the formation of the new sp^3 bond. When the α-substituent is bulky (entry E), reduction of the corresponding radical is no longer a competing reaction.

We have shown that allylic and homoallylic ester radicals can be viable reactive species in the intramolecular reaction with suitably disposed activated and unactivated olefins.[14] The overall reaction can be formally related to the alkylation or Michael reaction of an ester enolate,[15] albeit via a free-radical intermediate (Scheme I). The resulting γ- and δ-lactones which can contain vicinal and/or alternating substituents should be valuable chirons for the synthesis of a variety of natural products derived from well-known biosynthetic routes.

Acknowledgment. We thank the NSERCC and the FCAR for generous financial assistance.

Supplementary Material Available: Physical constants, $[\alpha]_D$, ^1H NMR, ^{13}C NMR, mass, and elemental analyses, X-ray crystal structures, representative spectra, and selected experimental procedure (29 pages). Ordering information is given on any current masthead page.

(14) Reactions can be conveniently carried out on preparative scale as shown in the following example. To a magnetically stirred solution of **36** (1.3 g, 4.88 mmol) in dry benzene (245 mL, solution 0.02 M) was added AIBN (10 mg, 0.098 mmol), at room temperature, under argon atmosphere. A solution of triphenyltin hydride (2.91 g, 8.3 mmol) in dry benzene (170 mL, 0.049 M solution) was injected in four portions using a syringe pump, into the refluxing solution over 14 h. The solvent was removed by evaporation, and the residue was purified by flash chromatography (ethyl acetate/hexanes 5–13% hexanes gradient) to give a crystalline mixture of four isomers (596 mg, 86%) (ratio 9.5:1.1:1.0:0.6 by NMR), the major isomer being the anti/anti (see the supplementary material).

(15) For recent reviews, see: Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 111. Evans, D. A. *Science* **1988**, *240*, 420 and references cited therein.

Platinum-Catalyzed Intramolecular Hydrosilation of Allylamines: Formation of 1-Aza-2-silacyclobutanes and Application to Stereoselective Synthesis of 2-Amino Alcohols[1]

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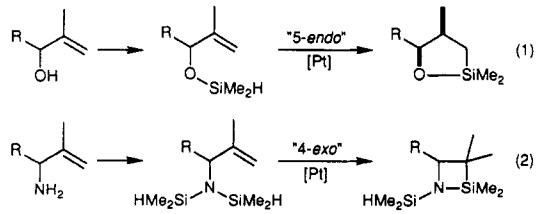
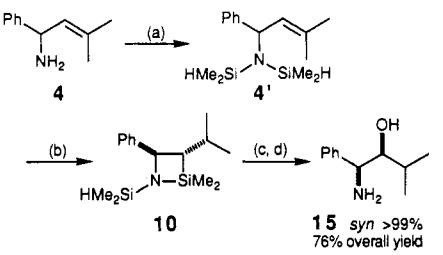
Summary: *N,N*-Bis(dimethylsilyl)allylamines undergo intramolecular hydrosilation in the presence of Pt-[{CH_2=CH)Me_2Si}$_2O$]$_2$ (0.2 mol %) to form four-membered cyclic compounds, 1-aza-2-silacyclobutane derivatives, which can be transformed into 2-amino alcohols by oxidation with 30% H_2O_2 in the presence of KF and $KHCO_3$.

We recently reported intramolecular hydrosilation of allyl alcohols as well as homoallyl alcohols forms five-membered ring compounds selectively (5-endo ring closure),[2] as exemplified by eq 1; the products can be transformed into 1,3-diols by hydrogen peroxide oxidation.[3] We now find, to our surprise, that platinum-catalyzed intramolecular hydrosilation of allylamines forms four-membered ring compounds, 1-aza-2-silacyclobutane derivatives, almost exclusively (4-exo ring closure),[2] as shown in eq 2. Reported herein are the regio- and stereoselective formation of 1-aza-2-silacyclobutanes and their application to the stereoselective synthesis of 2-amino alcohols.



Representative results are listed in Table I. Scheme I illustrates transformations of allylamine **4** (entry 4).

Scheme I[a]



[a] (a) *n*-BuLi (×2.2))/$ClSiMe_2H$ (×2.2)/Et_2O; (b) Pt[{(CH_2=CH)Me_2Si}$_2O$]$_2$ (0.2 mol %)/room temperature/0.5 h; (c) EDTA·2Na/hexane/room temperature; (d) 30% H_2O_2/KF/$KHCO_3$/MeOH/THF/room temperature/18 h.

