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Rhodium-Catalyzed Hydrosilylation of Internal Alkynes with Silane Reagents bearing Heteroatom Substituents. Studies on the Regio-/Stereochemistry and Transformation of the Produced Alkenylsilanes by Rhodium-Catalyzed Conjugate Addition

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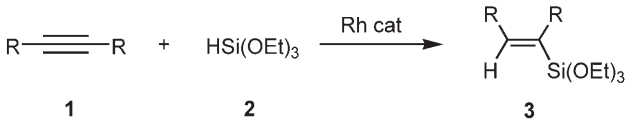
Abstract: Rhodium-catalyzed hydrosilylation of internal alkynes furnished (*E*)-1,2-disubstituted alkenylsilanes. The obtained alkenylsilane was subjected to reaction with α,β-unsaturated carbonyl compounds in the presence of a rhodium catalyst to undergo conjugate addition. One-pot hydrosilylation-conjugate addition with a rhodium catalyst was also performed.

Keywords: conjugate addition; 1,2-disubstituted alkenylsilanes; hydrosilylation; internal alkynes; rhodium

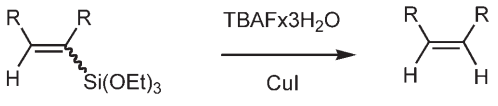
Hydrosilylation of alkynes serves as an important tool for the synthesis of alkenylsilanes, which can be transformed into a variety of organic molecules by transition metal-catalyzed carbon-carbon bond-forming reactions with organic electrophiles.[1] We have been studying the use of rhodium complexes as a catalyst for the hydrosilylation of alkynes and found that a rhodium catalyst was effective for the regio- and stereoselective hydrosilylation of terminal alkynes.[2] Our further interest has turned to investigation of the reaction of internal alkynes, which form 1,2-disubstituted alkenylsilanes.[3] We herein report that with the use of a rhodium complex as a catalyst the hydrosilylation of internal alkynes took place at room temperature. Further reactions of the thus formed 1,2-disubstituted alkenylsilanes with several α,β-unsaturated carbonyl compounds in the presence of a rhodium complex were also studied.

The reaction of diphenylethyne (**1a**) with triethoxysilane (**2**) was carried out in the presence of 0.5 mol % of $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) at room temperature. The corresponding alkenylsilane (**3a**) was obtained after stirring for 3 h [Eq. (1)]. Hydrosilylation of 3-hexyne (**1b**) with **2** also proceeded stereoselectively to give (*E*)-3-triethoxysilyl-hex-3-ene (**3b**) in a quantitative yield. The reaction proceeded efficiently without solvent. Worthy of note is that the reaction took place at room temperature with a small amount of the rhodium catalyst (0.025–0.5 mol %). By contrast, the similar reaction with a platinum catalyst, $(n\text{-}Bu_4N)_2PtCl_6$, did not proceed at room temperature.



(1)

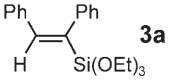
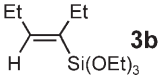
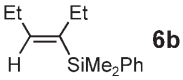
The stereochemistry of the product was found to be the *E*-form, which was confirmed by treatment of **3a** with tetra-*n*-butylammonium fluoride (TBAF) in the presence of CuI to give stilbene (**4a**) ($Z/E = 9:1$), suggesting that *cis*-addition of H–Si took place [Eq. (2)].(4) [4] To confirm the stereochemistry of **3b**, whose desilylation led to the rather volatile 3-hexene, hydrosilylation of dodecyne (**1c**) was carried out and the desilylation of **3c** with TBAF afforded (Z)-6-dodecene (**4c**) in 81% yield. The formation of **4c** was also confirmed by comparison with the authentic sample, which was synthesized by a Wittig reaction of hexanal and the phosphonium salt of 1-bromohexane. The stereochemical outcome of hydrosilylation contrasts to that with a ruthenium catalyst reported by Trost to induce the *trans*-addition.[5,6]



R = Ph; 87% (Z/E = 9:1)
R = n-C_5H_{11}; 81% (Z/E = 100:0)

(2)

Table 1. Rhodium-catalyzed hydrosilylation of internal alkynes.[a]

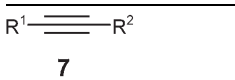
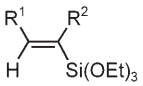
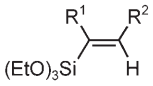
Alkyne (R)	Silane	Catalyst	Time [h]	Product	Yield [%]
Ph (**1a**)	$HSi(OEt)_3$ (**2**)	$[Rh(cod)Cl]_2$ (0.25)	3	 **3a**	99
	2	(0.025)	24	**3a**	84
Et (**1b**)	**2**	$[Rh(cod)Cl]_2$ (0.25)	3	 **3b**	83
	$HSiMe_2Ph$ (**5**)	$[Rh(cod)Cl]_2$ (0.25)	1	 **6b**	99
	5	$RhCl(PPh_3)_3$ (0.5)	3	**6b**	94
	5	$RhI(PPh_3)_3$ (0.5)	3	**6b**	84

[a] Unless noted, the reaction was carried out with an internal alkyne (1.0 mmol) and silane (1.0 mmol) at room temperature for 3 h.

