suggest that changes in the Mo oxidation states during substrate turnover may be coupled to pterin oxidation/reduction reactions. The nature of the quinonoid dihydropterin stabilization is currently under study by experiments in progress. We are also investigating H_4Pterin reductions of other dioxomolybdenum model complexes.

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1-Silylvinyl Radical Cyclization: Silicon-Mediated Regio- and Stereoselective Hydroacylation and Hydrovinylation of Allyl Alcohols[1]

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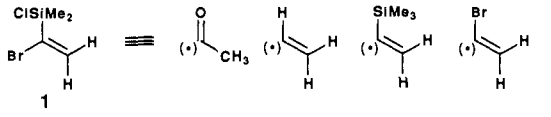
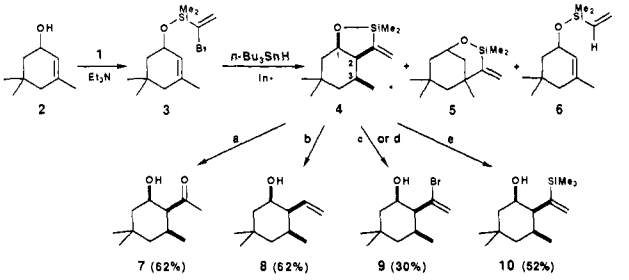
Radical cyclization has recently become a new useful methodology for carbon–carbon bond formation, especially for efficient synthesis of carbocyclic compounds and for regio- and stereoselective introduction of functionalized carbon chains.[2] Utility of vinyl radical cyclization has also been demonstrated by Stork's work.[3] Described herein is the first demonstration of 1-silylvinyl radical[4] cyclization as new tools for regio- and stereoselective hydroacylation[5] or hydrovinylation[6] of allyl alcohols.

The reagent for the purpose is 1-bromovinyldimethylsilyl chloride (**1**),[7] a new member of multifunctional silicon reagents[8] (Scheme I). Typical transformations starting with isophorol (**2**) are summarized in Scheme II. The hydroxy group is silylated with **1** to give **3**. When refluxed (80 °C, 8 h) with tri-*n*-butylstannane (1.2 equiv) in the presence of azobisisobutyronitrile (AIBN) (5 mol%) in benzene, **3** gave a mixture of a five-membered ring product **4**[9] (5-exo)[10] as the major cyclization product,

Scheme I

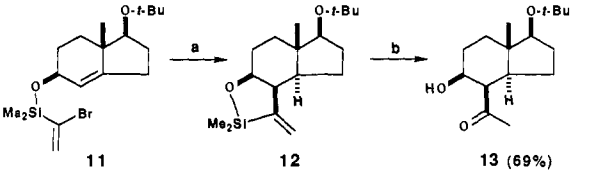


Scheme II[a]



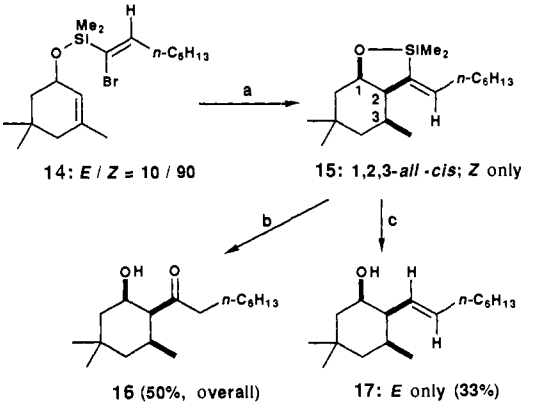
[a] (a) 30% H_2O_2/KF/$KHCO_3$/MeOH/THF/room temperature/1 day; (b) *t*-BuOK/DMSO–H_2O (17:1)/room temperature/2 days; (c) NBS/DMF/0 °C to room temperature/1 day; (d) (1) Br_2/CCl_4/0 °C; (2) KHF_2/MeOH/room temperature/1 day; (e) MeLi/Et_2O.

Scheme III[a]



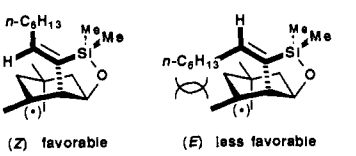
[a] (a) 0.02 M solution; *n*-Bu_3SnH (×1.2)/AIBN/benzene/reflux/4 h; (b) 30% H_2O_2 (×8)/KF (×4.4)/$KHCO_3$ (×4.4)/MeOH/THF/room temperature/15 h.

Scheme IV[a]



[a] (a) *n*-Bu_3SnH/*n*-Bu_3B/benzene/room temperature/24 h; (b) 30% H_2O_2/KF/$KHCO_3$/MeOH/THF/room temperature; (c) *t*-BuOK/DMSO–H_2O (17:1)/room temperature.

