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Triethylborane Induced Intramolecular Hydrogermylation of Homoallylic Alcohols and Homopropargylic Alcohols

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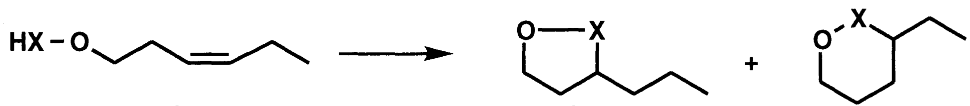
Whereas platinum-catalyzed hydrogermylation of 3-hexenoxydipropylgermane provided five-membered ring product (5-propyl-1-germa-2-oxacyclopentane) as a main product, triethylborane induced radical cyclization gave six-membered ring product (6-ethyl-1-germa-2-oxacyclohexane) selectively.

We recently reported that triphenylgermane readily adds to terminal acetylenes or terminal olefins in the presence of a catalytic amount of Et_3B to give alkenyltriphenylgermanes or alkyltriphenylgermanes, respectively, with excellent control of regio- and stereoselectivities.[1] Triphenylgermyl radical attacks the terminal carbon of these substrates selectively. Here we wish to report the intramolecular hydrogermylation of olefinic or acetylenic alcohols whose regioselectivity depends on the position of the $C=C$ or $C\equiv C$ bond and the substitution pattern of carbon-carbon multiple bonds.

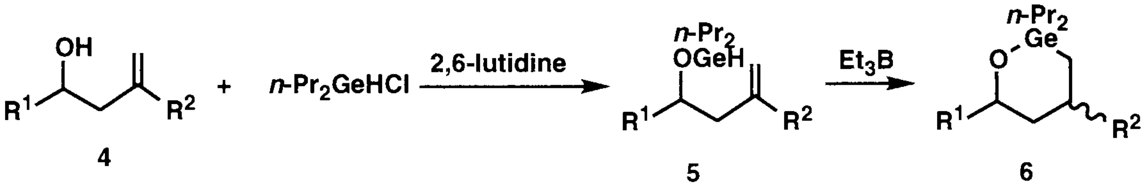
The platinum-catalyzed intramolecular hydrosilylation of **1a** has been reported to give the five-membered ring compound **2a** exclusively in 92% yield.[2] Meantime, hydrogermylation of **1b** in the presence of platinum catalyst[3] gave a mixture of five-membered ring product **2b** and six-membered ring product **3b** (**2b** : **3b** = 88 : 12) in only 28% yield. In contrast, a triethylborane initiated reaction[4] afforded 1-germa-2-oxacyclohexane **3b** selectively (**2b** : **3b** = 14 : 86)[5,6] in good yield. This facile intramolecular reaction shows sharp contrast to the intermolecular hydrogermylation of olefins which has been applicable only to terminal olefins because of the low reactivity of internal olefins.[7]



1 **2** **3**

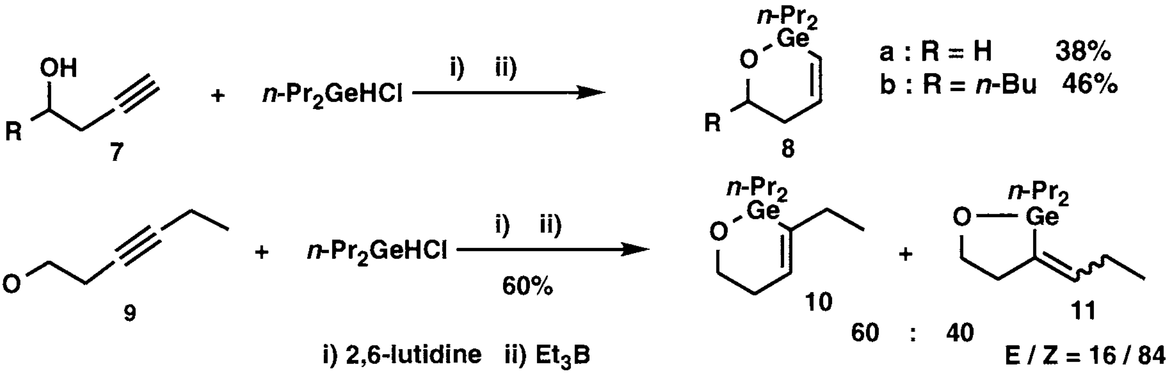
1a : X = Me_2Si	H_2PtCl_6	92%	100 : 0
1b : X = n-Pr_2Ge	H_2PtCl_6	28%	88 : 12
1b : X = n-Pr_2Ge	Et_3B	83%	14 : 86

