Thermolysis of *β*-Siloxyalkylboranes: Formation of Alkenes and/or Silyl Enol Ethers

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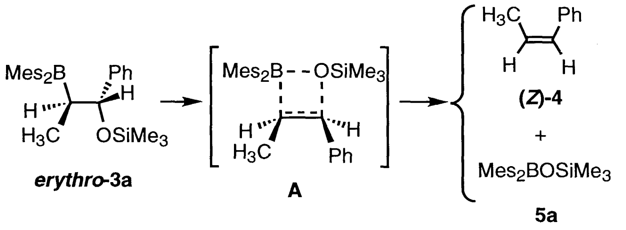
erythro-Trimethylsilyl ether **3a** underwent stereospecific and quantitative *syn*-elimination of trimethylsiloxy(dimesityl)borane upon heating to give (*Z*)-β-methylstyrene like the corresponding hydroxy borane **1**, whereas the thermolysis of *t*-butyldimethylsilyl ether **3c** afforded mainly (*Z*)-silyl enol ether **6** by elimination of dimesitylborane. Triethylsilyl ether **3b** gave a mixture of both products. These results indicate that two elimination reactions via a four-centered transition state proceed competitively depending on the steric bulkiness of the silyl group.

In the course of our study on oxetanes[1] bearing a highly coordinate main group element at the neighboring position we recently achieved the synthesis of a tetracoordinate 1,2-oxaboretanide, an intermediate of boron-Wittig reaction under basic conditions.[2] We also disclosed that on heating β-hydroxy boranes undergo *syn*-elimination of a hydoxyborane to give stereospecifically the corresponding olefins under neutral conditions.[3] We now wish to report the thermolysis of β-siloxy boranes, which is controlled by the bulkiness of the silyl group.

According to the method reported for the preparation of *erythro*-trimethylsilyl ether **3a**,[2,4] triethylsilyl and *t*-butyldimethylsilyl ethers (**3b** and **3c**) were obtained in 42 and 61% yields, respectively,[5] by sequential treatment of *erythro*-Mes_2B-CHMeCPhHOH (*erythro*-**1**), with R_3SiCl (**2**) (**b**: R = Et; **c**: R_3 = *t*-$BuMe_2$) in the presence of imidazole in *N,N*-dimethylformamide and then with water.

In the ^1H NMR spectrum of **3** the signals assigned to *o*-CH_3 of two mesityl groups were broad, presumably because of the hindered rotation of the mesityl group. The degree of broadening increases in the order of **3c**>**3b**>**3a** with an increase in the bulkiness of the silyl groups.



Trimethylsilyl ether **3a** was heated around 100 °C in C_6D_6 to give (*Z*)-β-methylstyrene (**4**) and trimethylsiloxy(dimesityl)-borane (**5a**) quantitatively. Monitoring of the olefin formation by ^1H NMR showed that the reaction was the first order in **3a**. Temperature-dependence of the rate constants for **1** and **3a** led to the estimation of the activation parameters ($\Delta H^{\neq}$= 21.5±0.4 kcal mol^{-1}, $\Delta S^{\neq}$= -14.1±1.0 e.u. for **1**[6]; $\Delta H^{\neq}$= 24.6±0.4 kcal mol^{-1}, $\Delta S^{\neq}$= -16.3±1.1 e.u. for **3a**), indicating that the reactions of both **1** and **3a** proceed via a similar reaction mechanism involving a four-centered rigid transition state (for the reaction of **3a**, see **A**) judging from similar activation parameters with negative activation entropies. Although non-stereoselective elimination of trimethylsiloxyborane under neutral conditions[4] and *anti*-elimination under acidic conditions[7] were reported, the present reaction is the first example for stereospecific *syn*-elimination of a siloxyborane. The fact that the reaction was retarded by an introduction of the silyl group prompted us to investigate on the steric effect of silyl groups.

Thermolysis of **3c** having the bulkiest silyl group among **3a-c** gave mainly (*Z*)-silyl enol ether **6c**[5] along with only a small amount of **4**, while that of **3b** afforded a mixture of **4** and **6b**, as shown in Table 1. The stereochemistry of **6b,c** was determined to be (*Z*)-configuration by different NOE experiments.

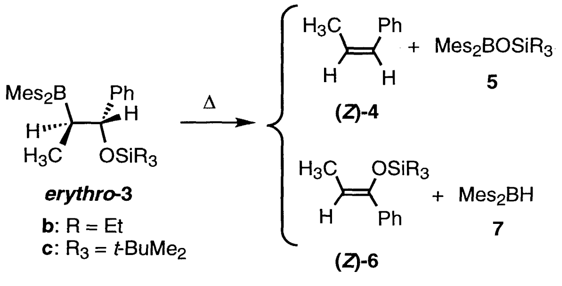


Table 1. Thermolysis of β-Siloxyalkylboranes **3a-c**

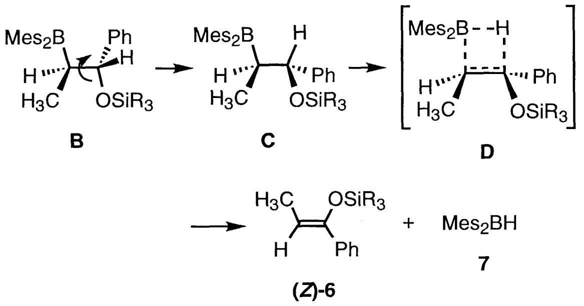
compounds	solvents	temp/°C	time/h	products (yields[a]/%)
3a	C_6D_6	130	2	(*Z*)-**4** (100)
3b	C_6D_6	145	24	(*Z*)-**4** (32) (*Z*)-**6b** (68)
	toluene-d_8	180	9	(*Z*)-**4**[b] (17) (*Z*)-**6b** (83)
3c	toluene-d_8	170	12.5	(*Z*)-**4** (<5) (*Z*)-**6c** (>95)

[a] Determined by ^1H NMR spectroscopy. [b] The ratio of (*Z*)/(*E*) was 88/12. A separate experiment showed that thermal isomerization between (*Z*)- and (*E*)-**4** took place under the reaction conditions.

