A Selective Synthesis of (*E*)-Vinylsilanes by Cationic Rhodium Complex-Catalyzed Hydrosilylation of 1-Alkynes and Tandem Hydrosilylation/Isomerization Reaction of Propargylic Alcohols to β-Silyl Ketones

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Received December 12, 1994[⊗]

(*E*)-Vinylsilanes were obtained with high selectivities by $[Rh(COD)_2]BF_4/2PPh_3$-catalyzed hydrosilylation of 1-alkynes with triethylsilane. A wide range of 1-alkynes were used. The hydrosilylation of propargylic alcohols with triethylsilane gave (*E*)-γ-silyl allylic alcohols **2h**–**r**, a useful source of a chiral alcohol, with high selectivities in excellent yields. The reaction can be carried out without protecting the alcohol functionality. The resulting (*E*)-γ-silyl allylic alcohols could be transformed into β-silyl ketones. The isomerization was also catalyzed by $[Rh(COD)_2]BF_4/2PPh_3$. Furthermore, the tandem hydrosilylation–isomerization of secondary propargylic alcohols could be carried out in a one-pot procedure.

Introduction

Vinylsilanes have received considerable interest as versatile synthetic intermediates.[1] The electrophilic substitution of vinylsilanes is one of the most useful methods for the stereoselective synthesis of substituted alkenes. Recently an intramolecular variant was successfully applied to synthesis of cyclopentenones.[2] Various methods for the preparation of vinylsilanes have been extensively studied. Of the methods, the most straightforward and simple is hydrosilylation of alkynes.[3] However, the method often encounters selectivity problems due to the difficulty in controlling the regio- and stereoselectivity in the addition of the Si–H bond to a carbon–carbon triple bond. The hydrosilylation of 1-alkyne can produce isomers including stereoisomers. For example, platinum-catalyzed hydrosilylation of 1-pentyne with triethylsilane, a commonly used trialkylsilane, was reported to give an 89:11 mixture of (*E*)-1-(triethylsilyl)-1-pentene and 2-(triethylsilyl)-1-pentene.[3g] Complete control of the selectivity is generally difficult. Considerable effort have been devoted to the improvement of the selectivity.

Rhodium complexes have been attracting much attention as efficient catalysts for the hydrosilylation of alkynes,[4] since Ojima and co-workers found that $RhCl(PPh_3)_3$ effectively catalyzed the hydrosilylation of 1-alkynes.[4n] Neutral rhodium complex-catalyzed hydrosilylation of 1-alkynes has been known to give (*Z*)-vinylsilane as a major product via the trans addition of Si–H across the carbon–carbon triple bond. In contrast to an extensive amount of the work on neutral rhodium complex-catalyzed hydrosilylation of 1-alkyne, the same reaction catalyzed by cationic rhodium complex has not been reported.[5] During our hydrosilylation study, we first disclosed that cationic rhodium complex-catalyzed hydrosilylation of 1-hexyne with triethylsilane was highly selective, giving (*E*)-1-(triethylsilyl)-1-hexene as a product.[6] Thus, the cationic rhodium complex shows the opposite stereoselectivity to a neutral counterpart. This novel catalysis by $[Rh(COD)_2]BF_4/2PPh_3$ is expected to be quite a useful tool for the preparation of vinylsilanes. We wish to report herein a synthetic application of the catalysis in detail and then to describe a convenient route

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Table 1. Cationic Rhodium Complex-Catalyzed Hydrosilylation of 1-Alkynes with Et_3SiH[a]

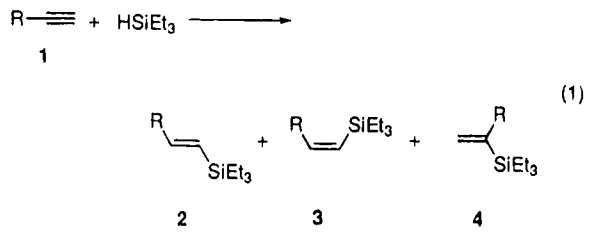
entry	substr	R =	conditions	yield/%[b]	product ratio[c] 2	3	4
1	**1a**	*n*-butyl	room temperature, 30 min	90	99	1	0
2	**1b**	*n*-hexyl	room temperature, 30 min	90	97	3	0
3	**1c**	*n*-octyl	room temperature, 30 min	95	96	4	0
4	**1d**	$CH_2CH_2CH_2Cl$	room temperature, 30 min	87	95	5	0
5[d]	**1e**	$CH_2C(CH_2CH{=}CH_2)(CO_2Et)_2$	50 °C, 16 h	78	100	0	0
6	**1f**	Ph	0 °C, 3 h	62	98	2	0
7	**1g**	$CH_2CH_2CH_2Ph$	room temperature, 20 h	83	97	3	0

[a] A mixture of **1** (8 mmol), $HSiEt_3$ (12 mmol), $[Rh(COD)_2]BF_4$ (0.016 mmol), PPh_3 (0.032 mmol), and acetone (12 mL) was stirred under argon. [b] Isolated yield. [c] Determined by 270 MHz ^1H NMR. [d] **1e** (4 mmol), $HSiEt_3$ (6 mmol), $[Rh(COD)_2]BF_4$ (0.08 mmol), PPh_3 (0.016 mmol), and acetone (6 mL).

to β-silyl ketone by the tandem hydosilylation/isomerization.

Results and Discussion

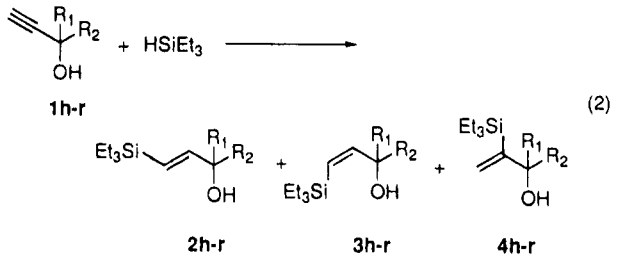
Highly Selective Hydrosilylation of 1-Alkynes. The hydrosilylation of 1-alkyne may give three isomeric vinylsilanes (eq 1). The selectivity depends on many factors, e.g., substituents on the alkyne, hydrosilane, the catalyst metal species, reaction temperature, and solvent.



(1)

We found that $[Rh(COD)_2]BF_4/2PPh_3$-catalyzed hydrosilylation of 1-alkynes with triethylsilane is highly selective, giving **2**, where the triethylsilyl group is substituted at a terminal vinylic carbon and the stereochemistry of the double bond is *E*. The results of the hydrosilylation of 1-alkynes with triethylsilane are summarized in Table 1. (*E*)-Vinylsilanes **2** were obtained in excellent yields with high selectivities. The reactions of **1a**−**d** were rapid and completed within 30 min (entries 1−4). The reaction of **1e** was sluggish and required more forcing conditions to give a product (entry 5). The presence of functional groups such as chloro or ethoxycarbonyl in the alkyl chain did not affect the (*E*)-selectivity of the reaction. The hydrosilylation of phenylacetylene (**1f**) was accompanied by polymerization.[7] A yellow insoluble solid was obtained with a hydrosilylation product. Lowering the reaction temperature did not suppress the polymerization completely. The reaction of phenylacetylene at 0 °C gave **2f** in moderate yield (entry 6). The reaction of 5-phenyl-1-pentyne (**1g**), where the phenyl group is away from the triple bond, gave **2g** in 83% yield (entry 7). No polymerization occurred. The reaction required a rather longer reaction time than that of 1-hexyne (**1a**). Acetone was used as a solvent. Although a cationic rhodium complex can catalyze hydrosilylation of ketones,[8] acetone was not hydrosilylated under the reaction conditions.

