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Selective Synthesis of (*Z*)-1-Ethylidene-2-silylcycloalkanes by Palladium-Catalyzed Hydrosilylation of 1-Vinylcycloalkenes[1]

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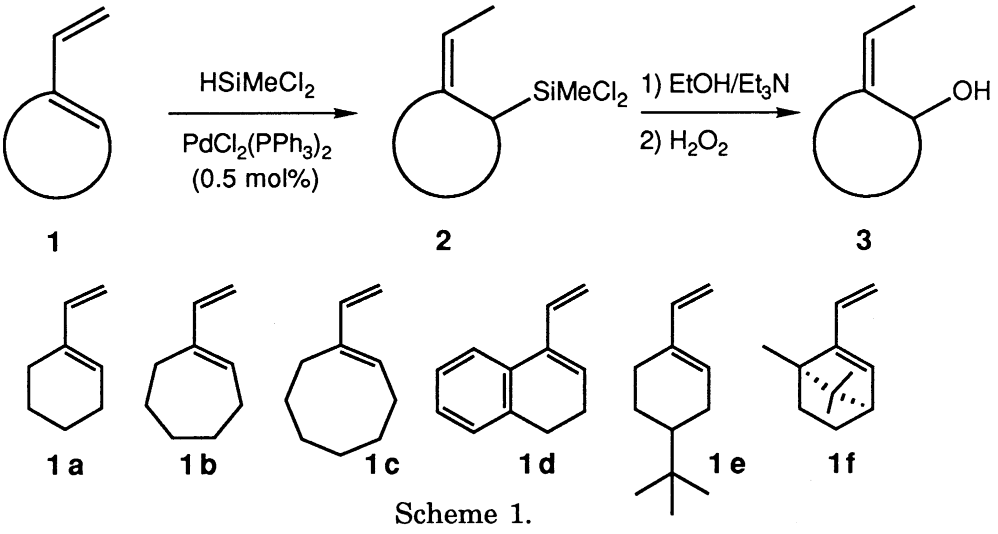
Hydrosilylation of 1-vinylcycloalkenes with methyldichlorosilane in the presence of a palladium catalyst proceeded with high regio- and stereoselectivity to give (*Z*)-1-ethylidene-2-silylcycloalkanes in high yields.

It is well documented that allylsilanes are highly useful reagents in organic synthesis, reacting with a wide variety of electrophiles in a regiospecific manner.[2,3] The synthetic utility of the allylsilanes is critically dependent on their availability. Although several reports have appeared on the preparation of allylsilanes,[2] methods for selective synthesis of substituted allylsilanes with definite regio- and/or stereochemistry remain to be developed. Described herein is a highly regio- and stereoselective synthesis of (*Z*)-1-ethylidene-2-silylcycloalkanes, which was achieved by palladium-catalyzed hydrosilylation of 1-vinylcycloalkenes (Scheme 1).[4,5]

Starting 1-vinylcycloalkenes **1** were prepared in high yields by palladium-catalyzed elimination of 1-vinylcycloalkyl acetylacetates,[6] which were obtained by treatment of 1-vinylcycloalkanols with diketene in pyridine. We have examined several palladium complexes for their catalytic activity and selectivity in the reaction of 1-vinylcyclohexene (**1a**) with hydrosilanes.



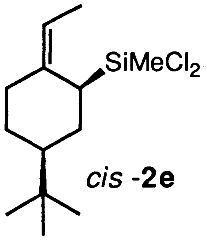
Scheme 1.