Scheme V



a six-membered isomer **5**[9] (6-endo),[10] and a direct reduction product **6**. While with 0.4 M *n*-Bu_3SnH the direct reduction was the major course of the reaction (**4**:**5**:**6** = 25:2:73), the cyclization proceeded efficiently (**4**:**5**:**6** = 80:8:12) under high dilution con-

(1) Silafunctional Compounds in Organic Synthesis. 42. Part 41: Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955.

(2) (a) Curran, D. P. *Synthesis* **1988**, 417 and 489. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. (c) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911. Silylmethyl radical cyclization has been used for hydroxymethylation or methylation of allyl alcohols. (d) Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298. (e) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (f) Stork, M.; Sofia, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6826. (g) Koreeda, M.; George, I. A. *J. Am. Chem. Soc.* **1986**, *108*, 8098.

(3) (a) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (c) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. (d) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. (e) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (f) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829.

(4) Formation of 1-silylvinyl radical intermediates via radical addition to silylacetylenes: (a) Curran, D. P.; Rakiewics, D. M. *Tetrahedron* **1985**, *41*, 3943. (b) Choi, J.-K.; Hart, D. J. *Tetrahedron* **1985**, *41*, 3935. Tin hydride reduction of 1-iodoalkenylsilanes has recently been shown to proceed nonstereospecifically. (c) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143.

(5) Transition-metal-catalyzed hydroacylation of olefins has been known. Recent papers: (a) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451. (b) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936. (c) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 6229.

(6) Transition-metal-catalyzed hydrovinylation: Buono, G.; Siv, C.; Peiffer, G.; Triantaphylides, C.; Denis, P.; Mortreux, A. Petit, F. *J. Org. Chem.* **1985**, *50*, 1781.

(7) Compound **1** was readily prepared from commercially available $[(CH_2{=}CH)Me_2Si]_2O$ by the following reactions: Bromination (neat, −78 °C), followed by dehydrobromination (Et_2NH, reflux, 3 h) gave $[(CH_2{=}CBr)Me_2Si]_2O$ (bp 70 °C/3 mmHg; 71%) which was heated with $MeSiCl_3$ (2/3 equiv) at 50 °C for 3 days in the presence of 5 mol% of HMPA. Direct distillation from the reaction mixture gave **1** in 52% overall yield (bp 80 °C/120 mmHg).

(8) Review: Tamao, K. *J. Synth. Org. Chem., Jpn.* **1988**, *46*, 861.

(9) In ^1H NMR (400 MHz, $CDCl_3$), **4** showed the NOE (6%) between the 3-Me (1.244, d, J = 7.3 Hz) and the lower field proton of the two olefin protons (5.499, t, J = 2.6 Hz and 5.916, t, J = 2.6 Hz). **5**: The bridgehead Me appeared as a singlet at 1.079.

(10) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

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ditions (0.02 M), keeping the **4**:**5** ratio nearly constant.[11] In the presence of n-Bu_3B (20 mol%) as a radical initiator[3e] (0.02 M, benzene, 25 °C, 24 h), the product distribution was not greatly affected, but the five- to six-membered ring ratio was somewhat improved: **4**:**5**:**6** = 76:5:19. The cyclization reactions were, therefore, carried out under the latter two dilution conditions.

The 1,2,3-all-cis stereochemistry in **4**, especially the high stereocontrol at the 3-position, is consistent with the approach of tin hydride from the less hindered convex side of the cis fused bicyclic system, as pointed out already by Stork.[2e,3b]

The mixture of products, containing the major five-membered ring product **4** (ca. 80%), was subjected without purification to further transformations of the cyclic vinylalkoxysilane moiety, some results being shown in Scheme II. Thus, the hydrogen peroxide oxidation[12] under the standard condition proceeded smoothly to form acetyl derivative **7** in 62% overall yield based on **3** in a stereochemically pure form. Basic cleavage[2f,13] and brominolysis[14] of the Si–alkenyl bond in **4** to the respective parent vinyl group (**8**) and 1-bromovinyl group (**9**) and cleavage of the Si–oxygen bond by methylation to the 1-trimethylsilylvinyl group (**10**) were also achieved. These results demonstrate that the present overall transformations are synthetically equivalent to the regio- and stereoselective hydroacylation and hydrovinylation of allylic alcohols, in which the acyl and vinyl groups are introduced onto the olefin carbon atom near the hydroxy group.

The hydroacylation has been applied to the bicyclic allyl alcohol derivative **11** to form the stereochemically pure **13** in high overall yield, as shown in Scheme III. The resulting ketone **13** should be an important intermediate for the total synthesis of vitamin D metabolites.[15]

A new stereochemical aspect characteristic of the 1-silylalkenyl radical cyclization has also been obtained. Thus, as shown in Scheme IV, the Z-rich (Si/R trans rich) mixture of the 1-bromo-1-octenylsilyl derivative **14**[16] gave, under similar conditions, the five-membered ring closure product **15** which had only the Z(Si/R cis) octenyl group. The result may be explained by rapid equilibration between the E- and Z-alkenyl radicals, the latter being sterically favored in the addition to olefin, as illustrated in Scheme V.[17] The product **15** could be converted into the E-octenyl derivative **17** by the basic desilylation procedure without loss of stereochemistry as well as into the 1-octanoyl derivative **16** by the hydrogen peroxide oxidation (Scheme IV).