The results obtained here have proven that $[Rh(COD)_2]BF_4/2PPh_3$ is one of the most selective catalysts for the hydrosilylation of a 1-alkyne. Our attention has been directed to the hydrosilylation of propargylic alcohols (eq 2). The reaction gives γ-silyl allylic alcohols as products, which are recognized as useful building blocks, particularly as a source of chiral secondary alcohols.[9] The



(2)

selective hydrosilylation of propargylic alcohols opens a direct route to γ-silyl allylic alcohols. Usually, a two-step synthesis from propargylic alcohol is used:[10] C-silylation followed by a stereoselective reduction.[11] The hydrosilylation route is more convenient, because the product can be obtained in a one-pot reaction of propargylic alcohols with hydrosilane. For synthetic purposes, the hydrosilylation of propargylic alcohols using the Speier catalyst has given no satisfactory results.[12] Recently, some improvement was made by the use of a platinum(0) complex.[13] However, the reaction still has a limitation: dimethylphenylsilane, a more reactive hydrosilane, must be used to obtain the product in greater than 95% selectivity. The selectivity is decreased considerably when trialkylsilanes are used.

Propargylic alcohols **1h**−**r** were subjected to hydrosilylation catalyzed by $[Rh(COD)_2]BF_4/2PPh_3$. The re-

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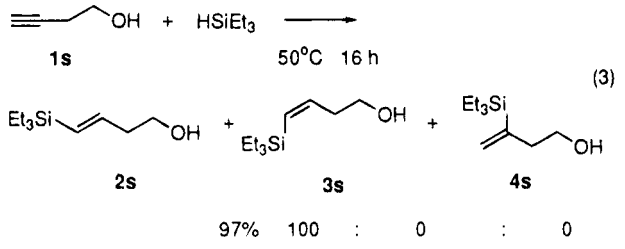
Table 2. Cationic Rhodium Complex-Catalyzed Hydrosilylation of Propargylic Alcohol with Et_3SiH[a]

entry	substrate	R_1 =	R_2 =	conditions	yield/%[b]	product ratio[c] 2	3	4
1[d]	**1h**	H	H	room temperature, 30 min	90	>99	1	0
2	**1i**	H	n-C_5H_{11}	50 °C, 4 h	95	>99	1	0
3	**1j**	H	cyclohexyl	50 °C, 16 h	94	98	2	0
4	**1k**	H	CH_2CH_2Ph	50 °C, 16 h	91	100	0	0
5	**1l**	H	Ph	50 °C, 16 h	94	95	2	3
6	**1m**	H	(*E*)-CH_3CH=CH	50 °C, 3 h	87	100	0	0
7	**1n**	H	(E)-PhCH=CH	50 °C, 2 h	90	100	0	0
8	**1o**	Me	Me	50 °C, 4 h	82	100	0	0
9	**1p**	Me	n-butyl	50 °C, 16 h	84	100	0	0
10	**1q**	$-(CH_2)_5-$		50 °C, 16 h	92	100	0	0
11	**1r**	Me	Ph	50 °C, 16 h	94	100	0	0

[a] A mixture of propargylic alcohol (4 or 8 mmol), Et_3SiH (6 or 12 mmol), acetone (6 or 12 mL), $[Rh(COD)_2]BF_4$ (0.5 mol %), and PPh_3 (1 mol %) was stirred under argon. [b] Isolated yield. [c] Determined by 270-MHz ^1H NMR. [d] $[Rh(COD)_2]BF_4$ (0.2 mol %), PPh_3 (0.4 mol %).

sults are summarized in Table 2.[14] Rhodium complexes have been reported to catalyze the dehydrogenative silylation of alcohols.[15] In all cases listed in Table 2, silylation of the hydroxyl group did not occur.[4a] It is noteworthy that the reaction proceeds well without protecting the alcohol functionality. The hydrosilylation of propargylic alcohols **1h**–**r** was highly selective, giving (*E*)-1-(triethylsilyl)-1-alken-3-ols **2h**–**r** in excellent yields. The hydrosilylation of propargyl alcohol (**1h**) was rapid at room temperature and completed in 30 min, as for 1-hexyne (**1a**), but other alcohols **1i**–**r** appeared to be less reactive. It was necessary to raise the reaction temperature to 50 °C to obtain the product in a high yield. Either secondary or tertiary propargylic alcohols gave the corresponding product in excellent yield. In the case of substrates bearing a carbon–carbon double bond, the reaction occurred chemoselectively at a carbon–carbon triple bond to give β-silyl bis-allylic alcohol (entries 6 and 7). The double-bond geometry of the starting alcohol was completely retained in each case. β-Silyl bis-allylic alcohols were reported to be useful starting materials for the synthesis of cyclopentenones, because they were easily oxidized to β-silyl-substituted divinyl ketones, which readily cyclized to give cyclopentenones.[2] Our hydrosilylation provides a more convenient and direct route to such alcohols. 1-Alkynols **1s** and **1t** were hydrosilylated similarly to give (*E*)-1-(triethylsilyl)-1-alkenol (eqs 3 and 4).



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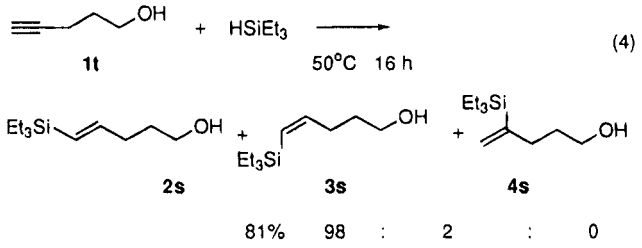
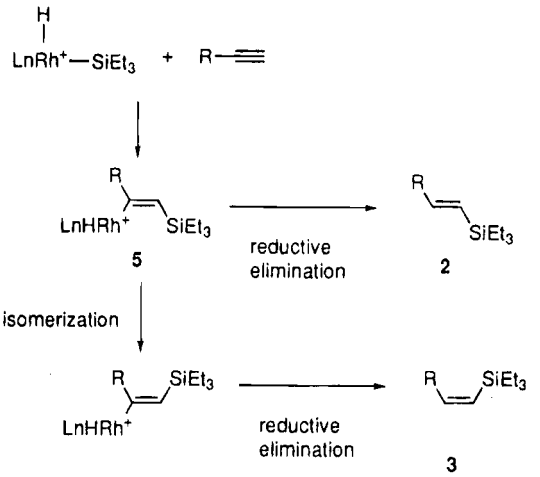


(4)

The (*E*)-selectivity described here can be explained according to the mechanism proposed by Ojima[4b] and Crabtree[3i] (Scheme 1). (*E*)-Vinylsilane (**2**) is formed by reductive elimination from the (β-silylalkenyl)rhodium complex **5**, which is formed by the insertion of alkyne into the rhodium–silicon bond. It is known that a positive charge on the metal center promotes reductive elimination.[16] The cationic rhodium complex has a positive charge on the metal center, generated by the dissociation of BF_4 ligand.[17] As a consequence, reductive elimination leading to (*E*)-vinylsilane (**2**) is much faster than isomerization leading to (*Z*)-vinylsilane (**3**).

