ORGANIC
LETTERS

2000
Vol. 2, No. 13
1887−1889

Highly Stereoselective and Efficient Hydrosilylation of Terminal Alkynes Catalyzed by [$RuCl_2$(*p*-cymene)$]_2$

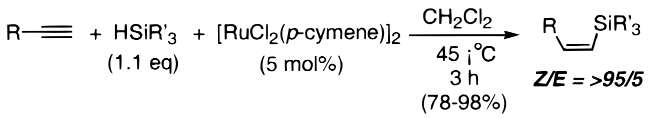
Youngim Na and Sukbok Chang*

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

sbchang@mm.ewha.ac.kr

Received April 19, 2000

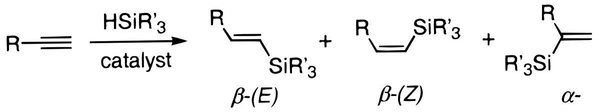
ABSTRACT



With [$RuCl_2$(*p*-cymene)$]_2$ as a catalyst, extremely high regio- and stereoselectivity was observed in the hydrosilylation reaction of various terminal alkynes under mild conditions to afford β-(*Z*)-vinylsilanes in excellent yields. A dramatic directing effect was also observed when alkynes having a hydroxyl group at the β position to the triple bond were employed as a substrate, and in these cases regioisomeric α-vinylsilanes were generated with excellent selectivity.

Organosilanes play an important role in chemistry as versatile building blocks.[1] Hydrosilylation of multiple bonds, therefore, represents a useful class of catalytic processes performed on both laboratory and industry scales. Vinylsilanes, widely used intermediates for organic synthesis, could be efficiently prepared by the transition metal catalyzed addition of silanes to alkynes.[2,3] The major consideration in this conversion is selectivity, the control of which, although highly desirable, is not an easy task in most cases. For example, hydrosilylation of monosubstituted alkynes may give a primary mixture of three isomeric vinylsilanes (Scheme 1).

Scheme 1



β-(*E*)-Vinylsilanes, the thermodynamic products, are usually formed as a major isomer in most of the transition metal catalyzed reactions developed. On the other hand, generation of β-(*Z*)-isomers *with a practical selectivity* is regarded much more challenging in most user-friendly hydrosilylation reactions. Although the regiocontrol reported is excellent in some cases,[4] the regioselectivity, in most metal-catalyzed hydrosilylations, is capriciously affected by various factors such as types of alkynes and silanes, catalytic metal species, and reaction conditions including solvent or temperature. Considering its potential utility in synthetic organic chemistry, an efficient catalytic system for the highly selective formation of β-(*Z*)-vinylsilanes is strongly desirable. In this Letter we report our results toward this goal.

Although ruthenium complexes are known to be generally less reactive in hydrosilylation reactions compared to other late transition metals,[5] we envisioned that this property could be developed into a highly selective catalyst system. Among

---

(1) (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, S., Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 29. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 7. (c) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375 and references therein.

(2) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (b) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 197. (c) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992; p 130.

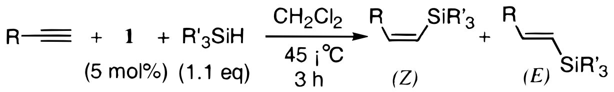
(3) For Lewis acids catalyzed hydrosilylations see: (a) Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356. (b) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 1339. (c) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494.

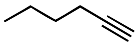
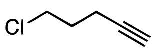
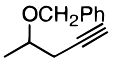
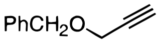
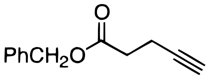
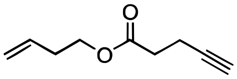
(4) For example see: (a) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909. (b) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045.

10.1021/ol0059697 CCC: $19.00

various easily available ruthenium complexes examined for hydrosilylation of alkynes, $[RuCl_2(p\text{-cymene})]_2$ (**1**)[6] exhibited remarkably high *β*-(*Z*)-selectivity under mild reaction conditions (Table 1). The stereochemistry of the double bond in products was unambiguously determined on the basis of the coupling constants (*J*) of ^1H NMR spectra.[7]

Table 1. Hydrosilylation of Terminal Alkynes Catalyzed by **1**[a]



entry	alkyne	silane (R')	(*Z*)/(*E*)[b]	yield (%)[c]
1	Ph—≡	Ph	96:4	94
2		Et	96:4	81
3		Ph	98:2	98
4		Et	96:4	88
5	4-Me-C_6H_4—≡	Ph	95:5	83
6		Ph	96:4	87
7		Ph	96:4	89
8		Ph	98:2	78
9		Ph	96:4	85
10		Ph	97:3	91

[a] All reactions were carried out at 0.5 M concentration under N_2 atmosphere. [b] Ratios were determined by ^1H NMR integration of the reaction mixture, and no α-isomer was observed in all cases. [c] Isolated yields of pure *β*-(*Z*)-products after column chromatography on silica gel.

