Communications

Anti-Hydrosilylation Reactions of Alkynes Catalyzed by Palladium Nitrate

Dong Hwan Kim and Young-ae W. Park*

*Department of Chemistry, Sangmyung University, Seoul 110-743, Korea. *E-mail: ywhang@smu.ac.kr*
Received November 28, 2005

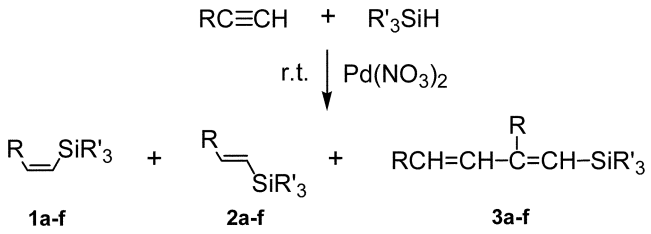
Key Words : *Anti*-hydrosilylation, Alkyne, Tertiary silane, Palladium nitrate, Dialkynylated silane

Hydrosilylation of alkynes catalyzed by transition metal complexes is the most effective method for the preparation of vinylsilanes that might be the excellent precursors to silicon polymers.[1] Although thermodynamically stable *syn*-hydrosilylation products are generally observed in this type of reactions,[2] changing catalyst and reaction conditions can lead to an unusually high degree of *anti*-hydrosilylation.[3,4] We performed the hydrosilylation reactions of RC≡CH (R = Ph, $C_{10}H_{21}$) with R'_3SiH (R'_3 = Et_3, *t*-$BuMe_2$, Me_2Ph) in the presence of 2 mol % palladium nitrate at room temperature. Initially, $Pd(NO_3)_2$-phosphine was used as the catalyst in order to expand our previous works since it had been found to be an effective catalyst for the activation of both aromatic and aliphatic carbon-hydrogen bonds in our laboratory.[5] However, palladium(II) was reduced to palladium(0) in the presence of phosphine in this work and the reaction did not proceed further. Here we report the unusual *anti*-hydrosilylation reactions of alkynes with R_3SiH using $Pd(NO_3)_2$ as the catalyst without phosphine, which has rarely been reported in this kind of reactions previously.

The *cis* and *trans* products (**1** and **2**, respectively) were obtained along with dialkynylated silanes (**3**) as described in Scheme 1 and the results are summarized in Table 1.

As shown in Table 1, it is unusual that thermodynamically less stable *cis* isomers **1** derived from *anti*-hydrosilylation were obtained almost exclusively over *trans* isomers **2** for the entries 1, 2, 4 and 5 with selectivity of 96-99%. More surprisingly, only *anti*-hydrosilylation product **1** was observed at the beginning of the reaction in GC analysis and it was slowly converted to **2**, of which ratios reached 1 to 4% at most and the ratios were unchanged since then. Usually, the reaction mechanism has been reported to proceed through the initial *syn*-addition of the hydrosilanes to alkynes giving the *trans* product, followed by isomerization to the *cis* product, even in the case of the other predominant *anti*-hydrosilylation reactions.[3,7,8] In fact, the isomerization of *cis* product to *trans* product was first observed by Watanabe *et al.*, but the selectivity was not high enough.[4] The investigation of the reaction mechanism in this work is in progress and will be published later.

It is noteworthy that the above results were observed only for the aliphatic silanes. In the case of aromatic silane, Me_2PhSiH, the reactions with PhC≡CH and $C_{10}H_{21}C$≡CH gave 62 : 38 and 49 : 51, respectively, in the ratios of the



a R = Ph, R'_3 = Et_3 **d** R = $C_{10}H_{21}$, R'_3 = Et_3
b R = Ph, R'_3 = *t*-$BuMe_2$ **e** R = $C_{10}H_{21}$, R'_3 = *t*-$BuMe_2$
c R = Ph, R'_3 = Me_2Ph **f** R = $C_{10}H_{21}$, R'_3 = Me_2Ph

Scheme 1

Table 1. Hydrosilylation of alkynes with tertiary silanes in the presence of $Pd(NO_3)_2$[a]

Entry	Reactants		Reaction time (h)	Products ratio (%)[b]		Conversion yields (%)[b]
	R	R'_3		Vinyl silanes (**1** : **2**)	Dialkynylated silanes (**3**)	
1	Phenyl	Et_3	3	70 (96:4)	30	100
2	Phenyl	*t*-$BuMe_2$	12	53 (99:1)	47	93
3	Phenyl	Me_2Ph	24	92 (62:38)	8	71
4	$C_{10}H_{21}$	Et_3	3	75 (98:2)	24	100
5	$C_{10}H_{21}$	*t*-$BuMe_2$	12	80 (98:2)	19	82
6	$C_{10}H_{21}$	Me_2Ph	24	91 (49:51)	9	70