Scheme 1



To obtain further evidence that a positive charge on the metal center plays a crucial role in determining the (*E*)-selectivity, the effect of the counter anion on the hydrosilylation of 1-hexyne with triethylsilane was examined. $[Rh(COD)]BPh_4/2PPh_3$ and $[Rh(COD)_2]BF_4/2PPh_3$ were used as catalysts. The BPh_4^- anion cannot fully dissociate because of π-bond coordination to rhodium in a η^6-fashion through one of the arene groups.[18] On the other hand, BF_4^- can dissociate easily to form a positive charge. The reaction was carried out using each

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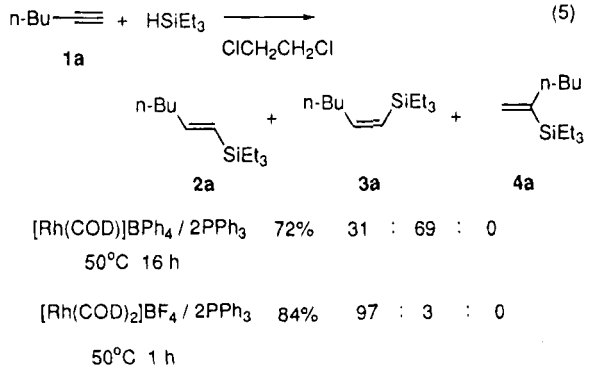
(18) (a) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339. (b) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069.

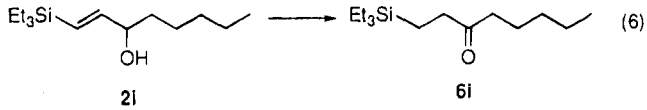
catalyst under the same reaction conditions (eq 5). The



[Rh(COD)]BPh_4/2PPh_3-catalyzed reaction gave (*Z*)-vinylsilane **3a** as a major product in 69% selectivity. The selectivity is similar to that of the neutral rhodium complex-catalyzed hydrosilylation. In contrast, the [Rh(COD)$_2$]BF_4/2PPh_3-catalyzed reaction gave (*E*)-vinylsilane **2a** with 97% selectivity. The result clearly indicates that a positive charge on the metal center, generated by the dissociation of the BF_4^- anion, is responsible for the fast reductive elimination leading to (*E*)-vinylsilane **2**.

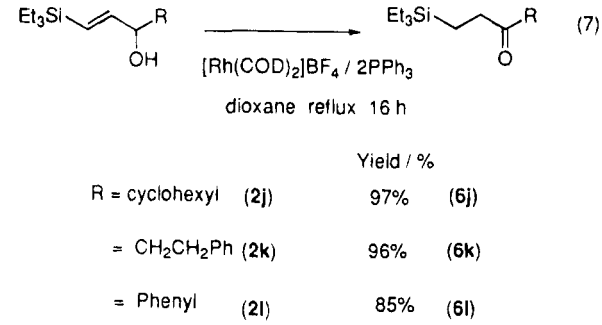
Isomerization of β-Silyl Allylic Alcohols. The isomerization of alkenes is known to be effectively catalyzed by certain transition metal complexes.[19] From a synthetic point of view, the isomerization of allylic alcohols to carbonyl compounds[20] is important. With γ-silyl allylic alcohols in hand, we attempted to isomerize the alcohols to β-silyl ketones, versatile synthetic intermediates.[21] They are usually prepared by the reaction of α,β-unsaturated ketones with a silyl cuprate[22] or by the reaction of lithium enolates of ketones with (trimethylsilyl)methyl iodide.[21d] These methods require a stoichiometric amount of organometallics. The catalytic synthesis is desired.

The isomerization of (*E*)-1-(triethylsilyl)-1-octen-3-ol (**2i**) gave 1-(triethylsilyl)octan-3-one (**6i**) as a product (eq 6). Catalytic activities of several transition metal com-



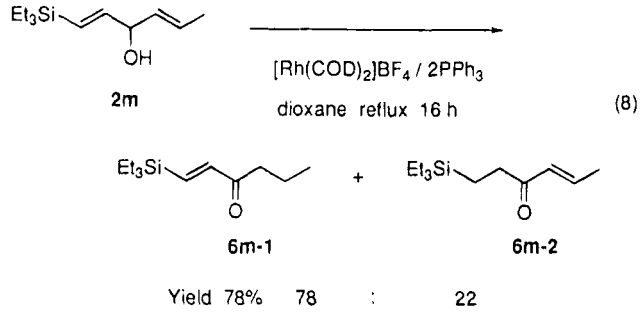
plexes and the effect of reaction conditions on the isomerization were examined. The results are summarized in Table 3. [Rh(COD)$_2$]BF_4/2PPh_3 was the most effective of the metal complexes surveyed. The reaction under reflux in dioxane gave the product in quantitative yield (entry 1). Lowering the reaction temperature resulted in a considerable decrease in the yield of **6i** (entries 2 and 3). The reaction catalyzed by $HRh(PPh_3)_4$, which was reported to be an efficient catalyst for a similar isomerization,[23] gave the product in 65% yield (entry 5). Other neutral rhodium complexes were much less effective (entries 6–8). $RuCl_2(PPh_3)_3$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ did not show any catalytic activity.

The isomerization of **2j–l** was carried out under reflux in dioxane in the presence of a catalytic amount of [Rh(COD)$_2$]BF_4/2PPh_3 (eq 7). β-Silyl ketones **6j–l** were



obtained. The yields of the products were nearly quantitative. The reaction proceeded well even when the substrate bore a bulky substituent such as cyclohexyl at the allylic position.

