J. Am. Chem. Soc. **1995,** *117,* 4415−4416

Organoyttrium-Catalyzed Sequential Cyclization/Silylation Reactions of 1,5-Dienes and 1,6-Dienes

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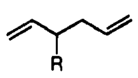
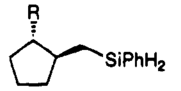
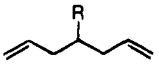
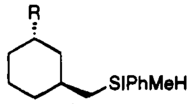
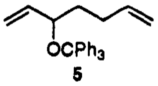
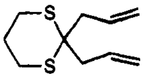
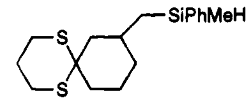
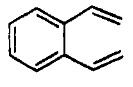
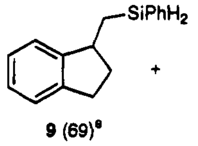
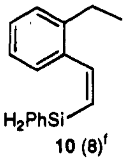
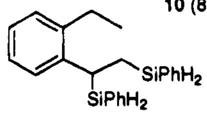
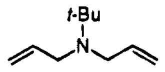
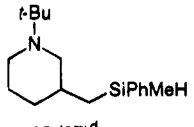
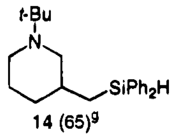
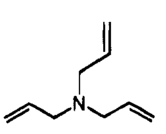
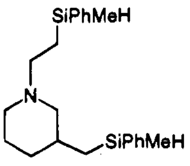
Received December 5, 1994

The conversion of acyclic dienes to cyclized organosilanes through a cyclooligomerization/silylation process allows rapid access to functionalized carbocycles and heterocycles from readily available starting materials. Radical cyclization reactions provide one means to accomplish this overall transformation.[1] However, metal-catalyzed routes provide advantages in terms of the various selectivities deemed desirable in these reactions. Although several lanthanide metal-catalyzed cyclization reactions of dienes have been developed[2] and many hydrosilylation reactions of alkenes are also known,[3] the integration of these two protocols into a unified process is rare.[4]

Building upon previous studies on organoyttrium-catalyzed cyclooligomerization[2a] and hydrosilylation reactions,[3a] a catalytic cycle in which these two processes were merged appeared feasible. The proposed catalytic cycle is outlined in Scheme 1, with the individual steps in the process being well documented.[2,5]

Initial cyclization reactions of this type were explored with 3-phenyl-1,5-hexadiene (**1c**) using Cp*$_2$YCH(SiMe$_3$)$_2$ (Cp* = Me$_5$C$_5$) as a precatalyst.[6] The reaction was very sluggish (5 days) but provided a good yield of the desired product (94% of **2c**) with high diastereoselectivity (10.6:1). The rate of the reaction could be increased considerably by adding a catalytic quantity of tetrahydrofuran (THF) to the reaction mixture. With this improvement, it became advantageous to use the easily prepared Cp*$_2$YCH$_3$·THF complex as the precatalyst, in which the requisite quantity of THF was already incorporated. This complex was used in the remainder of the study.[7] In a typical reaction using this protocol, 1,5-hexadiene (**1a,** 0.5 M in cyclohexane) and 1.1 equiv of phenylsilane in the presence of 5 mol % of Cp*$_2$YCH$_3$·THF provided an essentially quantitative yield of (phenylsilyl)methylcyclopentane (**2a**) within 1 h at room

Table 1. Cp*$_2$YMe·THF-Catalyzed Cyclization/Silylation Reactions of Substituted Dienes

substrate[a]	product(s) (isoltd yield (%), diastereoselectivity)[b]	reaction time (h)
 **1a** R = H	 **2a** (100)	1
1b R = OTBDMS	**2b** (75, 4:1)	1
1c R = Ph	**2c** (74, 9:1)	1
1d R = OCPh$_3$	**2d** (71, 24:1)	1
1e R = OBn	**2e** (76, 3.5:1)[c]	13
 **3a** R = H	 **4a** (98)[d]	1
3b R = OTBDMS	**4b** (99, 1.5:1)[d]	2
3c R = OCPh$_3$	**4c** (99, 2:1)[d]	2
 **5**	complex mixture	
 **6**	 **7** (99)[d]	1
 **8**	 +  + **9** (69)[e] **10** (8)[f]  **11** (5)	12
 **12**	 **13** (97)[d]	2
12	 **14** (65)[g]	20
 **15**	 **16** (90)[h]	1