The reaction with terminal olefins such as **5a**, **5b**, and **5c** proceeded in a highly regioselective manner to provide six-membered ring compounds **6a**, **6b**[8] and **6c**, exclusively in good yields. Treatment of **5d** with Et_3B afforded the corresponding endo ring-closure product **6d** in 84% yield as a 55/45 isomeric mixture. The crude germyl ether **5**, derived from chlorodipropylgermane and alcohol **4** having terminal olefinic linkage in the presence of 2,6-lutidine, was treated with triethylborane in hexane without purification because of their thermal instability.[9]

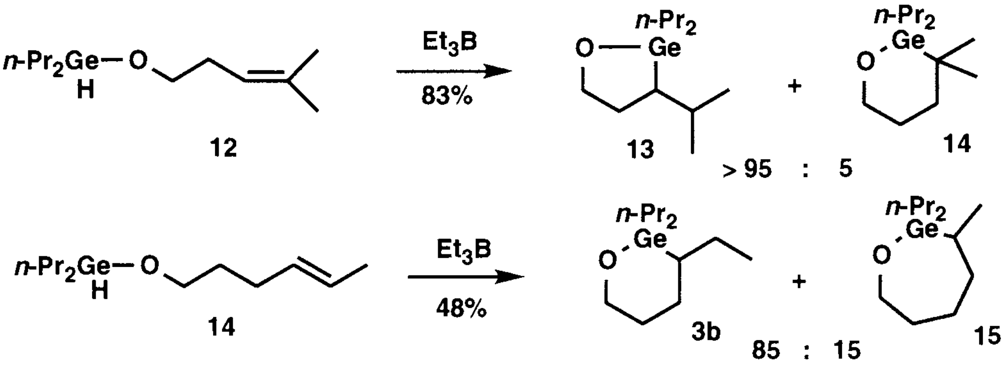


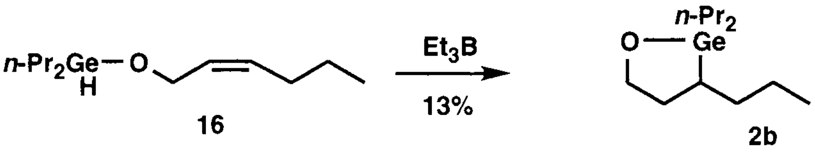
a : $R^1 = R^2 = H$ 85% b : R^1 = n-Bu $R^2 = H$ 87%
c : R^1 = Ph $R^2 = H$ 81% d : R^1 = Ph R^2 = Me 84%

In a similar fashion, the terminal acetylenic alcohol **7** provided the six-membered product **8** exclusively upon successive treatment with *n*-Pr_2GeHCl-2,6-lutidine and triethylborane as in the case of the homoallylic alcohols **4**, although the yields of **8** were inferior to those of the corresponding germyl ether **6**. The use of internal acetylenic substrate **9** resulted in the formation of a mixture of six-membered ring product **10** and five-membered one **11**.[10]