The isomerization of β-silyl bis-allylic alcohol **2m** gave a 78:22 mixture of two isomeric β-silyl ketones (eq 8). The



major product was ketone **6m–1**, derived from the isomerization of a double bond bearing the methyl substituent. The less hindered double bond of the two possible reaction sites reacted predominantly. These ketones were easily separated by column chromatography. The hydrosilylation/isomerization sequence is useful for the synthesis of a vinylsilane bearing a carbonyl functionality.[24]

Tadem Hydrosilylation/Isomerization of Propargylic Alcohols. Since both the hydrosilylation and the

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Table 3. Isomerization of (*E*)-1-(Triethylsilyl)-1-octen-3-ol (2i) to 2-(Triethylsilyl)-3-octanone (6i)[a]

entry	catalyst	conditions	yield of 6i/%[b]
1	$[Rh(COD)_2]BF_4/2PPh_3$	dioxane, reflux	100
2	$[Rh(COD)_2]BF_4/2PPh_3$	dioxane, 50 °C	1
3	$[Rh(COD)_2]BF_4/2PPh_3$	$ClCH_2CH_2Cl$, reflux	8
4	$[Rh(COD)_2]BF_4/2PPh_3$	toluene, reflux	68
5	$HRh(PPh_3)_4$	dioxane, reflux	65
6	$HRh(CO)(PPh_3)_3$	dioxane, reflux	17
7	$RhCl(PPh_3)_3$	dioxane, reflux	1
8	$[Rh(COD)Cl]_2$	dioxane, reflux	1

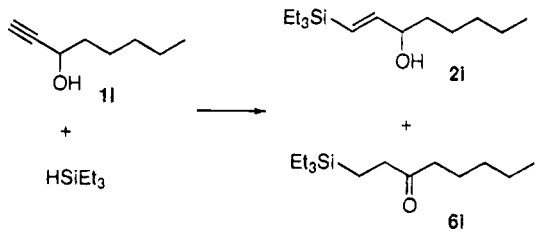
[a] A mixture of **2i** (1 mmol), catalyst (0.01 mmol), and solvent (3 mL) was stirred under argon for 16 h. [b] Determined by GLC.

Table 4. Tadem Hydrosilylation/Isomerization of 1i Catalyzed by $[Rh(COD)_2]BF_4/2PPh_3$[a]

entry	conditions	Et_3SiH/1i	yield of 2i/%[b]	yield of 6i/%[b]
1[c]	acetone, 50 °C, 16 h	1.5	95[d]	0
2	dioxane, reflux, 5 h	1.5	36	9
3	toluene, reflux, 16 h	1.5	33	1
4	diethyl ketone, reflux, 16 h	1.5	26	39
5	diethyl ketone, reflux, 16 h	2.0	0	61[d,e]
6	diethyl ketone, reflux, 16 h	4.0	0	58

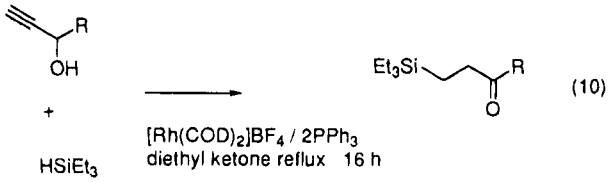
[a] A mixture of **1i** (2 mmol), Et_3SiH (1.5–4.0 equiv), $[Rh(COD)_2]BF_4$ (0.02 mmol), PPh_3 (0.04 mmol), and solvent (3 mL) was stirred under argon. [b] Determined by GLC. [c] **1i** (8 mmol), $HSiEt_3$ (12 mmol), $[Rh(COD)_2]BF_4$ (0.04 mmol), PPh_3 (0.08 mmol), and acetone (6 mL). [d] Isolated yield. [e] Silyl ether **7i** was obtained in 21% yield.

isomerization are successfully catalyzed by the same catalyst system, it was expected that the β-silyl ketone could be obtained from a one-pot reaction of secondary propargylic alcohol with triethylsilane (eq 9). A series



(9)

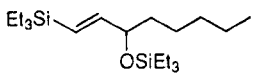
of reactions of 1-octyn-3-ol (**1i**) with triethylsilane were carried out under various conditions to optimize the yield of β-silyl ketone. The results are summarized in Table 4. The reaction at 50 °C for 16 h did not give β-silyl ketone **6i** (entry 1). The hydrosilylation product was obtained. When the reaction was carried out under reflux in dioxane or toluene, the starting material **1i** was consumed (eq 10). The hydrosilylation product **2i** was



(10)

		Yield / %	
R = cyclohexyl	(1j)	64%	(6j)
= CH_2CH_2Ph	(1k)	54%	(6k)
= Phenyl	(1l)	53%	(6l)

obtained in a decreased yield, and the yield of β-silyl ketone **6i** was quite low (entries 2 and 3). The reaction under reflux in diethyl ketone for 16 h gave a β-silyl ketone in 39% and the hydrosilylation product in 26% yield (entry 4). Diethyl ketone was found to be a more suitable solvent. The yield of β-silyl ketone **6i** was improved by increasing the ratio of triethylsilane relative to alcohol **1i**. Employing 2 or 4 equiv of triethylsilane relative to **1i** gave a moderate yield of β-silyl ketone **6i** (entries 5 and 6). Excess amounts of triethylsilane, however, led the formation of the silyl ether of the hydrosilylation product by the dehydrogenative silylation of the alcohol functionality.[16] Triethylsilyl ether **7i** was obtained in 21% yield.



7l

The tandem hydrosilylation/isomerization of propargylic alcohols described here is the first example. Recently a tadem hydrosilylation/isomerization of aliphatic 1-alkynes and 1-alkoxy-2-propynes catalyzed by $Rh_2(pfb)_4$ was reported.[4a] However, a 60-min addition of alkyne to a solution containing a hydrosilane and $Rh_2(pfb)_4$ is necessary for the formation of allylic silanes. Our tadem reaction has no such experimental limitation. The reactants can be added as usual at once.

Using our procedure, secondary propargylic alcohols were subjected to the tandem hydrosilylation/isomerization (eq 10) and moderate yields of β-silyl ketones were obtained in a one-pot procedure.

In conclusion, $[Rh(COD)_2]BF_4/2PPh_3$ is a useful tool for the synthesis of (*E*)-vinylsilanes. The procedure is quite simple, and a wide range of 1-alkynes can be used. The catalyst is easily accessible. Furthermore, a one-pot synthesis of β-silyl ketones from propargylic alcohol and hydrosilane is possible by the tandem hydrosilylation/isomerization.

Experimental Section

Materials. All reagents were dried and purified before use by the usual procedures. $[Rh(COD)_2]BF_4$,[25] $[Rh(COD)]BPh_4$,[18a] $HRh(PPh_3)_4$,[26] $HRh(CO)(PPh_3)_3$,[27] $RhCl(PPh_3)_3$,[28] $[Rh(COD)Cl]_2$,[29] $RuCl_2(PPh_3)_3$,[30] $Pd(PPh_3)_4$,[31] and $Pt(PPh_3)_4$ [32] were prepared by literature methods. 1-Alkynes and 1-alkynols (**1a**, **1b**, **1c**, **1d**, **1f**, **1g**, **1h**, **1i**, **1o**, **1r**, **1s**, **1t**) were purchased. 1-Alkyne (**1e**) was prepared by the reaction of diethyl sodioallylmalonate with propargyl bromide. 1-Alkynols (**1j**, **1k**, **1l**, **1m**, **1n**, **1p**, **1q**) were prepared by the reaction of ethynylmagnesium bromide with the corresponding aldehydes or ketones. Ethynylmagnesium bromide was purchased. Triethylsilane was purchased.