Reaction of phenylacetylene with triphenylsilane (1.1 equiv) in CH_2Cl_2 was effectively catalyzed by **1** (5 mol %), and the alkyne was completely consumed within 2 h at 45 °C.[8] Analysis of the crude reaction mixture by ^1H NMR indicated that the *β*-(*Z*)-adduct was formed with significantly high selectivity over the other isomers (*β*-(*Z*):*β*-(*E*):α- = 96: 4:0). Other silyl derivatives such as fully silylated alkanes or silylalkynes were not detected in this reaction. The reaction rate was slowed at lower temperatures, and ca. 30% conversion was observed after 12 h at 25 °C under otherwise identical conditions. Although CH_2Cl_2 was most conveniently used as a solvent in the reaction, other solvents such as benzene, 1,2-dichloroethane, or toluene could also be employed without affecting either activity or selectivity. Employment of other silanes such as triethylsilane as a silylating source resulted in similar regio- and stereoselectivity, although with slightly lower isolated yields compared to the reactions with triphenylsilane (entries 2 and 4). The extremely high selectivity for the formation of the *β*-(*Z*)-isomer was maintained to a very similar extent in the hydrosilylation of various other alkynes examined. The presence of functional groups such as chloro, alkoxy, or ester in the alkyl chain did not affect the *β*-(*Z*) selectivity in the reactions. It is especially noteworthy that the triple bond is exclusively hydrosilylated in the presence of an olefinic bond. For example, reaction of 3-butenyl-4-pentynoate with triphenylsilane afforded the *β*-(*Z*)-adduct with extremely high chemo-, regio-, and stereoselectivity (entry 10).

In the course of the present study, we observed a very interesting and dramatic directing effect of a hydroxyl group, if it is suitably positioned to the triple bond, on the regioselectivity. For example, hydrosilylation of 3-butyn-1-ol with a trialkylsilane gave the α-isomeric product instead of *β*-adducts with excellent selectivity (α-:*β*-(*Z*) = 98:2) in the presence of **1** (5 mol %) at 45 °C (entry 1 in Table 2). No trace of the corresponding *β*-(*E*)-vinylsilane was detected by NMR spectroscopy in this reaction. However, the same reaction with the O-protected alkyne provided the regioisomeric product, *β*-(*Z*)-vinylsilane, as a major isomer (entry 2). This implies that the dramatically changed selectivity for the formation of the Markovnikov's product in the reaction of 3-butyn-1-ol was caused by the directing effect of the hydroxyl group, presumably through the coordination of the carbinol oxygen to a ruthenium metal intermediate.[9] The rather low isolated yields from the reaction of alkynes having a hydroxyl group in Table 2 were mainly due to the competitive O-silylation.[10]

Although the selectivity for the α-regioisomer was moderate in the reaction of a secondary propargylic alcohol (entry 3), an alkyne substrate having a hydroxyl group *β* to the triple bond was hydrosilylated to afford the α-product with excellent selectivity (entry 4). Upon increasing the chain length between the hydroxyl group and the triple bond, the

---

(5) (a) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377. (b) Adams, R. D.; Barnard, T. S. *Organometallics* **1998**, *17*, 2567.

(6) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans*. **1974**, 233.

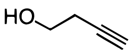
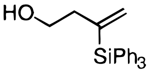
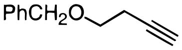
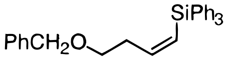
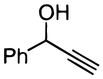
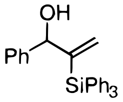
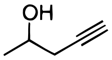
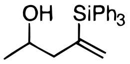
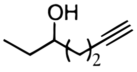
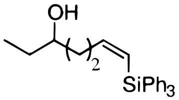
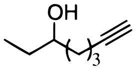
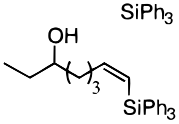
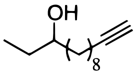
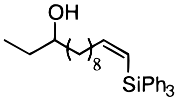
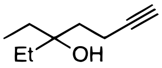
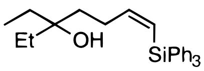
(7) Values for *J* were obtained in the range of 13−15 Hz for the double bond of *β*-(*Z*), 18−20 Hz for *β*-(*E*), and 1.1−2.6 Hz for α-isomers, which are in good agreement with those reported in the literature.[2−4]

