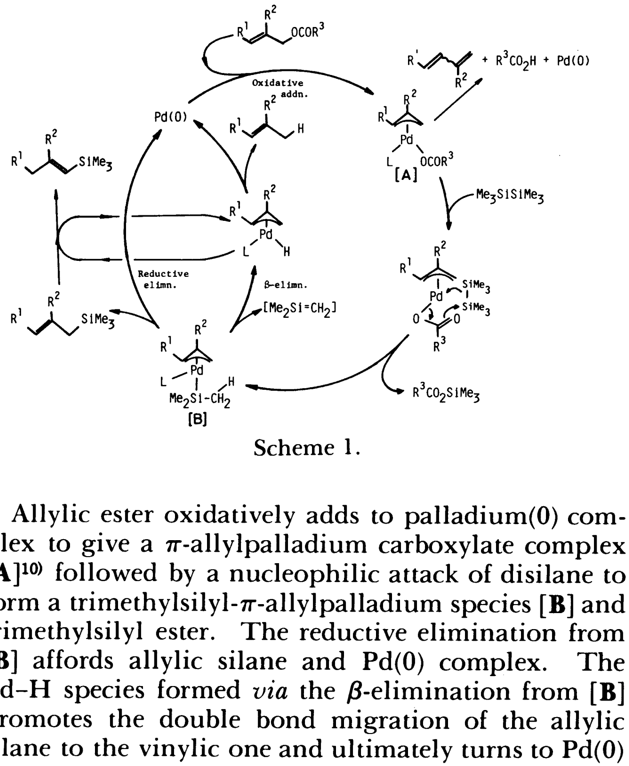
Conditions
A) 150 °C–2 h (no reaction)
B) Pd(PPh$_3$)$_4$—150 °C–2 h (no reaction) (2)
C) Pd(PPh$_3$)$_4$-AcOH—160 °C–2 h (20%)

conditions (Eq. 2).

Allyltrimethylsilane, **3a**, was isomerized to (*E*)-1-propenyltrimethylsilane, **5**, in a 20% conversion under the conditions C where palladium hydride was an actual active species.8) This suggests the double bond migration of **3a** to **5** occurs by way of the addition-elimination of Pd–H formed by β-elimination from intermediary Pd–SiMe$_3$ species.

The applicability of the present method is however limited to the allylic esters having no *primary* or *secondary* alkyl group at the γ-position of allylic moiety. When R^1 was *primary* or *secondary* alkyl group, treatment of **1** with Pd(0) or Rh(I) complex gave the conjugated diene even in the presence of excess amounts of hexamethyldisilane. These results well agreed with those reported by Tsuji *et al.*9)

From the results mentioned above, the following mechanism would be proposed for the conversion of allylic esters to the allylic silanes catalyzed by Pd(0) complex (Scheme 1).



Scheme 1.

Allylic ester oxidatively adds to palladium(0) complex to give a π-allylpalladium carboxylate complex [**A**]10) followed by a nucleophilic attack of disilane to form a trimethylsilyl-π-allylpalladium species [**B**] and trimethylsilyl ester. The reductive elimination from [**B**] affords allylic silane and Pd(0) complex. The Pd–H species formed *via* the β-elimination from [**B**] promotes the double bond migration of the allylic silane to the vinylic one and ultimately turns to Pd(0) with formation of the alkene such as propylene or β-methylstyrene.

Experimental

All reactions were conducted in Pyrex sealed tubes under nitrogen atmosphere.

Synthesis of (E)-*Cinnamyltrimethylsilane (entry 12).* Tetrakis(triphenylphosphine)palladium (62.8 mg, 0.054 mmol) was placed in a Pyrex tube equipped with a three-way stopcock. After the atmosphere was replaced with nitrogen, hexamethyldisilane (0.70 g, 4.78 mmol) and cinnamyl acetate (0.87 g, 4.94 mmol) were added. Then the tube was sealed and heated at 160 °C for 10 h. Bulb to bulb distillation of the resultant mixture gave trimethylsilyl acetate4) (0.60 g, 95%), ^{1}H-NMR (CCl$_4$) δ=0.20 (9H, s), 1.97 (3H, s). Purification of the residue by column chromatography (silica gel, benzene) afforded (*E*)-cinnamyltrimethylsilane6) (0.72 g, 79%), bp 234 °C; IR (CCl$_4$) 960 cm^{-1} (*trans* CH=CH); ^{1}H-NMR (CCl$_4$) δ=0.05 (9H, s), 1.63 (2H, m), 6.10 (2H, m), 7.11 (5H, bs).