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 270 and 67.8 MHz, respectively, with Me_4Si as internal standard. IR spectra were obtained as liquid films. GC analyses were performed with 3-mm ×

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2-m glass columns packed with either 20% SE-30 on 60/80 mesh Chromosorb W, AW-DMCS, or 5% OV-17 on 60/80 mesh Chromosorb W, AW-DMCS. Column chromatography was carried out on 70–230 mesh silica gel. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

General Procedure for the Hydrosilylation of 1-Alkynes. A two-necked flask equipped with a magnetic stirring bar was charged with $[Rh(COD)_2]BF_4$ (16.2 mg, 0.04 mmol) and PPh_3 (21.0 mg, 0.08 mmol) . The reactor was evacuated and filled with argon. Acetone (12.0 mL) was added to the flask. The mixture was stirred for 5 min. 1-Alkyne (8 mmol) was added via a syringe, followed by similar addition of triethylsilane (1.395 g, 12 mmol). The mixture was stirred under the conditions shown in Tables 1 and 2. The progress of the reaction was monitored by GLC. After the reaction was completed, the solution was concentrated in vacuo. The products were isolated by column chromatography. Samples for elemental analyses were purified by preparative gas chromatography.

(*E*)-1-(Triethylsilyl)-1-hexene (2a):[4b,f] ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.86–0.97 (m, 12H), 1.24–1.43 (m, 4H), 2.07–2.16 (m, 2H), 5.53 (dt, 1H, J = 18.5, 1.3 Hz), 6.02 (dt, 1H, J = 18.5, 6.3 Hz); ^{13}C NMR δ 3.6, 7.4, 14.0, 22.2, 31.1, 36.8, 125.5, 148.8.

(*Z*)-1-(Triethylsilyl)-1-hexene (3a):[4b,f] ^{1}H NMR δ 0.59 (q, 6H, J = 7.9 Hz), 0.86–0.99 (m, 12H), 1.25–1.39 (m, 4H), 2.03–2.12 (m, 2H), 5.37 (dt, 1H, J = 14.2, 1.3 Hz), 6.36 (dt, 1H, J = 14.2, 7.3 Hz); ^{13}C NMR δ 4.8, 7.5, 14.0, 22.5, 32.0, 33.9, 124.9, 150.3.

(*E*)-1-(Triethylsilyl)-1-octene (2b):[4a] ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.16–1.52 (m, 8H), 2.11 (q, 2H, J = 6.3 Hz), 5.53 (dt, 1H, J = 18.8, 1.3 Hz), 6.03 (dt, 1H, J = 18.8, 6.3 Hz); ^{13}C NMR δ 3.6, 7.4, 14.1, 22.6, 28.8 (2C), 31.7, 37.1, 125.5, 148.8. Anal. Calcd for $C_{14}H_{30}Si$: C, 74.25; H, 13.35; Si, 12.40. Found: C, 73.97; H, 13.49.

(*Z*)-1-(Triethylsilyl)-1-octene (3b):[4a] ^{1}H NMR δ 0.61 (q, 6H, J = 7.9 Hz), 0.89 (t, 3H, J = 6.9 Hz), 0.95 (t, 9H, J = 7.9 Hz), 1.19–1.39 (m, 8H), 2.09 (q, 2H, J = 6.6 Hz), 5.38 (d, 1H, J = 14.2 Hz), 6.38 (dt, 1H, J = 14.2, 6.6 Hz); ^{13}C NMR δ 4.8, 7.5, 14.1, 22.7, 29.1, 29.8, 31.8, 34.2, 124.9, 150.4.

(*E*)-1-(Triethylsilyl)-1-decene (2c): ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.27–1.41 (m, 12H), 2.11 (q, 2H, J = 6.6 Hz), 5.53 (dt, 1H, J = 18.8, 1.7 Hz), 6.03 (dt, 1H, J = 18.8, 6.3 Hz); ^{13}C NMR δ 3.6, 7.4, 14.1, 22.7, 28.9, 29.2, 29.3, 29.5, 31.9, 37.1, 125.5, 148.8. Anal. Calcd for $C_{16}H_{34}Si$: C, 75.50; H, 13.47; Si, 11.03. Found: C, 75.41; H, 13.26.

(*Z*)-1-(Triethylsilyl)-1-decene (3c): ^{1}H NMR δ 0.61 (q, 6H, J = 7.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 0.94 (t, 9H, J = 7.9 Hz), 1.27–1.36 (m, 12H), 2.09 (q, 2H, J = 7.3 Hz), 5.38 (dt, 1H, J = 14.2, 1.3 Hz), 6.37 (dt, 1H, J = 14.2, 7.3 Hz); ^{13}C NMR δ 4.7, 7.5, 14.1, 22.7, 29.3, 29.5, 29.6, 29.8, 31.9, 34.1, 124.9, 150.4.

(*E*)-5-Chloro-1-(triethylsilyl)-1-pentene (2d): ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.91 (t, 9H, J = 7.9 Hz), 1.86 (quintet, 2H, J = 7.3 Hz), 2.26 (q, 2H, J = 7.3 Hz), 3.51 (t, 2H, J = 6.3 Hz), 5.61 (d, 1H, J = 18.8 Hz), 5.98 (dt, 1H, J = 18.8, 6.3 Hz); ^{13}C NMR δ 3.4, 7.3, 31.6, 34.0, 44.3, 127.6, 146.1. Anal. Calcd for $C_{11}H_{23}ClSi$: C, 60.37; H, 10.59; Cl, 16.20; Si, 12.84. Found: C, 60.55; H, 10.57; Cl, 16.23.

(*Z*)-5-Chloro-1-(triethylsilyl)-1-pentene (3d): ^{1}H NMR δ 0.63 (q, 6H, J = 7.3 Hz), 0.95 (t, 9H, J = 7.3 Hz), 1.86 (quintet, 2H, J = 7.3 Hz), 2.26 (q, 2H, J = 7.3 Hz), 3.54 (t, 2H, J = 7.3 Hz), 5.48 (dt, 1H, J = 14.2, 1.3 Hz), 6.33 (dt, 1H, J = 14.2, 7.3 Hz); ^{13}C NMR δ 4.6, 7.5, 31.2, 32.6, 44.5, 127.0, 147.7.

(*E*)-4,4-Bis(ethoxycarbonyl)-1-(triethylsilyl)-1,6-heptadiene (2e): ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.92 (t, 9H, J = 7.9 Hz), 1.25 (t, 6H, J = 7.3 Hz), 2.64 (d, 2H, J = 7.3 Hz), 2.71 (d, 2H, J = 6.6 Hz), 4.18 (q, 4H, J = 7.3 Hz), 5.07 (m, 1H), 5.12 (m, 1H), 5.59–5.75 (m, 1H), 5.69 (d, 1H, J = 18.8 Hz), 5.86 (dt, 1H, J = 18.8, 6.6 Hz); ^{13}C NMR δ 3.3, 7.2, 14.1, 36.8, 39.9, 57.2, 61.1, 119.0, 132.0, 132.4, 141.3, 170.7; IR 1730 cm^{-1}. Anal. Calcd for $C_{19}H_{34}O_4Si$: C, 64.36; H, 9.67; O, 18.05; Si, 7.92. Found: C, 64.47; H, 9.63.