(8) **Representative Experimental Procedure.** To a solution of the *p*-cymene Ru complex (30.6 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added triphenylsilane (286.5 mg, 1.1 mmol), and the mixture was stirred for 15 min at 45 °C before addition of phenylacetylene (102.1 mg, 1.0 mmol). The reaction mixture was stirred at the same temperature for 2.5 h under N_2 atmosphere. After evaporation of the solvent under reduced pressure, the crude mixture was chromatographed on silica gel to afford the analytically pure (*Z*)-1-triphenylsilyl-2-phenylethene (341 mg, 94%): ^1H NMR (250 MHz, $CDCl_3$) δ 7.82 (1H, d, $J = 15.3$ Hz), 7.66−7.33 (15H, m), 7.26−6.99 (5H, m), 6.43 (1H, d, $J = 15.3$ Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 150.8, 138.4, 136.2, 135.5, 129.8, 128.3, 127.9, 125.7; HRMS (EI) calcd for $C_{26}H_{22}Si$ 362.1492 (M^+), found 362.1490.

(9) For precedent examples of directional effects by an existing carbonyl group on hydrosilylation see: (a) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc*. **1974**, *96*, 3684. (b) Murai, T.; Kimura, F.; Tsutsui, K.; Hasegawa, K.; Kato, S. *Organometallics* **1998**, *17*, 926.

(10) The relative rate between the triple-bond addition vs O-silylation was ca. 2:1 in ^1H NMR competitive experiments using equivalent molecular amounts of 1-hexyne, 1-butanol, and triphenylsilane in the catalyst system employed here. Those of secondary and tertiary alcohols vs terminal alkynes were ca. 5:1 and >10:1, respectively.

Table 2. Hydroxyl Group Directed Hydrosilylation of Alkynes[a]

entry	alkyne	β-(*Z*):α-[b]	major product	yield (%)[c]
1		2:98		47
2		>99:1		89
3		13:87		60
4		2:98		59
5		92:8		53
6		96:4		61
7		98:2		86
8		98:2		69

[a] Alkynes (1.0 equiv), silane (1.3 equiv), 5 mol % of catalyst **1**, CH_2Cl_2 (0.5 M), 45 °C, 3 h (N_2 atmosphere). [b] Determined by ^1H NMR integration of the reaction mixture. [c] Isolated yields of the major isomer after column chromatography on silica gel.

directing effect induced by the hydroxyl group was, as expected, significantly diminished and the high selectivity for the formation of *β*-(*Z*)-adducts recovered completely (entries 5−7). On the other hand, a tertiary hydroxyl group exhibited little directing effect on the regioselectivity regardless of its position relative to the triple bond. For example, hydrosilylation of 3-ethyl-6-heptyn-3-ol gave the corresponding *β*-(*Z*)-vinylsilane as an almost sole product (entry 8). The significantly reduced directing effect in this case can be attributed to the hindrance of the tertiary hydroxyl group for coordination to a ruthenium metal intermediate, presumably due to steric reasons.

As suggested in most reported transition metal catalyzed reactions, the present hydrosilylation seems to proceed via initial activation of the H−Si bond of a trialkylsilane by the catalyst **1**.[11] Mixing of a trialkysilane with a stoichiometric amount of the ruthenium complex **1** in $CDCl_3$ produces a singlet peak at −10.0 ppm in the ^1H NMR spectrum (in less than 10 min at 45 °C), which corresponds to a ruthenium hydride.[12] Upon addition of an alkyne to the generated ruthenium hydride solution, vinylsilanes are produced immediately and quantitatively with the same selectivity as in the catalytic case. No isomerization of one vinylsilane to other isomers occurred by the catalyst **1** under the reaction conditions employed here. Although the origin of the extremely high selectivity is not clear now, the catalytic hydrosilylation protocol described here is characterized by its excellent chemo-, regio-, and stereoselectivity, functional group compatibility, and mild reaction conditions, and therefore it should be an attractive and practical alternative for the selective preparation of vinylsilanes.

Acknowledgment. We thank the Center for Molecular Design and Synthesis (CMDS) at KAIST for support of this research.

Supporting Information Available: ^1H and ^{13}C NMR, IR, and mass spectroscopic data for all vinylsilane compounds obtained in this study. This material is available free of charge via the Internet at http:/pubs.acs.org.

OL0059697

---

(11) For discussions on mechanistic aspects of hydrosilylation reaction see: (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177. (c) Hofmann, P.; Meier, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, *490*, 51. (d) Uozumi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137. (e) Dash, A. K.; Wang, J. Q.; Eisen, M. S. *Organometallics* **1999**, *18*, 4724 and ref 5a.

(12) (a) Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Organometallics* **1999**, *18*, 3981. (b) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D. *Organometallics* **1998**, *17*, 5607.