Dehydrogenative Silylation of 1,5-Dienes with Hydrosilanes Catalyzed by $RhCl(PPh_3)_3$

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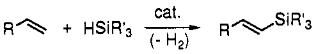
Summary: The reaction of 1,5-dienes with hydrosilanes using $RhCl(PPh_3)_3$ as a catalyst gives 1-silyl-1,5-dienes as the result of dehydrogenative silylation instead of the usual hydrosilylation products.

Catalyzed addition of hydrosilanes to olefins is known as hydrosilylation.[1] Less common is dehydrogenative silylation, i.e., the reaction that produces vinylsilanes directly from hydrosilanes and olefins (eq 1). Although formation of vinylsilanes as rather undesirable, unexpected byproducts in hydrosilylation had been observed from time to time,[2] no example of the exclusive formation of vinylsilanes had been reported until we found $Ru_3(CO)_{12}$ catalysts for styrenes.[3] Later, we reported the $Co_2(CO)_8$ catalyst for acrylic acid esters[4] and $Fe_3(CO)_{12}$ for styrenes.[5] A suitable combination of the olefin structure, a hydrosilane, and a catalyst seems essential for highly selective dehydrogenative silylation to take place. To find further examples of such substrate–catalyst combinations is very important, not only because dehydrogenative silylation is intrinsically interesting[6] but also because it provides an easy access to vinylsilanes, which are versatile synthetic intermediates.[7]



(1)

In our search for the effect of the chelating substrate in catalytic reactions, we have now found that the reaction of 1,5-dienes[8] with hydrosilanes involves dehydrogenative silylation when $RhCl(PPh_3)_3$ is used as the catalyst. Typically, a solution of 1,5-hexadiene (40 mmol, 3.28 g), $HSiEt_2Me$ (5 mmol, 0.73 mL), and $RhCl(PPh_3)_3$ (0.025 mmol, 23 mg) in benzene (5 mL) was heated at 80 °C for 30 min.[9] GLC analysis showed the formation of 1-(diethylmethylsilyl)-1,5-hexadiene (**1a**;[9,10] 90% yield) along with a small amount of its double-bond isomer, 1-(diethylmethylsilyl)-1,4-hexadiene (**2a**; 9%, $E/Z = 1/1$), as well

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(8) Among nonconjugated dienes, 1,5-dienes are known to serve as good bidentate ligands in transition-metal complexes. See: Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, Chapter 38.6.

(9) Typical procedure: The apparatus consisted of a 10-mL two-necked flask, a reflux condenser equipped with an argon inlet, an inlet tube sealed with a septum rubber, and a magnetic stirring bar. In the flask was placed $RhCl(PPh_3)_3$ (23 mg, 0.025 mmol), and then argon was charged. To the flask were added benzene (5 mL), diethylmethylsilane (5 mmol, 0.73 mL), 1,5-hexadiene (40 mmol, 3.28 g), and tridecane (0.11 g) as an internal standard. The resulting solution was heated at 80 °C for 0.5 h. The products, **1a** and **2a**, were isolated by distillation, and purifications of the products were carried out by preparative GLC. The assignment for **1a** is supported by spectroscopic and analytical data: bp 75–80 °C/20 mmHg; ^1H NMR ($CDCl_3$) δ –0.05 (s, 3 H, $SiCH_3$), 0.55 (q, $J = 7.8$ Hz, 4 H, $SiCH_2$), 0.92 (t, $J = 7.8$ Hz, 6 H, $SiCCH_3$), 2.13–2.23 (m, 4 H, CH_2CH_2), 4.96 (dt, $J = 10.3$, 1.9 Hz, 1 H, *cis*-C=CH), 5.02 (dt, $J = 17.6$, 1.9 Hz, 1 H, *trans*-C=CH), 5.61 (dt, $J = 18.6$, 1.4 Hz, 1 H, SiCH=C), 5.82 (ddt, $J = 17.6$, 10.3, 6.2 Hz, 1 H, $CH_2{=}C\mathit{H}$), 6.04 (dt, $J = 18.6$, 5.9 Hz, 1 H, SiC=CH); IR (neat) 3084 w, 2950 s, 2916 s, 2880 s, 1656 m, 1620 s, 1462 m, 1418 m, 1381 w, 1328 w, 1250 s, 1014 s, 990 s, 968 m, 912 s, 796 s, 746 m, 718 m, 670 w cm^{-1}; MS *m/e* 167 ($M^+ - CH_3$, 3), 153 ($M^+ - C_2H_5$, 100), 125 (29), 101 (25), 97 (46), 83 (14), 79 (25), 73 (77). Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.42; H, 12.38.