(*E*)-1-(Triethylsilyl)-2-phenylethene (2f): ^{1}H NMR δ 0.66 (q, 6H, J = 7.9 Hz), 0.99 (t, 9H, J = 7.9 Hz), 6.42 (d, 1H, J = 19.5 Hz), 6.89 (d, 1H, J =19.5 Hz), 7.18–7.44 (m, 5H); ^{13}C NMR δ 3.5, 7.4, 125.9, 126.3, 127.9, 128.5, 138.5, 144.9. Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15; Si, 12.86. Found: C, 76.75; H, 10.33.

(*Z*)-1-(Triethylsilyl)-2-phenylethene (3f). The characterization was carried out by comparison of its spectra with that in the literature.[3e]

(*E*)-1-(Triethylsilyl)-5-phenyl-1-pentene (2g): ^{1}H NMR δ 0.55 (q, 6H, J = 7.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.72 (quintet, 2H, J = 7.3 Hz), 2.16 (q, 2H, J = 7.3 Hz), 2.60 (t, 2H, J = 7.3 Hz), 5.57 (d, 1H, J = 18.8 Hz), 6.05 (dt, 1H, J = 18.8, 7.3 Hz), 7.13–7.28 (m, 5H); ^{13}C NMR δ 3.6, 7.4, 30.6, 35.4, 36.5, 125.7, 126.3, 128.3, 128.5, 142.5, 148.1. Anal. Calcd for $C_{17}H_{28}Si$: C, 78.39; H, 10.83; Si, 10.78. Found: C, 78.36; H, 11.09.

(*Z*)-1-(Triethylsilyl)-5-phenyl-1-pentene (3g). Compound **3g** could not be isolated in pure form. The ^{1}H-NMR spectrum was same as that of **2g** except δ 5.42 (d, 1H, J = 14.2 Hz), 6.40 (dt, 1H, J = 14.2, 7.3 Hz).

(*E*)-1-(Triethylsilyl)-1-propen-3-ol (2h): ^{1}H NMR δ 0.58 (q, 6H, J = 7.9 Hz), 0.94 (t, 9H, J = 7.9 Hz), 2.00 (br, 1H), 4.18 (dd, 2H, J = 4.3, 1.7 Hz), 5.85 (dt, J = 18.8, 1.7 Hz), 6.20 (dt, J = 18.8, 4.3 Hz); ^{13}C NMR δ 3.3, 7.2, 65.6, 125.6, 146.1; IR 3320 cm^{-1}. Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70; O, 9.28; Si, 16.30. Found: C, 62.43; H, 11.84.

(*Z*)-1-(Triethylsilyl)-1-propen-3-ol (3h): ^{1}H NMR δ 0.62 (q, 6H, J = 7.9 Hz), 0.95 (t, 9H, J = 7.9 Hz), 1.86 (br, 1H), 4.15 (dd, 2H, J = 6.6, 1.3 Hz), 5.63 (dt, J = 14.2, 1.3 Hz), 6.53 (dt, J = 14.2, 6.6 Hz); ^{13}C NMR δ 4.6, 7.4, 63.7, 128.5, 147.5; IR 3320 cm^{-1}.

(*E*)-1-(Triethylsilyl)-1-octen-3-ol (2i): ^{1}H NMR δ 0.57 (q, 6H, J = 7.9 Hz), 0.89 (t, 3H, J = 6.6 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.30–1.41 (m, 6H), 1.42–1.53 (m, 2H), 1.67 (br, 1H), 4.09 (qd, 1H, J = 6.6, 1.3 Hz), 5.76 (dd, 1H, J = 18.8, 1.3 Hz), 6.06 (dd, 1H, J = 18.8, 5.6 Hz); ^{13}C NMR δ 3.4, 7.3, 13.9, 22.6, 25.0, 31.7, 36.9, 75.0, 125.2, 150.2; IR 3330 cm^{-1}. Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47; O, 6.60; Si, 11.58. Found: C, 69.29; H, 12.63.

(*Z*)-1-(Triethylsilyl)-1-octen-3-ol (3i): ^{1}H NMR δ 0.63 (q, 6H, J = 7.9 Hz), 0.87–0.99 (m, 12H), 1.19–1.72 (m, 9H), 4.11 (m, 1H), 5.58 (dd, 1H, J = 14.2, 0.66 Hz), 6.32 (dd, 1H, J = 14.2, 8.9 Hz); ^{13}C NMR δ 4.8, 7.4, 14.0, 22.6, 25.1, 31.8, 37.2, 72.9, 128.2, 151.4; IR 3330 cm^{-1}.

(*E*)-3-Cyclohexyl-1-(triethylsilyl)-1-propen-3-ol (2j): ^{1}H NMR δ 0.55 (q, 6H, J = 7.9 Hz), 0.90 (t, 9H, J = 7.9 Hz), 1.07–1.44 (m, 6H), 1.62–1.80 (m, 6H), 3.82 (t, 1H, J = 5.6 Hz), 5.71 (dd, 1H, J = 18.8, 1.3 Hz), 6.02 (dd, 1H, J = 18.8, 5.6 Hz); ^{13}C NMR δ 3.4, 7.3, 26.11, 26.18, 26.5, 28.3, 28.8, 43.5, 79.4, 126.4, 148.7; IR 3350 cm^{-1}. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88; O, 6.29; Si, 11.03. Found: C, 70.54; H, 12.00.

(*Z*)-3-Cyclohexyl-1-(triethylsilyl)-1-propen-3-ol (3j). Compound **3j** could not be isolated in pure form. The ^{1}H-NMR spectrum was the same as that for **2j** except δ 5.65 (d, 1H, J = 14.2 Hz), 6.35 (dd, 1H, J = 14.2, 9.2 Hz).

(*E*)-1-(Triethylsilyl)-5-phenyl-1-penten-3-ol (2k): ^{1}H NMR δ 0.58 (q, 6H, J = 7.9 Hz), 0.94 (t, 9H, J = 7.9 Hz), 1.72 (br, 1H), 1.83 (dd, 1H, J = 7.9, 6.3 Hz), 1.86 (dd, 1H, J = 7.9, 6.3 Hz), 2.61–2.80 (m, 2H), 4.12 (q, 1H, J = 6.3 Hz), 5.79 (dd, 1H, J = 19.1, 1.3 Hz), 6.09 (dd, 1H, J = 19.1, 5.3 Hz), 7.14–7.30 (m, 5H); ^{13}C NMR δ 3.4, 7.4, 31.7, 38.6, 74.1, 125.7, 125.8, 128.41, 128.48, 142.0, 149.8; IR 3330 cm^{-1}. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21; O, 5.79; Si, 10.15. Found: C, 73.76; H, 10.23.