Table 1. Palladium-Catalyzed Hydrosilylation of 1-Vinylcycloalkenes[a)]

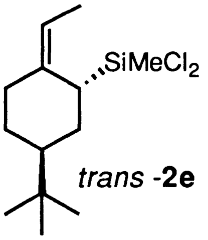
Entry	Diene 1	Hydrosilane	Reaction time / h	Product	Yield of **2** / %[b)]	Isomeric purity
1	**1a**	$HSiMeCl_2$	3	**2a**	84	>99/1
2	**1a**	$HSiCl_3$	30	**5a**[c)]	38	93/7[d)]
3	**1b**	$HSiMeCl_2$	19	**2b**	69	94/6[d)]
4	**1c**	$HSiMeCl_2$	4	**2c**	81	>99/1
5	**1d**	$HSiMeCl_2$	20	**2d**	48	>99/1
6	**1e**	$HSiMeCl_2$	19	**2e**	69	55/45 (*trans*/*cis*)
7	**1f**	$HSiMeCl_2$	20	**2f**	80	20/80 (*exo*/*endo*)

a) A mixture of diene **1** (2.0 mmol), hydrosilane (2.6 mmol), and $PdCl_2(PPh_3)_2$ (0.01 mmol) was heated at 80 °C in a degassed sealed glass tube. b) Isolated yield by distillation. c) Trichlorosilyl analogue of **2a**. d) The minor isomer is 1-(1-silylethyl)cycloalkene.

It was found that dichlorobis(triphenylphosphine)palladium(II) is a highly effective catalyst for the hydrosilylation with methyldichlorosilane. Thus, the reaction of **1a** with 1.3 equiv of methyldichlorosilane in the presence of 0.5 mol% of the palladium catalyst at 80 °C in a sealed tube gave 84% yield of (*Z*)-1-ethylidene-2-(methyldichlorosilyl)cyclohexane (**2a**)[7)] exclusively (entry 1 in Table 1). No isomeric hydrosilylation products were detected by GLC or ^1H NMR. The (*Z*) geometry of the carbon-carbon double bond was determined by NOE studies of allylic alcohol **3a**,[8)] which was obtained by the oxidative cleavage of carbon-silicon bond[9)] in **2a**. Lower regioselectivity was observed in the reaction with trichlorosilane, which gave 1-(1-trichlorosilylethyl)cyclohexene as a minor isomer (7%) (entry 2). The reaction of other 1-vinylcycloalkenes **1b-d** with methyldichlorosilane also proceeded with high selectivity to give corresponding (*Z*)-1-ethylidene-2-silylcycloalkanes **2b-d** in high yields[10)] (entries 3-5). Diastereoselectivity in the hydrosilylation was examined with substituted vinylcyclohexenes **1e** and **1f** (entries 6 and 7). The hydrosilylation took place from the less hindered face of diene moiety to give *trans*-**2e** and *exo*-**2f** preferentially, though the diastereoselectivity was not high.



cis -**2e**



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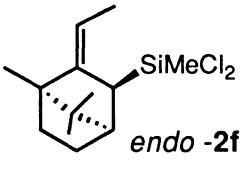
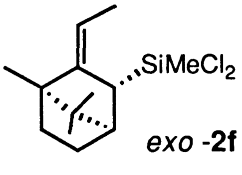
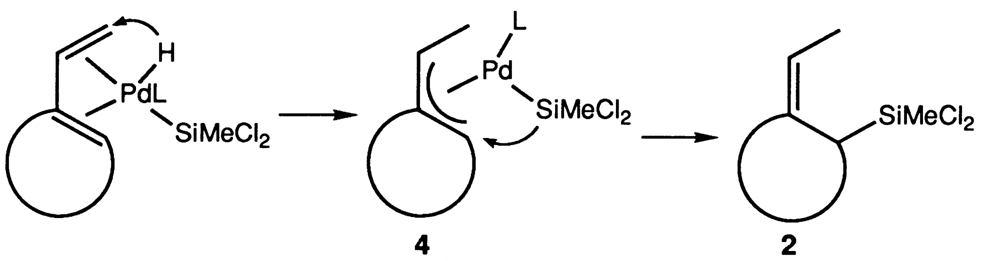