Table 1 summarizes the hydrosilylation of internal alkynes with several silane reagents. In contrast with our previous findings on the hydrosilylation of terminal alkynes, there is little advantage of the use of rhodium iodide concerning the stereoselectivity as well as the reactivity of rhodium catalyst.[2] Although other rhodium catalysts such as $RhCl(PPh_3)_3$ and $RhI(PPh_3)_3$ also affected the hydrosilylation, the reactions were slightly slower than with $[RhCl(cod)]_2$. In addition to alkoxysilane **2**, dimethylphenylsilane (**5**) underwent the hydrosilylation to give **6**.

We next investigated the hydrosilylation of unsymmetrical internal alkynes (**7**: $R^1C{\equiv}CR^2$). As shown in Table 2, several internal alkynes with different substituents were examined. It was not easy to control the regioselectivity with the differences of steric bulkiness. Although the regiochemistry in the reaction of phenyl(trimethylsilyl)ethyne (**7a**) with **2** was highly controlled to afford (*E*)-1-triethoxysilyl-1-trimethylsilyl-2-phenylethene (**8a**) exclusively, hydrosilylation of 1-trimethylsilyl-1-propyne (**7b**) or 1-trimethylsilyl-1-octyne (**7c**) afforded a mixture of regioisomers. On the other hand, it should be pointed out that the regioselectivity of the rhodium-catalyzed hydrosilylation was strongly influenced by the electronic effect of the substituent on the aromatic ring. In the reaction of triethoxysilane (**2**) with the 1-aryl-1-octyne **7d** bearing an electron-donating methoxy group the hydrosilylation afforded **8d** and **9d** in a ratio of 62:38. The reaction with unsubstituted **7e** resulted in a 42:58 ratio of **8e** and **9e**. By contrast, a drastic change of the regioselectivity was observed when an alkyne bearing an electron-withdrawing nitro group, e.g., **7f**, was employed as the substrate. Gevorgyan recently reported regiochemical studies on the palladium-catalyzed hydrostannylation of unsymmetrical internal alkynes.[6] The course of the regiochemistry was shown to be similar to that of the present rhodium-catalyzed hydrosilylaton.

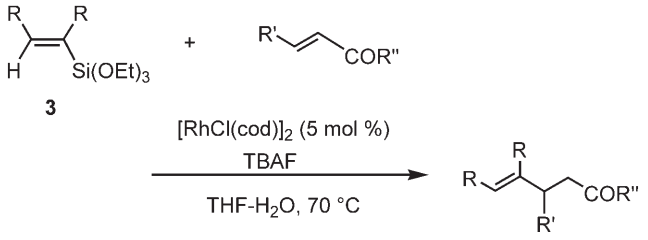
Table 2. Rhodium-catalyzed hydrosilylation of unsymmetrical internal alkynes.[a]

 **7** R^1	R^2	Yield [%] of (**8**+**9**)	Ratio[b] of **8**:**9**  **8**	:  **9**
TMS	C_6H_5	99	100	0
TMS	n-C_6H_{13}	99	24	84
TMS	Me	99	60	40
4-$MeOC_6H_4$	n-C_6H_{13}	92[b]	62	38
C_6H_5	$_n$-C_6H_{13}	86[b]	42	58
4-$O_2NC_6H_4$	n-C_6H_{13}	65[b]	11	89

[a] The reaction was carried out with 1.0 mmol of alkyne, 1.0 mmol of silane reagent, and 0.0025 mmol of $[RhCl(cod)]_2$ at room temperature.
[b] The ratio was estimated by ^1H NMR analysis.

Since the obtained 1,2-disubstituted alkenylsilanes possess heteroatom substituents on the silicon atom, these alkenylsilanes exhibit potential synthetic utility for further transformations to various organic molecules by transition metal-catalyzed reactions. As a representative application we studied the rhodium-catalyzed conjugate addition of **3** to α,β-unsaturated carbonyl compounds [Eq. (3)]. Rhodium-catalyzed conjugate addition of organosilicon reagents was recently demonstrated by Oi and Inoue, Murata and Masuda, Li, and our group.(7) [7] However, the reaction with 1,2-disubstituted alkenylsilanes has not been examined so far. Alkenylsilane **3b** was subjected to reaction with dimethyl fumarate (**10**) in the presence of TBAF and 5 mol % of $[RhCl(cod)]_2$ in THF. The reaction took place to yield the conjugate addition product **11** in 75% yield after stirring at 70 °C for 24 h. As shown in Table 3, the reaction of **3b** with dimethyl maleate (**12**) also afforded **11** in 78%