(10) All new products obtained here gave satisfactory spectral and analytical (C, H) data (see the supplementary material). The reactions run equally well with toluene as a solvent.

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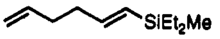
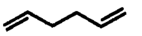
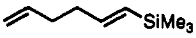
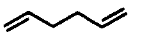
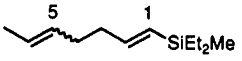
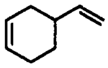
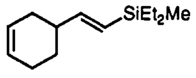
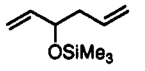
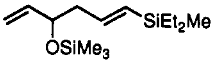
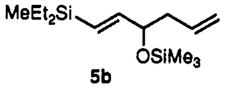
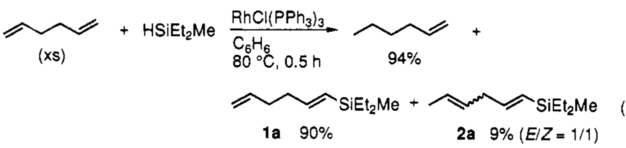
Table I. RhCl(PPh$_3$)$_3$-Catalyzed Reaction of 1,5-Dienes with Hydrosilanes[a]

entry no.	1,5-diene	product	yield, %[b] (stereochem at C$_1$)	total yield of byproducts, %
1		 **1a**	90 ($E > 98$)	9[c]
2[d]		 **1b**	85 ($E > 98$)	9[e]
3[f]		 **1c**	99 (E/Z = 92/8)	0
4	 (E/Z = 11/1)	 **3**	84 (E/Z at C$_5$ = 11/1)	7[e]
5		 **4**	90	9[g]
6	 	 **5a**	44	
		 **5b**	49	trace

[a] Reaction conditions: 1,5-dienes (40 mmol), HSiEt$_2$Me (5 mmol), RhCl(PPh$_3$)$_3$ (0.025 mmol), benzene (5 mL), 80 °C, 0.5-1 h. [b] Determined by GLC. [c] 1-Silyl-1,4-hexadiene. [d] HSiMe$_3$ was used as a hydrosilane. [e] Unidentified products. [f] HSi(OEt$_3$)$_3$ was used as a hydrosilane. [g] 1-Silyl-2-(4-cyclohexenyl)ethane.

as 1-hexene (94%), the yields being based on the hydrosilane (eq 2). Noteworthy was that no simple adduct, the



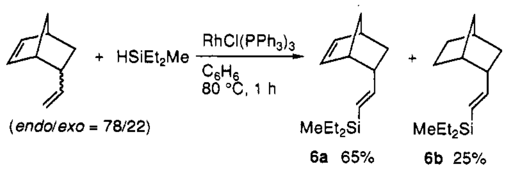
(2)