[a]The reactions were carried out at room temperature in toluene. The ratio of RCCH/R'_3SiH/Pd was 1/1/0.02. [b]Ratios and yields (based on alkynes reacted) of vinyl silanes and dialkynylated silanes were determined by GC using *n*-hexadecane as an internal standard.

anti- to the *syn*-hydrosilylation products (entries 3 and 6). Nile and his coworkers also found the similar results that good electron-donor ligands gave the *cis* product while good electron-acceptor ligands gave the *trans* product as the major species.[3c] These facts clearly indicate that the reactions of the aliphatic silanes in this work involve stereoselective *anti*-hydrosilylation to give the *cis* products.

For the entries 4 and 5, obtained were very small amounts of byproducts (1% yield) which were not listed in Table 1. They are assumed to be dehydrogenative silylation products from their GC-MS data, and the similar reactions were reported to arise from the initial insertion of the unsaturated substrate into the M-Si bond, followed by β-hydride elimination.[3a] The other byproducts of notice in this work were dialkynylated silanes, which were identified to be the isomeric mixtures by GC-MS, ^{1}H NMR and elemental analysis. This dialkynylation reaction is thought to take place by a sequence of dimerization and hydrosilylation of alkyne.[9,10] Although a number of bis-silylation reactions of unsaturated substrates have been reported,[11] dialkynylation of silane has rarely been reported before.

In summary, we found a very simple palladium(II) compound which catalyzed hydrosilylation of alkynes with the exclusive selectivity on the *anti*-hydrosilylation, and the *cis* products derived from *anti*-hydrosilylation were obtained unusually at the initial stage of the reactions. Obtained also were the rarely reported dialkynylated silanes along with dehydrogenated silylation products in a small amount.

Acknowledgement. Authors thank to Sangmyung University for the financial support in 2002.