Refinement and further applications are now under investigation.[18]

Acknowledgment. We thank Dr. M. R. Uskokovic for valuable discussions during his stay in Japan last November and H. Fujita for measurements of 400 MHz NMR.

Supplementary Material Available: Physical, spectroscopic, and selected analytical data for compounds **1**, **3**, **4**, **7**, **8**, **9**, **10**, **12**, **13**, **15**, **16**, and **17** (2 pages). Ordering information is given on any current masthead page.

(11) The dependence of the product distribution on the reagent concentrations in the vinyl radical cyclization reactions has already been discussed in connection with the reversibility of the reaction.[3c,d]

(12) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. (c) Reference 1 and our previous works cited therein.

(13) (a) Price, C. C.; Sowa, J. R. *J. Org. Chem.* **1967**, *32*, 4126. (b) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809.

(14) Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100.

(15) The 4α epimer has been used for the total synthesis of calciferol derivatives: Baggiolini, E. G.; Iacobelli, J. A.; Hennessy, B. M.; Uskokovic, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 2945.

(16) The corresponding chlorosilane as the silylating agent was prepared from (Z)-1-octenyldimethylethoxysilane by bromination and dehydrobromination, followed by treatment with acetyl chloride for ethoxysilane to chlorosilane conversion.

(17) Similar observations have been described for cyclization of 2-stannylalkenyl radicals.[3e,f]

(18) The silylvinyl radical cyclization has also been applied to acyclic allyl alcohols; the regio- and stereochemical studies are currently underway.

Determination of the Absolute Steric Course of a Solid-State Photorearrangement by Anomalous Dispersion X-ray Crystallography

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An interesting situation arises when compounds that rearrange through multiply degenerate reaction pathways in solution are studied in the solid state. In general, the degeneracy will be lifted in the crystal owing to its anisotropic environment, and the problem then becomes one of determining the extent to which each of the degenerate (solution) mechanisms contributes to the overall solid-state process. By solving such problems we learn much about the forces that control reactivity in molecular crystals. In this communication we report the case of a rearrangement that is 4-fold degenerate in solution but which follows a single mechanism in the crystal.

The reaction studied was the di-π-methane photorearrangement of dibenzobarrelene-11,12-diester **1** to the dibenzosemibullvalene derivative **4**.[1] This reaction occurs both in solution and the solid state, and its commonly accepted mechanism (path I) is shown in Scheme I.[2a] It is readily apparent that there are three additional and equivalent pathways (II–IV) for a total mechanistic degeneracy of four.

The approach to be taken in determining the relative importance of these four pathways to the solid-state rearrangement came from the realization that paths I and II lead to one enantiomer of **4**, whereas pathways III and IV give the other. Fortuitously, diester **1** crystallizes in a homochiral conformation in the chiral space group $P2_12_12_1$ and, as reported by us earlier,[1] undergoes stereospecific photorearrangement in the solid state to afford **4** in quantitative enantiomeric excess. This result establishes complete (I + II) vs (III + IV) discrimination in the crystal but does not differentiate between the two possibilities; neither does it indicate the relative importance of path I vs path II (or path III vs path IV).

In principle, it is possible to differentiate between pathways (I + II) and (III + IV) by determining the absolute configuration of the molecules in a reactant crystal and correlating this with the absolute configuration of the photoproduct generated by irradiation of that same crystal. To this end, a fragment of a large (55 mg) crystal of **1** was subjected to X-ray crystal structure analysis, taking account of anomalous dispersion, as described originally by Bijvoet.[3] At the same time, the remaining fragment was photolyzed and shown to give levorotatory **4** ($[\alpha]_D = -25.4°$, $CHCl_3$). Recrystallization of this material from ethanol gave prisms (mp 124–125 °C, space group $P4_12_12$ or $P4_32_12$) suitable for Bijvoet analysis. In both cases the anomalous dispersion is small ($\Delta f'' = 0.009$ for carbon, 0.032 for oxygen), but Hamilton's R factor ratio test[4a] favored one chirality for **1** and space group

(1) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648. The first example of this type of photorearrangement in solution (that of barrelene to semibullvalene) was reported by Zimmerman et al. (Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183). The first example of a solution phase dibenzobarrelene to dibenzosemibullvalene rearrangement was reported for the dimethyl diester of **1** by Ciganek (Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882).

(2) (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Chapter 16. The debate over whether 1,4-biradicals such as **2** represent true minima on the di-π-methane hypersurface [see (b) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597. (c) Adam, W.; Dorr, M.; Kron, J.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 7074. (d) Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900] does not affect the arguments presented in this paper.

(3) Bijvoet, J. M.; Peerdeman, A. F.; Van Bommel, J. A. *Nature* **1951**, *168*, 271.

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