endo -**2f**



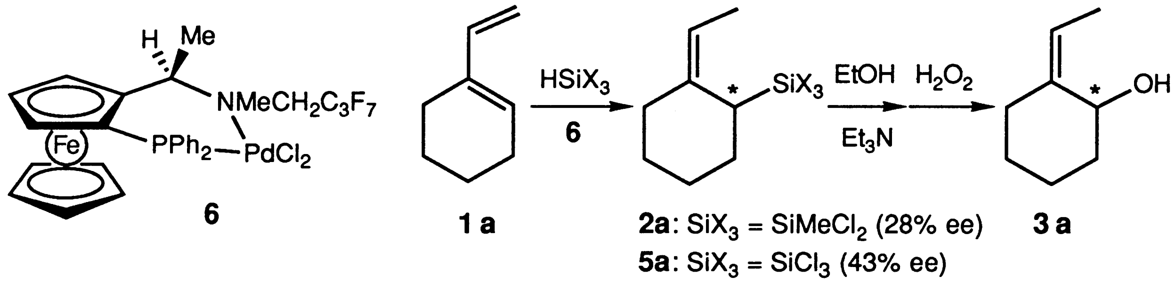
exo -**2f**

The high selectivity for forming (*Z*)-1-ethylidene-2-silylcycloalkanes may be illustrated by the catalytic cycle involving π-allylpalladium intermediate **4**, which is formed by regioselective hydropalladation of diene **1** in cisoid conformation[11] (Scheme 2). Attack of silyl group on π-allyl carbon at *cis* position in the square planar complex **4** before the isomerization of methyl group on the π-allyl from *anti* to *syn*[12] will form allylsilane **2** that has silyl group on the cycloalkane ring and (*Z*) configuration of the double bond.



Scheme 2.

Catalytic asymmetric hydrosilylation of **1a** was carried out in the presence of 0.2 mol% of chiral ferrocenylphosphine-palladium complex **6**[13] (Scheme 3). The reaction with methyldichlorosilane at 50 °C for 18 h gave **2a** selectively in 70% yield, whose enantiomeric purity was determined to be 28% ee by HPLC analysis of 3,5-dinitrophenylcarbamate of allyl alcohol **3a** with chiral stationary phase column (Sumipax OA-1000). The enantioselectivity was improved by using trichlorosilane instead of methyldichlorosilane, the hydrosilylation at 50 °C for 80 h giving (*Z*)-1-ethylidene-2-(trichlorosilyl)cyclohexane (**5a**) of 43% ee (81% yield),[14,15] together with a small amount (2%) of its regioisomer, 1-(1-trichlorosilylethyl)cyclohexene.



Scheme 3.

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5) Hydrosilylation of butadiene has been reported to give (*Z*)-2-butenylsilanes: M. Kira, T. Hino, and H, Sakurai, *Tetrahedron Lett.*, **30**, 1099 (1989).

6) Palladium-catalyzed elimination of allyl acetates forming 1,3-dienes has been reported: J. Tsuji, T. Yamakawa, M. Kaito, T. Mandai, *Tetrahedron Lett.*, **24**, 2075 (1978). We have found that the elimination of allyl acetylacetates proceeds under milder conditions than that of the corresponding acetates.

7) ^{1}H NMR (CDCl$_3$) of **2a**: 0.78 (s, 3 H), 1.0-2.4 (m, 8 H), 1.59 (dt, J = 7 and 1 Hz, 3 H), 2.6-2.8 (m, 1 H), 5.35 (broad q, J = 7 Hz, 1 H).

8) ^{1}H NMR (CDCl$_3$) of **3a**: 1.15-2.05 (m, 8 H), 1.65 (dd, J = 7.0 and 2.2 Hz, 3 H), 2.30-2.55 (m, 1 H), 4.77 (broad t, J = 2.8 Hz, 1 H), 5.27 (dq, J = 1.8 and 7.0 Hz, 1 H). Irradiation of the allylic methyl protons gave rise to 6.3% NOE enhancement at methine proton on the allylic carbon substituted with hydroxy group.

9) K. Tamao, E. Nakajo, and Y. Ito, *J. Org. Chem.*, **52**, 4412 (1987), and references cited therein.

