CHEMISTRY LETTERS, pp. 1485-1486, 1982. © The Chemical Society of Japan 1982

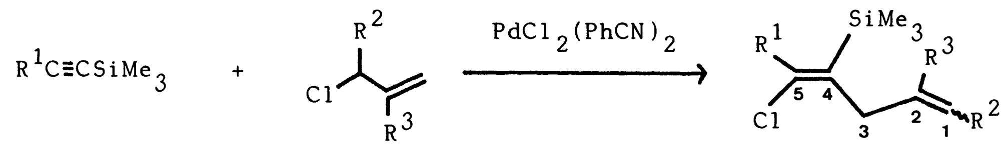
PALLADIUM(II)-CATALYZED CHLOROALLYLATION OF ALKYNYLSILANES. REGIO- AND STEREOSELECTIVE SYNTHESIS OF β-CHLOROALKENYLSILANES

Ryohei YAMAGUCHI,* Hiroshi KAWASAKI, Toshihide YOSHITOME, and Mituyosi KAWANISI
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606

Reactions of alkynyltrimethylsilanes with allylic chlorides in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ give regio- and stereoselectively 4-trimethylsilyl-5-chloro-1,4(E)-dienes in good yields.

Organosilicon compounds have found their versatile utility in organic synthesis and, among them, alkenylsilanes have turned out to be important synthetic intermediates.[1)] Meanwhile, hydro- and carbometallation of alkynylsilanes have been successfully applied to regio- and stereoselective synthesis of alkenylsilanes.[2)] Recent report by Kaneda et al.[3)] has promoted us to investigate palladium(II)-catalyzed reactions of alkynylsilanes, and we wish to report here that chloropalladation of alkynylsilanes provides a convenient synthetic method of β-chloroalkenylsilanes containing 1,4-diene moiety.

When a mixture of alkynylsilane (**1**) and dichlorobis(benzonitrile)palladium [$PdCl_2(PhCN)_2$] (0.05-0.1 eq) in an allylic chloride (**2**) solution was stirred at room temperature for 5-15 h, the reaction proceeded cleanly to give the corresponding chloroallylation product (**3**) in good yield with high regio- and stereoselectivity. The results are summarized in the Table.



1 **2** **3**

The products (**3**) were characterized by various spectral data including MS, IR, ^1H- and ^{13}C-NMR. Furthermore, **3** (R^2=R^3=H) could be easily converted to the corresponding 1,4-enyne (**4**) upon treatment with Bu_4NF in THF.[4)]

$$3 \xrightarrow{Bu_4NF} RC\equiv CCH_2CH=CH_2$$

4

a $R=C_4H_9-$ (57%)
b $R=C_5H_{11}-$ (73%)
c $R=C_6H_{13}-$ (84%)[5)]

Table. Chloroallylation of Alkynylsilanes

	1	**2**		**3**	
	R^1	R^2	R^3	Yields(%)$^{a)}$	Selectivity(%)$^{b,c)}$
a	C_4H_9	H	H	79	>98
b	C_5H_{11}	H	H	87	>98
c	C_6H_{13}	H	H	91	>98
d	C_4H_9	H	CH_3	79	97
e	C_6H_{13}	H	CH_3	94	95
f	C_4H_9	CH_3	H	84	>98$^{d)}$
g	C_6H_{13}	CH_3	H	92	>98$^{d)}$

a) Isolated yields. b) Selectivity referring to the 4,5-double bond shown in the first Scheme. c) Determined by glc. d) E/Z ratio was ca. 55/45 at the 1,2-double bond shown in the first Scheme.

A typical procedure is as follows: To a solution of 1-hexynyltrimethylsilane (616 mg; 4 mmol) in allyl chloride (4 ml) was added $PdCl_2(PhCN)_2$ (77 mg; 0.2 mmol) and the dark orange solution was stirred at room temperature overnight. Allyl chloride was removed under reduced pressure and the residue was chromomatographed on alumina. Elution by hexane gave 5-chloro-4-trimethylsilylundeca-1,4(E)-diene (**3a**, 725 mg; 79%); MS *m/e*: 232, 230 (M^+). IR (neat): 2900, 1630, 1590, 1460, 1250, 905, 840, 755 cm^{-1}. ^{1}H-NMR δ(CCl_4): 5.60-6.10(1H, m), 4.72-5.20(2H, m), 3.03(2H, d, J=6 Hz), 2.30-2.63(2H, m), 0.70-1.90(7H, m), 0.17(9H, s). ^{13}C-NMR δ($CDCl_3$): 144.3(s), 135.7(d), 131.3(s), 114.9(t), 40.0(t), 37.7(t), 31.0(t), 22.4(t), 14.0(q), 0.5(q). Anal. Found: C, 62.54; H, 9.98%. Calcd for $C_{12}H_{23}ClSi$: C, 62.43; H, 10.04%.

We thank Dr. Kiitiro Utimoto for helpful discussions.

References
1) E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981.
2) Ref. 1), pp. 48-54.
3) K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, and S. Teranishi, J. Org. Chem., **1979**, *44*, 55.
4) For fluoride ion induced β-elimination of β-chlorotrimethylsilylethene, see R. F. Cunico and E. M. Dexheimer, J. Amer. Chem. Soc., **1972**, *94*, 2868.
5) Spectral data for **4c** are as follows; MS *m/e*: 150 (M^+). IR (neat): 2900, 1630. 1460, 1415, 985, 910 cm^{-1}. ^{1}H-NMR δ(CCl_4): 5.50-6.13(1H, m), 4.90-5.45(2H, m), 2.87(2H, m), 2.13(2H, m), 0.63-1.80(11H, m). ^{13}C-NMR δ($CDCl_3$): 133.6(d), 115.5(t), 82.8(s), 76.7(s), 31.5(t), 29.2(t), 28.7(t), 23.2(t), 22.6(t), 18.9(t), 14.0(q). This compound (**4c**) was also identical with the authentic sample which was prepared by a coupling reaction of 1-octynylmagnesium bromide with allyl bromide in the presence of a catalytic amount of CuI.

(Received July 14, 1982)