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(Citation)
Polyhedron, 19(5):567-568

(Issue Date)
2000-03

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90000450

Stereodivergent Hydrosilylation of 1-Alkynes Catalyzed by $RhI(PPh_3)_3$ Leading to (*E*)- and (*Z*)-Alkenylsilanes and the Application to Polymer Synthesis

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Abstract

Hydrosilylation of 1-alkynes catalyzed by $RhI(PPh_3)_3$ gives (E)- and (Z)-alkenylsilanes in a stereodivergent manner by switching the reaction conditions and the order of the addition of the reagents. The reaction is also applied to the synthesis of silicon containing polymers with (E) and (Z) main-chain structrues via polyaddition.

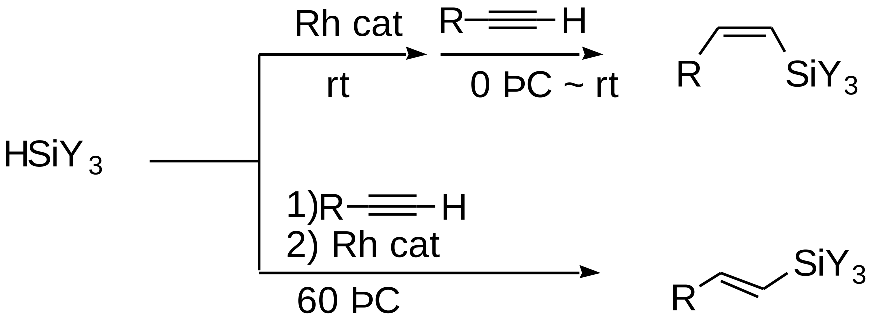
Key words: Hydrosilylation, $RhI(PPh_3)_3$, Stereodivergent, Alkenylsilanes, Polyaddition

Hydrosilylation serves as one of the most fundamental reaction in organosilicon chemistry. The reaction proceeds by the catalysis of a variety of transition metals and control of the reactivity and the selectivity in the hydrosilylation have been a major concern in synthetic organic chemistry as well as organometallic chemistry.[1,2] The hydrosilylation of a terminal alkyne with a hydrosilane, for example, would form regio- and stereochemical isomers.

We found that the use of $RhI(PPh_3)_3$ as a catalyst for the hydrosilylation of a terminal alkyne furnishes E and Z-alkenylsilanes in stereochemically divergent manners by switching the order of the addition of the reagents and reaction conditions.[4]

The process is illustrative in Scheme 1. When an alkyne was added to a pretreated mixture of a hydrosilane and the rhodium catalyst at room temperature for 2 h, (*Z*)-alkenylsilane was obtained in a good yield (>99%) with an excellent stereoselectivity (>99:1). On the other hand, reaction of the mixture of a hydrosilane, an alkyne, and the catalyst at 60 ˚C lead to (*E*)-product (>99% yield, >99% selectivity).

Scheme 1



The results on the stereodivergnet hydrosilylation leading to E- and Z-alkenylsilanes are summarized in Table 1. The hydrosilylation is effective for a variety of hydrosilanes, namely, the ones with heteroatom substituent(s) such as a siloxy or an alkoxy group in contrast that most of the previous rhodium-catalyzed hydrosilylations have been examined with the use of triethylsilane.[1]

Table 1. Stereoselective hydrosilylation of 1-alkynes leading to *Z* and *E*-alkenylsilanes

alkyne	$\mathrm{HSiY_3}$	condn[a]	temp/˚C, time/h	ratio, *E*:*Z*
$\mathrm{PhC{\equiv}CH}$	$\mathrm{HSiMe_2OSiMe_3}$	A	rt, 2	1:100
		B	60, 1	100:0
	$\mathrm{HSiMe(OEt)_2}$	A	60, 48[b]	2:98
		B	60, 1	100:0
$\mathrm{4\text{-}MeOC_6H_4C{\equiv}CH}$	$\mathrm{HSiMe_2OSiMe_3}$	A	rt, 2	2:98
$\mathrm{4\text{-}MeOC_6H_4C{\equiv}CH}$	$\mathrm{HSiMe_2OSiMe_3}$	B	60, 2	100:0
$n\text{-}\mathrm{C_6H_{13}C{\equiv}CH}$	$\mathrm{HSiMe(OEt)_2}$	A	80, 48[c]	3:97

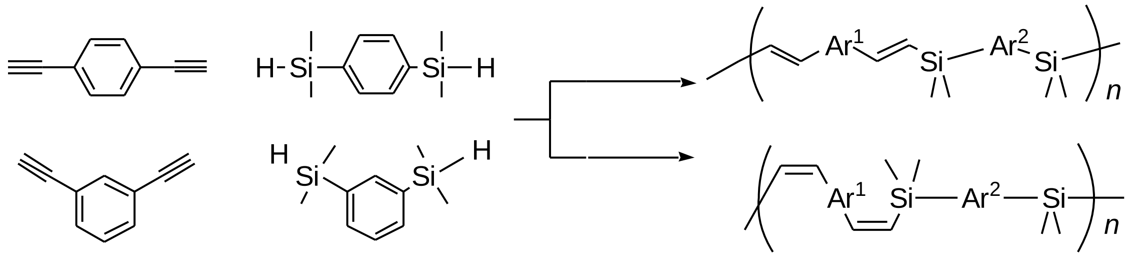
a) Condn A: Pretreatment of a hydrosilane with 0.1 mol% of the rhodium catalyst at rt for 2 h followed by the addition of an alkyne, B: The reaction with a mixture of a hydrosilane, an alkyne and the catalyst.
b) The amount of the rhodium catalyst: 0.01 mol%. c) The amount of the rhodium catalyst: 0.005 mol%.

The obtained alkenylsilanes were successfully subjected to transformation reactions of the carbon-silicon bond to a carbon-carbon bond via the palladium-catalyzed cross-coupling reaction with retention of the stereochemistry.[5]

Then, the stereodivergent hydrosilylation is applied to bis-alkynes with bis-hydrosilanes via polyaddition to afford the poly[(phenylene)-((E), or

(Z)-vinylene)-(silylene)]s. The reactions proceeded in a highly stereospecific manner as shown in Scheme 2 with the ratios of higher than 90%. The molecular weights and the molecular weight distributions were estimated by SEC analyses ranging 6000-20000 and 2.4-5.5, respectively. UV absorption and emission spectra of the polymers were also measured.[6]

Scheme 2



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