Thus, the amino group in **4** was converted into a bis(dimethysilyl)amino group by repeating *twice* a sequence of lithiation (*n*-BuLi) and silylation (HMe_2SiCl). The bis(silyl)amine **4'** was treated in dry ether with a catalytic amount (0.2 mol %) of Pt[{(CH_2=CH)Me_2Si}$_2O$]$_2$.[4] Intramolecular hydrosilation occurred exothermically at room temperature and was complete within 0.5 h, as monitored by ^1H NMR. Bulb-to-bulb distillation gave **10**[5] as a single trans isomer in 90% yield. Transformation to an amino alcohol was carried out, without isolation of **10**, as follows. After removal of the platinum catalyst by treatment with crystalline EDTA·2Na, **10** was subjected to the hydrogen peroxide oxidation under usual condition, followed by column chromatography, to afford the amino alcohol **15**[5] as a syn isomer in 76% overall yield.[6]

(1) Silafunctional Compounds in Organic Synthesis. 46. Part 45: Tamao, K.; Hayashi, T.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6533.

(2) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. 5-Endo and 4-exo ring closure modes observed in the hydrosilation products may be regarded as 6-endo and 5-exo modes, respectively, in transition-metal-containing intermediates.[3]

(3) (a) Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem Soc.* **1986**, *108*, 6090. (c) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712.

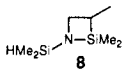
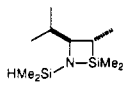
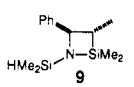
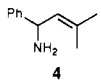
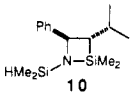
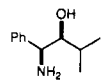
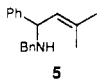
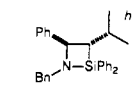
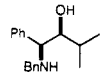
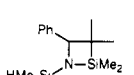
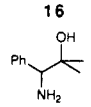
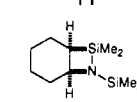
(4) Readily available from chloroplatinic acid: (a) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191. (b) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. The intramolecular hydrosilation proceeded rather slowly with $Pt(PPh_3)_4$ as a catalyst, while H_2PtCl_6·$6H_2O$-catalyzed reaction resulted in the formation of rather complex mixture.

(5) All new compounds showed satisfactory spectral and analytical data, as shown in the supplementary material.

(6) Stereochemistry and isomer ratios of 2-amino alcohols were determined by capillary GLC analysis and ^1H NMR spectroscopy of amino alcohol themselves or of their oxazolidone derivatives.

0022-3263/90/1955-3438$02.50/0

Table I. Transformation of Allylamine to 1-Aza-2-silacyclobutane and to 2-Allylamine[a]

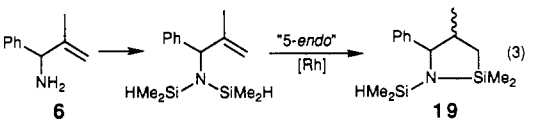
entry	allylamine	1-aza-2-silacyclobutane (major isomer)	yield,[b] % (stereoselectivity)	2-amino alcohol (major isomer)	overall yield,[c] % (stereoselectivity)
1	 1	 8	71[d,e]	...[f]	
2	 2		...[g]	 13	53 (77 : 23)
3	 3	 9	68 (87 : 13)	 14	77 (80 : 20)
4	 4	 10	90 (>99 : 1)	 15	76 (>99 : 1)
5	 5		...[g]	 16	50 (>99 : 1)
6	 6	 11	75[e]	 17	57
7	 7	 12	80 (>99 : 1)	 18	72 (>99 : 1)

[a] Intramolecular hydrosilation and hydrogen peroxide oxidation were carried out in essentially the same method as described in the text, unless otherwise mentioned. [b] Isolated yield based on allylamine, unless otherwise noted. Stereoisomeric ratios were determined by GLC. [c] Isolated overall yield based on allylamine. Stereoisomeric ratios were determined by capillary GLC. [d] Based on the disilylamine derivative. [e] Trace amounts (1–3% yield) of the regioisomer, 1-aza-2-silacyclopentane derivative, were detected by ^{1}H NMR. [f] Not examined. [g] Not isolated. [h] Silylated with $ClSiPh_2H$.