10) ^{1}H NMR (CDCl$_3$) spectra of allylsilanes **2b**-**2f** and allyl alcohols **3b**-**3e** are as follows: **2b**: 0.72 (s, 3 H), 0.9-2.4 (m, 10 H), 1.59 (d, J = 7 Hz, 3 H), 2.63 (dd, J = 12 and 6 Hz, 1 H), 5.45 (q, J = 7 Hz, 1 H). **2c**: 0.69 (s, 3 H), 1.1-2.6 (m, 13 H), 1.60 (d, J = 7 Hz, 3 H), 5.41 (q, J = 7 Hz, 1 H). **2d**: 0.61 (s, 3 H), 2.00 (d, J = 7 Hz, 3 H), 2.1-2.7 (m, 2 H), 2.7-3.3 (m, 2 H), 6.29 (q, J = 7 Hz, 3 H), 7.1-7.5 (m, 3 H), 7.5-7.7 (m, 1 H). **2e** (1 : 1 mixture of *trans* and *cis* isomers): 0.75, 0.79 (a pair of s, 3 H), 0.82, 0.86 (a pair of s, 9 H), 1.7-2.9 (m, 8 H), 1.60, 1.62 (a pair of d, J = 7 Hz, 3 H), 5.37 (q, J = 7 Hz, 1 H). *endo*-**2f**: 0.73 (s, 3 H), 0.85 (s, 6 H), 0.88 (s, 3 H), 1.2-2.6 (m, 6 H), 1.68 (dd, J = 7 and 2 Hz, 3 H), 5.22 (dq, J = 3 and 7 Hz, 1 H). **3b**: 1.0-2.5 (m, 11 H), 1.71 (d, J = 7.0 Hz, 3 H), 4.67 (dd, J = 8.5 and 2.4 Hz, 1 H), 5.46 (dq, J = 0.9 and 7.0 Hz, 1 H). **3c**: 1.1-2.0 (m, 11 H), 1.71 (d, J = 7 Hz, 3 H), 2.0-2.3 (m, 2 H), 4.58 (dd, J = 9 and 6 Hz, 1 H), 5.44 (q, J = 7 Hz, 1 H). **3d**: 1.35-2.4 (m, 2 H), 1.94 (d, J = 7.3 Hz, 3 H), 2.67 (ddd, J = 16.5, 5.1, and 3.4 Hz, 1 H), 3.07 (ddd, J = 16.5, 11.8, and 5.1 Hz, 1 H), 4.98 (broad s, 1 H), 6.26 (q, J = 7.3 Hz, 1 H), 7.0-7.3 (m, 3 H), 7.5-7.7 (m, 1 H). *trans*-**3e**: 0.86 (s, 9 H), 1.0-2.7 (m, 8 H), 1.65 (dd, J = 6.8 and 2.0 Hz, 3 H), 4.83 (broad t, J = 3 Hz, 1 H), 5.26 (dq, J = 1.9 and 6.8 Hz, 1 H). *cis*-**3e**: 0.86 (s, 9 H), 1.0-1.4 (m, 4 H), 1.5-2.3 (m, 4 H), 1.85 (dd, J = 7.0 and 0.9 Hz, 3 H), 4.35 (broad m, 1 H), 5.28 (dq, J = 1.1 and 7.0 Hz, 1 H).

11) We have previously proposed a similar π-allylpalladium intermediate in the asymmetric hydrosilylation of 1-phenyl-1,3-butadiene: T. Hayashi and K. Kabeta, *Tetrahedron Lett.*, **26**, 3023 (1985).

12) With respect to the alkyl group substituted at 2 position of the π-allyl.

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14) (*Z*)-1-Ethylidene-2-(triethoxysilyl)cyclohexane derived from **5a** has the optical rotation of $[\alpha]^{20}{}_{D}$ –25.1° (c 1.6, benzene). **3a**: $[\alpha]^{20}{}_{D}$ –40.5° (c 1.1, benzene).

15) The synthetic utility of optically active allylsilanes has been reported: a) T. Hayashi, M. Konishi, and M. Kumada, *J. Am. Chem. Soc.*, **104**, 4963 (1982); b) T. Hayashi, Y. Matsumoto, T. Kiyoi, Y. Ito, S. Kohra, Y. Tominaga, and A. Hosomi, *Tetrahedron Lett.*, **29**, 5667 (1988).

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