product expected from usual hydrosilylation, was obtained. The higher molar ratio of 1,5-diene to hydrosilane is an important factor to attain a high selectivity for the dehydrogenative silylation. When the reaction was carried out with the 1,5-hexadiene/HSiEt$_2$Me ratio equal to 1/1 or 1/4, a complex mixture including **1a**, **2a**, and the usual hydrosilylation products was obtained. Other rhodium complexes that also showed a high catalytic activity for eq 2 were Rh$_6$(CO)$_{16}$ (**1a**, 74% yield; **2a**, 25% yield), RhCl(PPh$_3$)$_2$(CO) (**1a**, 85%; **2a**, 15%), RhH(PPh$_3$)$_3$(CO) (**1a**, 90%; **2a**, 10%), RhCl$_3$·3H$_2$O (**1a**, 93%; **2a**, 5%), and [Rh(OAc)$_2$]$_2$ (**1a**, 74%; **2a**, 26%). The reaction of 1,5-hexadiene using Ru$_3$(CO)$_{12}$[3] or Co$_2$(CO)$_8$[4] gave a mixture of many products, including adducts of one and two molecules of HSiEt$_2$Me.

The vinylsilane formation of eq 2 seems to be specific to 1,5-dienes. The RhCl(PPh$_3$)$_3$-catalyzed reaction of 1,4-pentadiene or 1,6-hepatadiene with HSiEt$_2$Me under the same reaction conditions did not result in the exclusive formation of similar 1-silyl 1,ω-dienes.[11] The poor results with 1,4- and 1,6-dienes are not surprising, since these have poorer coordination ability compared to that of 1,5-dienes.[8] The results for several 1,5-dienes are shown in Table I. The use of HSi(OEt)$_3$ resulted in complete dehydrogenative silylation, giving a mixture of E and Z isomers of **1c** (entry 3). The reaction of 1,5-dienes in which one of the double bonds is substituted gave similar results (entries 4 and 5). In the case of 3-(trimethylsiloxy)-1,5-hexadiene, no regioselection was observed (entry 6). In all cases except for entry 3 shown in Table I, small amounts of byproducts, which were double-bond isomers and/or stereoisomers and hydrosilylation products, were detected by the GCMS analysis, but the structures of the byproducts were not fully elucidated.

As described above, the dehydrogenative silylation of eq 2 also produced 1-hexene (94% yield) based on the hydrosilane in which the two hydrogen atoms were transferred, one from the hydrosilane and another from 1,5-hexadiene. Initially, we expected the hydrogen transfer would take place in an intramolecular fashion to give 1-silyl-1-hexene, but this was not the case. These results can be accounted for by a larger binding constant of 1,5-hexadiene to the metal than those of **1a** and 1-hexene.

The importance of strong coordination ability of 1,5-diene to a metal was also observed in the reaction of 5-vinyl-2-norbornene. Thus, the reaction of 5-vinyl-2-norbornene (a 78:22 mixture of *endo* and *exo* isomers) with HSiEt$_2$Me under the same reaction conditions of eq 2 gave only products (**6a** and **6b**) arising from the *endo* starting material (eq 3). The presence of byproduct **6b** indicated



(3)

that an intramolecular hydrogen transfer took place to

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(11) 1,4-Pentadiene gave CH$_2$=CHCH$_2$CH=CHSiEt$_2$Me (14%), CH$_2$=CHCH$_2$CH$_2$CH$_2$SiEt$_2$Me (46%), and CH$_3$CH=CHCH$_2$CH$_2$SiEt$_2$Me (30%), while 1,6-heptadiene afforded CH$_2$=CHCH$_2$CH$_2$CH$_2$CH=CHSiEt$_2$Me (32%), CH$_3$CH=CHCH$_2$CH$_2$CH=CHSiEt$_2$Me (31%), and CH$_2$=CHCH$_2$CH$_2$CH=CHCH$_2$SiEt$_2$Me (19%).

some extent when the diene had a strongly coordinating site such as a norbornene moiety.

Efforts are currently underway to find further examples of the substrate–catalyst matching for selective dehydrogenative silylation.

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Supplementary Material Available: Text giving spectral data and elemental analysis data (5 pages). Ordering information is given on any current masthead page.

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