[a] All reactions were performed with 5 mol % catalyst and PhSiH$_3$ unless otherwise noted. [b] Isolated by distillation in >98% purity unless otherwise noted. The diastereoselectivity was determined on the crude reaction mixture by fused silica capillary gas chromatography. All of these compounds have been fully characterized spectroscopically (^{1}H NMR, ^{13}C NMR, IR), and elemental composition has been established by high-resolution mass spectrometry and/or combustion analysis. [c] The reaction was performed using 20 mol % catalyst at 90 °C in a sealed reaction vessel. The isolated yield includes 10% unwanted isomers, which were inseparable. [d] The reaction was performed with PhMeSiH$_2$. [e] The reaction was performed at 50 °C in a sealed reaction vessel. The yield was estimated by fused silica capillary gas chromatography after isolation of a mixture of **8** and **9**. [f] 8:1 mixture of cis to trans isomers. [g] The reaction was performed with Ph$_2$SiH$_2$. [h] The reaction was performed with 2.2 equiv of PhMeSiH$_2$.

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(5) (a) Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989,** *111,* 4108. (b) Gagne, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990,** *9,* 1716. (c) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987,** *6,* 2053.

(6) The precatalyst Cp*$_2$YCH$_2$(SiMe$_3$)$_2$ was prepared from Cp*$_2$Y(μ-Cl)$_2$(OEt$_2$)$_2$ by treatment with LiCH(TMS)$_2$ in toluene in a procedure similar to that utilized for the analogous lanthanum complex. (a) den Haan, K. H.; Teuben, J. H. *J. Organomet. Chem.* **1987,** *322,* 321. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985,** *107,* 8091.

(7) The precatalyst Cp*$_2$YCH$_3$·THF was synthesized in one pot by the reaction of YCl$_3$ (Cerac) with 2 equiv of Cp*Li (boiling THF, 8 h) followed by MeLi (−78 to 25 °C, 12 h) according to the general procedure reported in the following: den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987,** *327,* 31.

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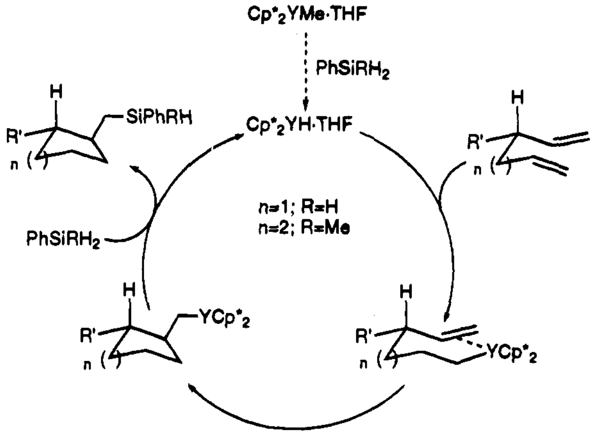
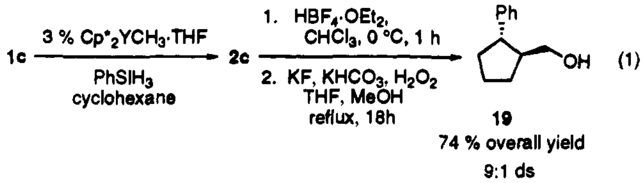
Scheme 1



temperature (Table 1).[8] As evidenced in Table 1, a variety of substrates could be efficiently converted to cyclized organosilanes in high yields and with excellent diastereoselectivities using this protocol.