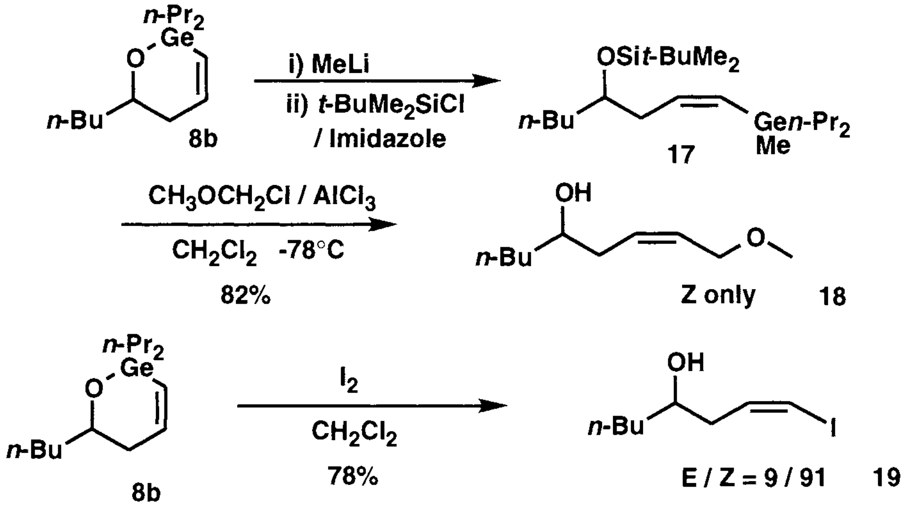


The germyl ether **12** having a trisubstituted olefinic moiety afforded the five-membered ring product **13** selectively. Whereas **14**, generated from 4-hexen-1-ol and chlorodipropylgermane, gave a mixture of six-membered ring product **3b** and seven-membered ring product **15** in an 85 : 15 ratio, germyl ether **16**, 2-hexenoxydipropylgermane afforded 1-germa-2-oxacyclopentane **2b** in only 13% yield along with unidentified complex products.





1-Germa-2-oxacyclohexanes or 1-germa-2-oxacyclopentanes were easily transformed into 4-trialkylgermyl-1-alkanols or 3-trialkylgermyl-1-alkanols upon treatment with alkyllithium or Grignard reagents.[6] Attempts to cleave carbon-germane bond of **2b** or **3b** oxidatively with various methods, which are effective for the oxidative cleavage of carbon-silicon bond,[12] resulted in the formation of a complex mixture and no desired diol was observed in the reaction mixture. However, alkenylgermane **8b** was converted into the corresponding ether **18** upon treatment with methyllithium followed by chloromethyl methyl ether in the presence of aluminium trichloride. In addition, treatment of **8b** with iodine in dichloromethane at 25 °C for 2 h gave the alkenyl iodide **19** (*E*/*Z* = 9/91) in 78% yield.[13]



A typical experimental procedure is as follows. A hexane solution of 1-octen-4-ol (**4b**, 0.19 g, 1.5 mmol) and 2,6-lutidine (0.16 g, 1.5 mmol) was added to a solution of chlorodipropylgermane (0.29 g, 1.5 mmol) in hexane (5 ml) at –78 °C. After stirring for 20 min at –78 °C, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and kept there for 30 min. Triethylborane (1.0 *M* hexane solution, 0.15 ml, 0.15 mmol) was added to the resulting mixture containing germyl ether **5b** and the reaction mixture was stirred at 25 °C for 2 h. The precipitate was filtered and filtrate was concentrated under reduced pressure. The residual oil was distilled (70 °C, bath temp, 1 Torr) to give cyclic germyl ether **6b** (0.37 g) in 87% yield.

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References

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2) K. Tamao, T. Tanaka, T. Nakajima, R. Sumiya, H. Arai, and Y. Ito, *Tetrahedron Lett.*, **27**, 3377 (1986).

3) Platinum catalyzed intermolecular hydrogermylation: K. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **25**, 3221 (1984); R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **40**, 73 (1972).