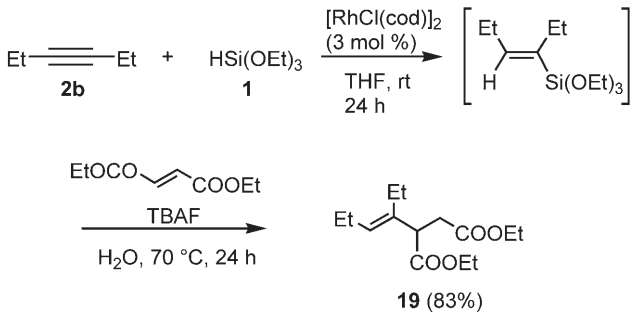
yield. Ethyl cinnamate (**13**) also reacted to afford the corresponding conjugate addition product **14** in 63% yield. The reaction of α,β-unsaturated ketone **15** also took place to yield **16**. In addition, 1,2-diphenylethenylsilane **3a** reacted with diethyl fumarate **17** to furnish **18** in 61% yield.



(3)

A one-pot procedure for the sequential rhodium-catalyzed hydrosilylation and conjugate addition was found to occur effectively. The reaction of 3-hexyne (**1b**) and triethoxysilane was carried out in the presence of 5 mol % of $[RhCl(cod)]_2$ at room temperature. After stirring for 24 h, TBAF and diethyl fumarate were added to the resulting reaction mixture, which was then heated at 70 °C and stirring was continued for further 24 h. Overall yield of the hydrosilylation-conjugate addition to afford **19** was 83% as shown in Scheme 1.

In conclusion, the hydrosilylation of internal alkynes was found to proceed at room temperature with a rhodium complex. The obtained 1,2-disubstituted alkenylsilane was subjected to further reaction with α,β-unsaturated carbonyl compounds leading to the conjugate addition products. The reactions were also carried out in one-pot successfully with a rhodium-catalyzed hydrosilylation-conjugate addition sequence.



Scheme 1.

Table 3. Rhodium-catalyzed conjugate addition of 1,2-disubstituted alkenylsilanes.[a]

Silane	Substrate	Product	Yield [%]
3b	MeOCO, COOMe (**10**)	Et, Et, COOMe, COOMe (**11**)	75
	COOMe, COOMe (**12**)		78
	Ph, OEt, O (**13**)	Et, Et, COOEt, Ph (**14**)	63
	Ph, Me, O (**15**)	Et, Et, COMe, Ph (**16**)	78
3a	EtOCO, COOEt (**17**)	Ph, Ph, COOEt, COOEt (**18**)	61

[a] The reaction was carried out with alkenylsilane (1.5 mmol), α,β-unsaturated carbonyl compound (0.5 mmol) and TBAF (1.5 mmol) with $[RhCl(cod)]_2$ (5 mol %) in THF (6 mL) and H_2O (2 mL) at 70 °C .

Experimental Section

One-Pot Hydrosilylation-Conjugate Addition of 1b and 2

To a solution of 3-hexyne (**1b**, 0.17 mL, 1.5 mmol) and $[RhCl(cod)]_2$ (12.4 mg, 0.025 mmol) in THF (4.5 mL) was added triethoxysilane (**2**, 0.28 mL, 1.5 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 24 h. Diethyl fumarate (**17**, 0.082 mL, 0.5 mmol), TBAF (1.5 mL of 1 M THF solution, 1.5 mmol), and 2 mL of water were added and the resulting mixture was heated at 70 °C for 24 h. After cooling to room temperature, the mixture was poured into diethyl ether (20 mL) and 1 M hydrochloric acid (20 mL) and the two phases were separated. The aqueous layer was extracted with diethyl ether twice and the combined organic layers were dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a crude oil, which was subjected to silica gel column chromatography to afford **19** as a colorless oil; overall yield: 105 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 6.8 Hz, 3H), 0.97 (t, J = 6.8 Hz, 3H), 1.23 (t, J = 5.7 Hz, 6H), 1.96–2.19 (m, 4H), 2.45 (dd, J = 16.8, 5.4 Hz, 1H), 2.90 (dd, J = 16.8, 10.2 Hz, 1H), 3.42 (dd, J = 10.2, 5.4 Hz, 1H), 4.10 (q, J = 5.7 Hz, 2H), 4.13 (q, J = 5.7 Hz, 2H), 5.28 (t, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 14.3, 14.4, 21.2, 23.2, 36.6, 47.8, 60.7, 60.9, 130.3, 137.2, 172.3, 173.7; anal. calcd. for $C_{14}H_{24}O_4$: C 65.60, H 9.44; found: C 65.16, H 9.32.

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