Noteworthy aspects of this transformation are the high regioselectivities and stereoselectivities in which the carbon–carbon bonds and a carbon–silicon bond are formed. For 1,5-dienes, the enhanced regioselectivity is attributed to initial olefin insertion of the organoyttrium hydride catalyst at the least sterically hindered olefin, followed by cyclization to provide 1,2-disubstituted cyclopentanes. The chairlike transition structure depicted in Scheme 1 accounts for the diastereoselectivities observed in these reactions.[9] Remarkably, the strongly Lewis acidic catalyst[2c,10] tolerates functional groups such as ethers, thioacetals, and tertiary amines. In the case of substituted 1,5-dienes, bulky substituents served to enhance the observed diastereoselectivities. Another useful feature of this reaction is the facile conversion of these phenylsilane products to synthetically more versatile alcohols (eq 1).[11] Products from these oxidation reactions are complementary to those provided by the recently reported titanium-catalyzed cascade carboalumination of dienes.[12]



The cyclization of 1,5-dienes proceeded efficiently in all instances except for the benzyloxy-substituted substrate **1e**, which required additional catalyst and substantially higher reaction temperatures. This may be due to deactivation of the catalyst through oxygen chelation after the initial olefin insertion event. The annulation reactions with 1,6-dienes also proceeded efficiently, albeit with lower diastereoselectivities. With 1,6-dienes, trapping the products with phenylsilane resulted in mixtures of silicon-bridged dimers. This problem was overcome with the use of phenylmethylsilane, which was sufficiently bulky to provide clean (monomeric) product formation. Diphenylsilane could also be used (product **14**), although with a substantial decline in rate and yield. Unfortunately, cyclized products could not be obtained from **5**, presumably because of steric considerations. Furthermore, as in a previous study,[2a] 4,4-dicyano-1,6-heptadiene and diallyldimethylsilane provided no cyclized material.

In conclusion, $Cp^*_2YCH_3{\cdot}THF$ has been shown to be an efficient catalyst for the annulation and subsequent silylation of substituted 1,5- and 1,6-dienes. Significantly, this process takes precedence over the dehydrogenative polymerization of the silanes, which is reported to be a remarkably facile process.[13] The reaction tolerates a number of functional groups and proceeds with excellent yields and diastereoselectivities. The relatively easy preparation of the precatalyst and subsequent in situ generation of the active hydride catalyst make this a synthetically useful one-pot procedure for preparing a number of functionalized five- and six-membered rings. Additionally, facile oxidation of the resulting phenylsilane to the corresponding alcohol allows for further functionalization.

Acknowledgment. We thank Dr. Manfred Julius, who performed the initial experiments in this area, and the National Institutes of Health for their generous support of this research.

Supplementary Material Available: Complete experimental details and spectral data for the cyclization reactions described herein (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[8] The general workup procedure involved filtration of the crude mixture through a small plug of Florisil prior to concentration by rotary evaporation and purification by flash chromatography and/or Kugelrohr distillation.

[9] The relative stereochemistry of the major and minor isomers of **2b** was assigned by comparison with published spectroscopic data of both isomers. (a) Fang, C.; Ogawa, T.; Suemune, H.; Sakai, K. *Tetrahedron: Asymmetry* **1991**, *2*, 389. (b) Kinast, G.; Tietze, L.-F. *Chem. Ber.* **1976**, *109*, 3626. (c) Finch, N.; Fitt, J. J.; Hsu, I. H. S. *J. Org. Chem.* **1975**, *40*, 206. (d) Favre, H.; LaPointe, J. P. *Can. J. Chem.* **1971**, *41*, 3851. (e) Penny, C. L.; Belleau, B. *Can. J. Chem.* **1978**, *56*, 2396. The relative stereochemistry of the major and minor isomers of **4c** was assigned on the basis of NOE difference experiments using the deprotected alcohol derivative of **4c**. See the supplementary material.

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