Two significant points deserve comment. (1) The selective formation of various kinds of 1-aza-2-silacyclobutane derivatives by a simple procedure is notable. Only a few compounds of this class have so far been prepared mainly by Wiberg in connection with the study of silicon–carbon and silicon–nitrogen double-bonded species.[7] The present reaction can afford rather simple mono-, di-, and trisubstituted 1-aza-2-silacyclobutanes, **8**–**11**, and bicyclic derivative **12**. While trans isomers are formed highly selectively or exclusively from acyclic allylamines (entries 2–4), a cis isomer is obtained exclusively from a cyclic allylamine (entry 7).[8] It is also worthwhile to note that a tertiary alkyl–silicon bond can readily be formed by the intramolecular hydrosilation, as exemplified by **11**, in view of difficulties encountered in preparation of *tert*-alkylsilicon compounds by traditional methods.[9] 1-Aza-2-silacyclobutanes obtained herein were all thermally stable and isolable by distillation; for example, **11** showed little sign of decomposition at 200 °C after several hours, in sharp contrast to the thermal lability of highly crowded compounds prepared by Wiberg, which generate silene species at 100 °C.[7,10]

(2) Conversion of 1-aza-2-silacyclobutanes into the corresponding 2-amino alcohols by hydrogen peroxide oxidation, with retention of configuration, proceeded smoothly in all cases, providing a new methodology for the regio- and stereoselective transformation of allylamines to the syn (threo) isomer of acyclic 2-amino alcohols or to the cis isomer of cyclic amino alcohols.[11] The stereoselectivity observed using acyclic allylamines appears to be determined by the size of the two substituents at 3- and 4-positions in the 1-aza-2-silacyclobutanes (entries 2–4).[12] The present transformation is not restricted to primary amines, but was also applied to the *N*-benzyl derivative **5** (entry 5); in this case, $ClSiPh_2H$ was more suitable as the silylating agent, with respect to the stability of the resulting silylamine, than $ClSiMe_2H$.

The mechanism for the selective formation of the 1-aza-2-silacyclobutane skeleton is remarkably intriguing, because we have also observed that intramolecular hydrosilation of **6** catalyzed by $RhCl(PPh_3)_3$ gives a 1:1 stereoisomeric mixture of 1-aza-2-silacyclopentanes **19** (5-endo ring closure) selectively with no formation of 1-aza-2-silacyclobutanes (eq 3).



6 19

The contrasting regioselectivities observed with Pt and Rh complexes as catalysts, as well as with allyl alcohols[3] and allylamines as substrates, strengthen the complexity of the hydrosilation mechanisms.[13] Much study is required before the mechanism for the regio and stereocontrolled intramolecular hydrosilation is clarified.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for the Grant-in-Aid for Special Project Research (No. 01649005).

Supplementary Material Available: Experimental procedures for transformation of **4** to **10** and to **15** and physical, spectral, and analytical data of compounds **4'**, **8**–**18**, and oxazolidone derivatives of amino alcohols (7 pages). Ordering information is given on any current masthead page.

(7) (a) Klingebiel, U.; Meller, A. *Z. Naturforsch.* **1976**, *31b*, 1545. (b) Wiberg, N.; Preiner, G.; Shieda, O. *Chem. Ber.* **1981**, *114*, 3518. (c) Wiberg, N.; Preiner, G.; Schurz, K. *Chem. Ber.* **1988**, *121*, 1407 and references cited therein.

(8) There is a distinct stereochemical difference in vicinal coupling constants for protons attached to the four-membered rings, as shown by the following data for **8**–**10**: $^3J_{cis}$ = 9.0–9.4 Hz and $^3J_{trans}$ = 5.0–5.4 Hz.

(9) Reaction of halosilanes with tertiary alkyllithium reagents has been virtually the only method for access to tertiary-alkylsilicon compounds. A new method by $AlCl_3$-catalyzed hydrosilation of certain tetrasubstituted olefins has recently been developed: Oertle, K.; Wetter, H. *Tetrahedron Lett.* **1985**, *26*, 5511.

(10) The thermal behavior of our 1-aza-2-silacyclobutanes is now under investigation in our laboratory.

(11) Stereoselective transformation of allylamines to 2-amino alcohols, e.g.: (a) Pauls, H. W.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1980**, *102*, 3956. (b) Kobayashi, S.; Isobe, T.; Ohno, M. *Tetrahedron Lett.* **1984**, *25*, 5078.

(12) Conversion of **11** to **17** provides the first example for the hydrogen peroxide oxidation of a tertiary-alkylsilicon bond.

(13) Mechanism of transition metal-catalyzed hydrosilation has recently been discussed in terms of two possibilities of hydrometalation and silylmetalation as the initial step and experimental data in accordance with the silylmetalation mechanism have been accumulated. Cr: (a) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Eng.* **1988**, *27*, 289. (b) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. Ru: (c) Kodama, T.; Kajikawa, Y.; Murakami, H.; Ohe, K.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *The 36th Symposium on Organometallic Chemistry, Japan*, Tokyo, September 1989; Abstracts, p 307. (d) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1987**, *52*, 4864. (e) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890. Rh: (f) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (g) Millan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. Ni: (h) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478.