(*E*)-1-(Triethylsilyl)-3-phenyl-1-propen-3-ol (2l): ^{1}H NMR δ 0.58 (q, 6H, J = 7.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 2.05 (br, 1H), 5.18 (dd, 1H, J = 5.0, 1.3 Hz), 5.94 (dd, 1H, J = 19.1, 1.3 Hz), 6.22 (dd, 1H, J = 19.1, 5.0 Hz), 7.24–7.35 (m, 5H); ^{13}C NMR δ 3.4, 7.3, 77.0, 126.1, 126.5, 127.7, 128.6, 142.7, 148.5; IR 3340 cm^{-1}. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74; O, 6.44; Si, 11.30. Found: C, 72.48; H, 9.87.

(*Z*)-1-(Triethylsilyl)-3-phenyl-1-propen-3-ol (3l). Compound **3l** could not be isolated in pure form. The ^{1}H-NMR spectrum was the same as that for **2l** except δ 5.70 (dd, 1H, J = 13.9, 0.7 Hz), 6.52 (dd, 1H, J = 13.9, 8.9 Hz).

2-(Triethylsilyl)-3-phenyl-1-propen-3-ol (4l). Compound **4l** could not be isolated in pure form. The ^{1}H-NMR spectrum was the same as that for **2l** except δ 5.53 (dd, 1H, J = 2.6, 1.3 Hz), 6.00 (dd, 1H, J = 2.6, 1.6 Hz).

(*E,E*)-1-(Triethylsilyl)-1,4-hexadien-3-ol (2m): ^{1}H NMR δ 0.55 (q, 6H, J = 7.9 Hz), 0.90 (t, 9H, J = 7.9 Hz), 1.68 (d, 3H, J = 6.6 Hz), 1.75 (br, 1H), 4.52 (t, 1H, J = 5.9 Hz), 5.46 (ddq, 1H, J = 15.2, 6.6, 1.3 Hz), 5.67 (dq, 1H, J = 15.2, 6.6 Hz), 5.77 (dd, 1H, J = 19.1, 1.3 Hz), 6.05 (dd, 1H, J = 19.1, 5.0 Hz); ^{13}C NMR δ 3.3, 7.3, 17.7, 75.4, 125.4, 127.4, 132.3, 148.3; IR 3330 cm^{-1}. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39; O, 7.53; Si, 13.22. Found: C, 67.57; H, 11.22.

(*E,E*)-1-(Triethylsilyl)-5-phenyl-1,4-pentadien-3-ol (2n): ^{1}H NMR δ 0.59 (q, 6H, J = 7.9 Hz), 0.95 (t, 9H, J = 7.9 Hz), 2.14 (br, 1H), 4.79 (t, 1H, J = 5.6 Hz), 5.90 (dd, 1H, J = 18.8, 1.3 Hz), 6.15 (dd, 1H, J = 18.8, 5.0 Hz), 6.22 (dd, 1H, J = 16.2, 6.6 Hz), 6.60 (dd, 1H, J = 16.2, 1.0 Hz), 7.19−7.39 (m, 5H); ^{13}C NMR δ 3.3, 7.3, 75.4, 126.4, 126.5, 127.6, 128.5, 130.49, 130.55, 136.7, 147.6; IR 3360 cm^{-1}. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55; O, 5.83; Si, 10.23. Found: C, 74.12; H, 9.40.

(*E*)-1-(Triethylsilyl)-3-methyl-1-buten-3-ol (2o): ^{1}H NMR δ 0.57 (q, 6H, J = 7.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.30 (s, 6H), 1.72 (br, 1H), 5.74 (d, 1H, J = 19.1 Hz), 6.18 (d, 1H, J = 19.1 Hz); ^{13}C NMR δ 3.4, 7.3, 29.4 (2C), 72.1, 120.4, 154.8; IR 3350 cm^{-1}. Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07; O, 7.98; Si, 14.02. Found: C, 65.70; H, 12.29.

(*E*)-1-(Triethylsilyl)-3-methyl-1-hepten-3-ol (2p): ^{1}H NMR δ 0.58 (q, 6H, J = 7.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.21−1.34 (m, 4H), 1.26 (s, 3H), 1.47−1.57 (m, 3H), 5.72 (d, 1H, J = 19.1 Hz), 6.09 (d, 1H, J = 19.1 Hz); ^{13}C NMR δ 3.4, 7.3, 14.0, 23.1, 26.1, 27.8, 41.9, 74.3, 121.1, 154.0; IR 3390 cm^{-1}. Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47; O, 6.60; Si, 11.58. Found: C, 69.63; H, 12.41.

1-((*E*)-2-(Triethylsilyl)ethenyl)-1-cyclohexanol (2q): ^{1}H NMR δ 0.53 (q, 6H, J = 7.9 Hz), 0.89 (t, 9H, J = 7.9 Hz), 1.22−1.66 (m, 11H), 5.75 (d, 1H, J = 19.1 Hz), 6.12 (d, 1H, J = 19.1 Hz); ^{13}C NMR δ 3.4, 7.3, 22.1 (2C), 25.5, 37.5 (2C), 72.7, 121.1, 154.8; IR 3380 cm^{-1}. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74; O, 6.65; Si, 11.68. Found: C, 69.74; H, 11.91.

(*E*)-1-(Triethylsilyl)-3-phenyl-1-buten-3-ol (2r): ^{1}H NMR δ 0.59 (q, 6H, J = 7.6 Hz), 0.93 (t, 9H, J = 7.6 Hz), 1.63 (s, 3H), 2.05 (br, 1H), 5.87 (d, 1H, J = 19.1 Hz), 6.34 (d, 1H, J = 19.1 Hz), 7.20−7.35 (m, 3H), 7.41−7.47 (m, 2H); ^{13}C NMR δ 3.4, 7.3, 29.3, 75.7, 122.2, 125.2, 126.8, 128.1, 146.5, 153.1; IR 3400 cm^{-1}. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98; O, 6.10; Si, 10.70. Found: C, 73.36; H, 9.95.

(*E*)-1-(Triethylsilyl)-1-buten-4-ol (2s): ^{1}H NMR δ 0.53 (q, 6H, J = 7.9 Hz), 0.90 (t, 9H, J = 7.92 Hz), 1.66 (br, 1H), 2.38 (qd, 2H, J = 6.3, 1.3 Hz), 3.65 (t, 2H, J = 6.3 Hz), 5.67 (dt, 1H, J = 18.8, 1.3 Hz), 5.99 (dt, 1H, J = 18.8, 6.3 Hz); ^{13}C NMR δ 3.4, 7.3, 40.3, 61.5, 130.1, 143.9; IR 3320 cm^{-1}. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90; O, 8.58; Si, 15.07. Found: C, 64.22; H, 11.86.

(*E*)-1-(Triethylsilyl)-1-penten-5-ol (2t): ^{1}H NMR δ 0.51 (q, 6H, J = 7.9 Hz), 0.89 (t, 9H, J = 7.9 Hz), 1.63 (quintet, 2H, J = 6.6 Hz), 2.08 (br, 1H), 2.17 (qd, 2H, J = 7.6, 1.3 Hz), 3.60 (t, 2H, J = 6.6 Hz), 5.55 (dt, 1H, J = 18.5, 1.3 Hz), 6.01 (dt, 1H, J = 18.5, 6.3 Hz); ^{13}C NMR δ 3.4, 7.3, 31.6, 33.2, 62.3, 126.5, 147.6; IR 3320 cm^{-1}. Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07; O, 7.98; Si, 14.02. Found: C, 65.88; H, 12.32.