4) The reaction mediated by AIBN (azobisisobutyronitrile, hexane reflux, 6 h) afforded a mixture of **2b** and **3b** (**2b** : **3b** = 22 : 78) in lower yield (<50%).

5) The reaction was performed with 0.1 *M* solution of **1b.** In higher concentration (1.0 *M*), the ratio of 5-exo/6-endo increased (**2b** : **3b** = 40 : 60). Thus, the six-membered ring product **3b** is thermodynamic one.

6) 1-Germa-2-oxacyclopentane **2b** was labile to acid and partially decomposed during purification by silica-gel column chromatography. Thus, the combined yield of **2b** and **3b** was determined after distillation of the crude product, and the ratio (**2b** : **3b**) was determined by ^{1}H NMR. An addition of methyllithium to a mixture of **2b** and **3b** gave a mixture of 3-dipropylmethylgermyl-1-hexanol and 4-dipropylmethylgermyl-1-hexanol.

7) Under more severe conditions (60 °C in benzene, 10 h), internal olefins isomerized by addition-elimination sequence of Ph_3Ge radical upon treatment with Ph_3GeH-Et_3B. See Ref. 1.

8) **6a**: Bp 65–67 °C (bath temp, 1.5 Torr, 1 Torr = 133.322 Pa); IR (neat) 2952, 2922, 2864, 1460, 1135, 1078, 1048, 1018, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.92–1.07 (m, 12H), 1.45–1.64 (m, 6H), 1.84–1.94 (m, 2H), 3.91 (t, J = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -13.91, 17.51, 17.74, 17.98, 23.50, 32.00, 67.12. Found: C, 51.77; H, 9.31%. Calcd for $C_{10}H_{22}GeO$: C, 52.02; H, 9.60%. **6b**: Bp 64–66 °C (bath temp, 0.8 Torr); IR (neat) 2952, 2924, 2860, 1459, 1142, 1071, 1057, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.83–1.12 (m, 15H), 1.12–1.79 (m, 13H), 2.01–2.13 (m, 1H), 3.61–3.70 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -12.58, 14.18, 17.09, 17.43, 17.66, 17.81, 19.21, 22.86, 22.93, 27.92, 36.26, 36.40, 75.53. Found: C, 58.57; H, 10.72%. Calcd for $C_{14}H_{30}GeO$: C, 58.59; H, 10.54%.

9) Distillation of **5a** (60 °C, bath temp, 1 Torr) resulted in a partial formation of **6a** along with **5a**. The ratio of **6a**:**5a** varied from 1:9 to 5:5 by changing the distillation conditions (bath temp). In addition, compounds **5a**, **5b**, and **5c** were sensitive to weak acid.and purification of these compounds by silica-gel column failed.

10) The structure of **10** was confirmed by the examination of ^{1}H NMR spectrum: δ 0.90–1.15 (m, 13H), 1.45–1.62 (m, 4H), 2.14 (qdt, J = 7.6, 1.5, 1.5 Hz, 2H), 2.20 (tdt, J = 5.1, 4.5, 1.5 Hz, 2H), 3.89 (t, J = 5.1 Hz, 2H), 6.42 (tt, J = 4.5, 1.5 Hz, 1H). Decoupling the two-protons triplet at δ 3.89 caused the multiplet at δ 2.20 to collapse to doublet triplet in the 300 MHz NMR spectrum of six-membered ring product **10**. The compound **11** as well as **2b** was not stable to silica-gel column purification. An addition of propylmagnesium bromide to a mixture of **10** and **11** provided 3-tripropylgermyl-3-hexen-1-ol (*E*/*Z* = 16/84) along with unchanged **10**. Major (*Z*) isomer was further transferred into (*E*)-3-hexen-1-ol (HI, benzene)[11] which was identical with a commercially available sample (Aldrich Chemical Company).

11) Protiodegermylation proceeded under the similar reaction conditions for protiodesilylation. K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, **1975**, 2825.

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