Synthesis of Allyltrimethylsilane and (E)-*1-Propenyltrimethylsilane (entry 1).* Pd(PPh$_3$)$_4$ (57.6 mg, 0.05 mmol), hexamethyldisilane (1.44 g, 10.05 mmol), and allyl acetate (1.02 g, 10.22 mmol) were placed in a Pyrex tube under N$_2$. After the tube was sealed and heated at 180 °C for 2 h, bulb to bulb distillation of the resultant mixture gave a mixture (2.40 g) of trimethylsilyl acetate4) (100%), allyltrimethylsilane6) (48%), and (*E*)-1-propenyltrimethylsilane7) (48%), IR (CCl$_4$) 982 cm^{-1} (*trans* CH=CH); ^{1}H-NMR (CCl$_4$) δ=0.02 (9H, s), 1.80 (3H, d, J=5 Hz), 5.44 (1H, d, J=19 Hz), 6.06 (1H, dq, J=19 and 5 Hz). Propylene was also detected from gas phase by GLC analysis in a 2% yield.

Isomerization of Allyltrimethylsilane to (E)-*1-Propenyltrimethylsilane.* To a benzene solution (1 ml) of Pd(PPh$_3$)$_4$ (66.2 mg, 0.057 mmol) and acetic acid (3 μl) was added allyltrimethylsilane (0.77 g, 6.75 mmol). After the mixture was heated at 160 °C for 2 h in a Pyrex sealed tube, ^{1}H-NMR measurement of the reaction mixture showed a 20% conversion of (*E*)-1-propenyltrimethylsilane.

The authors are grateful to the Toshiba Silicon Co. Ltd. for a generous gift of disilane residue in the direct synthesis.

References

1) For eample, H. Matsumoto, S. Nagashima, T. Kato, and Y. Nagai, *Angew. Chem., Int. Ed. Engl.*, **17**, 279 (1978); K. Yamamoto, S. Suzuki, and J. Tsuji, *Tetrahedron Lett.*, **21**, 1653 (1980); M. Lefort, C. Simmonet, M. Birot, G. Deleris, J. Donogues, and R. Calas, *ibid.*, **21**, 1857 (1980); H. Matsumoto, K. Shono, and Y. Nagai, *J. Organomet. Chem.*, **208**, 145 (1981).

2) For example, H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *Chem. Lett.*, **1975**, 887; H. Okinoshima, K. Yamamoto, and M. Kumada, *J. Organomet. Chem.*, **86**, C27 (1975); K. Tamao, T. Hayashi, and M. Kumada, *ibid.*, **114**, C19 (1976); K. Tamao, S. Okazaki, and M. Kumada, *ibid.*, **146**, 87 (1978); H. Watanabe, M. Kobayashi, K. Higuchi, and Y. Nagai, *ibid.*, **186**, 51 (1980).

3) H. Urata, H. Suzuki, Y. Moro-oka, and T. Ikawa, *J. Organomet. Chem.*, **234**, 367 (1982).

4) Yves Étienne, *C. R. Acad. Sci.*, **235**, 966 (1952).

5) N. E. Hoffman, A. Milling, Jr., and P. Parmelee, *Anal. Biochem.*, **32**, 386 (1969).

6) J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95**, 8678 (1973).

7) T. H. Chan and I. Fleming, *Synthesis*, **1979**, 761.

8) V. H. Hey and H. J. Arpe, *Angew. Chem.*, **85**, 968 (1973).

9) J. Tsuji, T. Yamakawa, M. Kaito, and T. Mandai, *Tetrahedron Lett.*, **1978**, 2075.

10) T. Yamamoto, O. Saito, and A. Yamamoto, *J. Am. Chem. Soc.*, **103**, 5600 (1981).

11) H. Matsumoto, T. Yako, S. Nagashima, T. Motegi, and Y. Nagai, *J. Organomet. Chem.*, **148**, 97 (1978).

12) Furfuryltrimethylsilane: Bp 149 °C. Found: C, 62.36; H, 9.03%. Calcd for C$_8$H$_{14}$OSi: C, 62.28; H, 9.15%. ^{1}H-NMR (CCl$_4$) δ=0.05 (9H, s), 2.03 (2H, s), 5.68 (1H, m), 6.10 (1H, m), 7.10 (1H, m).