(*Z*)-1-(Triethylsilyl)-1-penten-5-ol (3t). Compound **3t** could not be isolated in pure form. The ^{1}H-NMR spectrum was the same as that for **2t** except δ 5.39 (d, 1H, J = 14.2 Hz), 6.34 (dt, 1H, J = 14.2, 7.3 Hz).

General Procedure for the Isomerization of (*E*)-γ-Silyl Allylic Alcohols. A mixture of (*E*)-γ-silyl allylic alcohol (1.0 mmol), $[Rh(COD)_2]BF_4$ (4.1 mg, 0.01 mmol), PPh_3 (5.2 mg, 0.02 mmol), and dioxane (3.0 mL) was stirred under argon in a two-necked flask equipped with a magnetic stirring bar. The stirred mixture was heated for 16 h. Reaction temperatures are shown in Table 3, eqs 7 and 8. The progress of the reaction was monitored by GLC. After the reaction was completed, the solution was concentrated in vacuo. The products were isolated by column chromatography.

1-(Triethylsilyl)octan-3-one (6i): ^{1}H NMR δ 0.52 (q, 6H, J = 7.9 Hz), 0.74−0.80 (m, 2H), 0.89 (t, 3H, J = 7.3 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.21−1.37 (m, 4H), 1.58 (quintet, 2H, J = 7.3 Hz), 2.31−2.43 (m, 4H); ^{13}C NMR δ 3.1, 5.0, 7.3, 13.9, 22.4, 23.7, 31.4, 37.1, 42.0, 212.2; IR 1715 cm^{-1}. Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47; O, 6.60; Si, 11.58. Found: C, 69.04; H, 12.53.

1-Cyclohexyl-3-(triethylsilyl)propan-1-one (6j): ^{1}H NMR δ 0.52 (q, 6H, J = 7.9 Hz), 0.72−0.78 (m, 2H), 0.93 (t, 9H, J = 7.6 Hz), 1.13−1.43 (m, 5H), 1.65−1.83 (m, 5H), 2.32−2.44 (m, 3H); ^{13}C NMR δ 3.2, 4.8, 7.4, 25.7, 25.8, 28.7, 35.0, 50.3, 215.0; IR 1710 cm^{-1}. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88; O, 6.29; Si, 11.03. Found: C, 70.70; H, 12.08.

1-(Triethylsilyl)-5-phenylpentan-3-one (6k): ^{1}H NMR δ 0.49 (q, 6H, J = 7.6 Hz), 0.72−0.78 (m, 2H), 0.91 (t, 9H, J = 7.6 Hz), 2.28−2.35 (m, 2H), 2.76 (t, 2H, J = 7.6 Hz), 2.90 (t, 2H, J = 7.6 Hz), 7.14−7.30 (m, 5H); ^{13}C NMR δ 3.1, 5.0, 7.3, 30.0, 37.5, 43.5, 126.0, 128.3, 128.4, 141.2, 211.0; IR 1710 cm^{-1}. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21; O, 5.79; Si, 10.15. Found: C, 73.82; H, 10.31

1-(Triethylsilyl)-3-phenylpropan-3-one (6l): ^{1}H NMR δ 0.56 (q, 6H, J = 7.6 Hz), 0.90−1.00 (m, 11H), 2.90−2.96 (m, 2H), 7.42−7.58 (m, 3H), 7.93−7.98 (m, 2H); ^{13}C NMR δ 3.2, 5.8, 7.4, 33.0, 128.0, 128.5, 132.8, 136.8, 201.3; IR 1690 cm^{-1}. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74; O, 6.44; Si, 11.30. Found: C, 72.40; H, 9.53.

(*E*)-1-(Triethylsilyl)-1-hexen-3-one (6m-1): ^{1}H NMR δ 0.65 (q, 6H, J = 7.9 Hz), 0.95 (t, 3H, J = 7.3 Hz), 0.96 (t, 9H, J = 7.9 Hz), 1.65 (sextet, 2H, J = 7.3 Hz), 2.59 (t, 2H, J = 7.3 Hz), 6.51 (d, 1H, J = 19.1 Hz), 7.02 (d, 1H, J = 19.1 Hz); ^{13}C NMR δ 3.0, 7.1, 13.7, 17.6, 41.3, 143.4, 143.5, 200.2; IR 1670 cm^{-1}. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39; O, 7.53; Si, 13.22. Found: C, 67.66; H, 11.40.

(*E*)-1-(Triethylsilyl)-4-hexen-3-one (6m-2): ^{1}H NMR δ 0.53 (q, 6H, J = 7.9 Hz), 0.78−0.84 (m, 2H), 0.94 (t, 9H, J = 7.9 Hz), 1.90 (dd, 3H, J = 6.9, 1.7 Hz), 2.44−2.50 (m, 2H), 6.14 (dq, 1H, J = 15.8, 1.7 Hz), 6.85 (dq, 1H, J = 15.8, 6.9 Hz); ^{13}C NMR δ 3.1, 7.3, 5.4, 18.2, 34.6, 131.3, 142.0, 201.3.

General Procedure for the Tadem Hydrosilylation/Isomerization of 1-Alkyn-3-ols. A two-necked flask equipped with a magnetic stirring bar was charged with $[Rh(COD)_2]BF_4$ (8.1 mg, 0.02 mmol) and PPh_3 (10.5 mg, 0.04 mmol) . The reactor was evacuated and filled with argon. Solvent (3.0 mL) was added to the flask. The mixture was stirred for 5 min. 1-Alkyn-3-ol (2.0 mmol) was added via a syringe, followed by similar addition of triethylsilane. The mixture was stirred under the conditions shown in Table 4 and eq 10. The progress of the reaction was monitored by GLC. After the reaction was completed, the solution was concentrated in vacuo. The products were isolated by column chromatography.

(*E*)-3-(Triethylsiloxy)-1-(triethylsilyl)-1-octene: ^{1}H NMR δ 0.54 (q, 6H, J = 7.9 Hz), 0.57 (q, 6H, J = 7.3 Hz), 0.86 (t, 3H, J = 6.9 Hz), 0.90 (t, 9H, J = 7.3 Hz), 0.93 (t, 9H, J = 7.9 Hz), 1.16−1.51 (m, 8H), 4.02 (q, 1H, J = 5.9 Hz), 5.65 (dd, 1H, J = 18.8, 1.0 Hz), 5.98 (dd, 1H, J = 18.8, 5.9 Hz); ^{13}C NMR δ 3.5, 4.9, 6.8, 7.3, 14.0, 22.6, 25.0, 31.8, 38.0, 76.1, 124.5, 150.9.

Acknowledgment. We are grateful for a Grant-in-Aid for Science Research (06750893) from the Ministry of Education, Science and Culture of Japan and a Research Grant from Kihara Memorial Yokohama Foundation for the Advancement of Life Sciences.

JO9421034