References and Notes

1. Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578.
2. (a) Chauhan, M.; Hauck, B. J.; Keller, L. P.; Boudjouk, P. *J. Organomet. Chem.* **2002**, *645*, 1. (b) Goldberg, Y.; Alper, H. *Tetrahedron Lett.* **1995**, *36*, 369.
3. (a) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (c) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299.
4. Watanabe, H.; Kitabara, T.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1977**, *139*, 215.
5. (a) Hwang, S. W.; Park, Y. *J. Ind. Eng. Chem.* **2000**, *6*, 125. (b) Shin, J. A.; Park, Y.; Park, Y. S.; Woo, J. W. *J. Ind. Eng. Chem.* **2001**, *7*, 337.
6. The ^{1}H NMR (250 MHz) spectra of vinylsilanes (**1** and **2**) or dialkynylated products (**3**) were taken as the isomeric mixtures, and the isomers of the dialkynylated products were described as **A** and **B**, since the stereochemistry could not be determined from the NMR spectral data. (2,4-Diphenylbuta-1,3-dienyl)triethylsilane (**3a**). Isomer **A** (62%). ^{1}H NMR: δ 7.28-7.25 (m, 10H), 7.12 (d, J = 15.8 Hz, 1H), 6.07 (d, J = 15.8 Hz, 1H), 5.98 (s, 1H), 0.88 (t, J = 7.9 Hz, 9H), 0.34 (q, J = 7.9 Hz, 6H); GC-MS: m/z 320 (M^+), 291, 189, 161. Isomer **B** (38%). ^{1}H NMR: δ 7.28-7.25 (m, 11H), 6.45 (d, J = 15.8 Hz, 1H), 5.75 (s, 1H), 1.08 (t, J = 7.9 Hz, 9H), 0.82 (q, J = 7.9 Hz, 6H); GC-MS: m/z 320 (M^+), 291, 189, 161; Anal. Calc. for $C_{22}H_{28}Si$ (Mixture of isomers **A** and **B**): C, 82.4; H, 8.8. Found: C, 82.3; H, 8.6. (*Z*)-*t*-Butyldimethylstyrylsilane (**1b**). ^{1}H NMR: δ 7.55 (d, J = 15.4 Hz, 1H), 7.58-7.31 (m, 5H), 5.94 (d, J = 15.4 Hz, 1H), 0.98 (s, 9H), 0.00 (s, 6H); GC-MS: m/z 218 (M^+), 161. *t*-Butyl(2,4-diphenylbuta-1,3-dienyl)dimethylsilane (**3b**). Isomer **A** (89%). ^{1}H NMR: δ 7.58-7.31 (m, 10H), 6.92 (d, J = 16.3 Hz, 1H), 5.88 (s, 1H), 5.84 (d, J = 16.3 Hz, 1H), 0.75 (s, 9H), −0.48 (s, 6H); GC-MS: m/z 320 (M^+), 263. Isomer **B** (11%). ^{1}H NMR: δ 7.58-7.31 (m, 11H), 6.30 (d, J = 16.1 Hz, 1H), 5.62 (s, 1H), 0.80 (s, 9H), 0.13 (s, 6H); GC-MS: m/z 320 (M^+), 263. (*Z*)-Dodec-1-enyltriethylsilane (**1d**). ^{1}H NMR: δ 6.30 (dt, J = 14.1, 7.3 Hz, 1H), 5.38 (dt, J = 14.1, 1.3 Hz, 1H), 2.09 (q, J = 6.9 Hz, 2H), 1.4-1.2 (m, 16H), 0.94 (t, J = 7.9 Hz, 9H), 0.88 (t, J = 6.9 Hz, 3H), 0.61 (q, J = 7.9 Hz, 6H); GC-MS: m/z 282 (M^+), 253, 225, 87. (2-Decyltetradeca-1,3-dienyl)triethylsilane (**3d**). Isomer **A** (97%). ^{1}H NMR: δ 6.00 (d, J = 15.7 Hz, 1H), 5.67 (dt, J = 15.7, 6.8 Hz, 1H), 5.28 (s, 1H), 2.27-2.15 (m, 2H), 2.13-2.05 (q, J = 6.7 Hz, 2H), 1.20-1.50 (m, 32H) 0.95 (t, J = 7.9 Hz, 9H), 0.88 (t, J = 6.8 Hz, 6H), 0.61 (q, J = 7.9 Hz, 6H); GC-MS: m/z 448 (M^+), 419, 391, 307, 181, 115, 87. Isomer **B** (3%). GC-MS: m/z 448 (M^+), 419, 391, 307, 181, 115, 87. (*Z*)-*t*-Butyl(dodec-1-enyl)dimethylsilane (**1e**). ^{1}H NMR: δ 6.37 (dt, J = 14.2, 7.4 Hz, 1H), 5.47 (dt, J = 14.2, 1.3 Hz, 1H), 2.11 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.95-0.85 (m, 12H), 0.09 (s, 6H); GC-MS: m/z 282 (M^+), 225, 99, 85. *t*-Butyl(2-decyltetradeca-1,3-dienyl)dimethylsilane (**3e**). Isomer **A** (93%). ^{1}H NMR: δ 6.00 (d, J = 15.7 Hz, 1H), 5.67 (dt, J = 15.7, 6.9 Hz, 1H), 5.36 (s, 1H), 1.4-1.2 (m, 32H), 0.95-0.85 (m, 15H), 0.09 (s, 6H); GC-MS: m/z 448 (M^+), 391. Isomer **B** (7%). GC-MS: m/z 448 (M^+), 391. (*Z*)-Dodec-1-enyldimethylphenylsilane (**1f**). ^{1}H NMR: δ 7.6-7.5 (m, 5H), 6.44 (dt, J = 14.0, 7.4 Hz, 1H), 5.63 (dt, J = 14.0, 1.1 Hz, 1H), 2.19 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.87 (t, J = 6.9 Hz, 3H), 0.39 (s, 6H); GC-MS: m/z 302 (M^+), 287, 161, 135. (*E*)-Dodec-1-enyldimethylphenylsilane (**2f**). ^{1}H NMR: δ 7.4-7.3 (m, 5H), 6.14 (dt, J = 18.5, 6.2 Hz, 1H), 5.74 (dt, J = 18.6, 1.4 Hz, 1H), 2.19 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.87 (t, J = 6.9 Hz, 3H), 0.34 (s, 6H); GC-MS: m/z 302 (M^+), 287, 161, 135.
7. Dickers, H. M.; Hazeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91.
8. (a) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 1133. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.
9. (a) Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 1584.
10. Kawanami, Y.; Yamamoto, K. *Synlett* **1995**, 1232.
11. (a) Murai, S.; Chatani, N. *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 421. (b) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Fujimoto, K.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933. (c) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353.