The results indicate that *syn*-elimination of dimesitylborane (**7**) giving silyl enol ethers **6b,c** via a four-membered transition state can compete with *syn*-elimination of siloxydimesitylborane (**5**) when **3b,c** having a silyl group larger than trimethylsilyl were used.

Since it is reasonably considered that **3b** and **3c** in solution also have conformation **B** like *erythro*-**3a** in the crystalline state,[8] elimination of **7** most likely occurs via a transition state **D** reached from an eclipsed conformer **C** which is in turn formed by rotation of the C-C bond of the most stable conformer **B**.

It is obvious that there exists some interaction between oxygen and boron atoms in the transition state giving **4**. Since such a transition state becomes unfavorable with increasing the bulkiness of the silyl group, the elimination[9] proceeds via another transition state **D** in the reactions of **3b** and **3c** to afford (*Z*)-**6**, with the ratio of **4**/**6** being reduced upon increasing the bulkiness of the silyl group.



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References and Notes

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5 Physical and spectral data of **3c** and **6c** are shown as typical examples: **3c**: colorless crystals; mp 111.7-113.4 °C (decomp); ^{1}H NMR ($\mathrm{CDCl_3}$, 500.1 MHz) δ -0.39 (s, 3H, $\mathrm{SiC\underline{H}_3}$), -0.07 (s, 3H, $\mathrm{SiC\underline{H}_3}$), 0.80 (s, 9H, $\mathrm{SiC(C\underline{H}_3)_3}$), 1.27 (d, ^3J = 7.9 Hz, 3H, $\mathrm{SiCHC\underline{H}_3}$), 2.00 (brs, 12H, *o*-$\mathrm{C\underline{H}_3}$ of Mes), 2.24 (s, 6H, *p*-$\mathrm{C\underline{H}_3}$ of Mes), 2.89 (dq, ^3J = 7.9, 8.3 Hz, 1H, $\mathrm{SiC\underline{H}CH_3}$), 4.80 (d, ^3J = 8.3 Hz, 1H, $\mathrm{C\underline{H}O}$), 6.69 (s, 4H, *m*-H of Mes), and 6.96-7.06 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 125 MHz) δ -5.0 (q, $\mathrm{Si\underline{C}H_3}$), -4.5 (q, $\mathrm{Si\underline{C}H_3}$), 13.5 (q, $\mathrm{\underline{C}H_3}$ of Mes), 18.2 (s, $\mathrm{SiC(\underline{C}H_3)_3}$), 21.0 (q), 23.1 (q), 25.9 (s, $\mathrm{Si\underline{C}(CH_3)_3}$), 44.9 (d, $\mathrm{Si\underline{C}H}$), 77.5 (d, $\mathrm{\underline{C}HO}$), 126.4 (d), 127.2 (d), 127.5 (d), 128.4 (d), 137.8 (s), 138.7 (s), 142.5 (s), and 146.0 (s). Anal. Found: C, 78.45; H, 9.28%. Calcd for $\mathrm{C_{33}H_{47}BOSi\cdot 1/2H_2O}$: C, 78.08; H, 9.53%. **6c**: colorless viscous oil: ^{1}H NMR ($\mathrm{CDCl_3}$, 500.1 MHz) δ -0.05 (s, 6H, $\mathrm{Si(C\underline{H}_3)_2}$), 0.98 (s, 9H, $\mathrm{SiC(C\underline{H}_3)_3}$), 1.72 (d, ^3J = 6.8 Hz, 3H, $\mathrm{=CHC\underline{H}_3}$), 5.18 (q, ^3J = 6.8 Hz, 1H, $\mathrm{=C\underline{H}CH_3}$), 7.21 (t, ^3J = 7 Hz, 1H, *p*-H of Ph), 7.27 (t, ^3J = 7 Hz, 2H, *m*-H of Ph), and 7.41 (t, ^3J = 7 Hz, 2H, *o*-H of Ph). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 125 MHz) δ -4.1 (q, $\mathrm{Si\underline{C}H_3}$), 11.7 (q, $\mathrm{\underline{C}H_3}$), 18.3 (s, $\mathrm{Si\underline{C}(CH_3)_3}$), 25.9 (q, $\mathrm{SiC(\underline{C}H_3)_3}$), 105.8 (d, $\mathrm{=\underline{C}HCH_3}$), 125.7 (d), 127.3 (d), 127.7 (d), 128.4 (s), 139.8 (s), and 150.2 (s). HRMS (70 eV) *m/z* Found: 248.1584. Calcd for $\mathrm{C_{15}H_{24}OSi}$, $\mathrm{M^+}$: 248.1596.

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7 G. L. Larson, E. Hernández, C. Alonso, and I. Nieves, *Tetrahedron Lett.*, **1975**, 4005.

8 The X-ray crystallographic analysis of *erythro*-**3a** showed that it has a structure where dimesitylboryl and trimethylsiloxyl groups are *anti*-periplanar to each other; see, the supplementary materials in Ref. 2.

9 This type of retrohydroboration is known as a key step of thermal isomerization of alkylboranes: for a review, see: A. Pelter and K. Smith, "Comprehensive Organic Chemistry," ed by D. H. R. Barton, W. D. Ollis, Pergamon, Oxford (1979), Vol.3, Chapter 14.3, pp 860-861.