Control Factors of Two Reaction Modes of Pentacoordinate 1,2-Oxasiletanides, the Peterson Reaction and Homo-Brook Rearrangement

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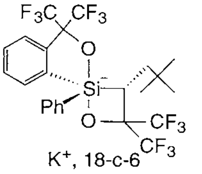
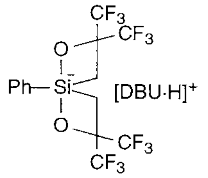
Thermolyses of pentacoordinate 1,2-oxasiletanides with or without a neopentyl group at the 3-position in the presence of a proton source afforded the corresponding olefin and/or alcohol, indicating that they are the intermediates of both the Peterson reaction and homo-Brook rearrangement which are two possible modes in the reaction of β-hydroxyalkylsilanes with bases.

For the reaction of β-hydroxyalkylsilanes with bases, two reaction modes are possible. One is an olefin formation reaction known as the Peterson reaction, which has been widely utilized to synthesize geometrically defined olefins.[1] On the other hand, when the reaction is carried out in the presence of a proton source, intramolecular 1,3-rearrangement of a silyl group from carbon to oxygen atoms followed by protonation (homo-Brook rearrangement) takes place to give the corresponding silyl ether.[2] Both reaction modes have been thought to proceed via pentacoordinate 1,2-oxasiletanides (i.e. oxetanes bearing a pentacoordinate silicon at the neighboring position). Indeed we have reported the synthesis of pentacoordinate 1,2-oxasiletanide **1a** and its thermolysis giving the corresponding olefin quantitatively. These facts indicate that **1a** is a real intermediate of the Peterson reaction under basic conditions.[3] On the other hand, we have synthesized a pentacoordinate silicate containing two oxasiletane rings (i.e. spirobis[1,2-oxasiletanide] **2**), and found that **2** acts as an intermediate of homo-Brook rearrangement.[4] The reactivity difference between **1a** and **2** prompted us to investigate effects of the substituent at the 3-position and a counter cation on the reaction of pentacoordinate species. Here, we report that they show reactivity as the intermediates of both the Peterson reaction and homo-Brook rearrangement.

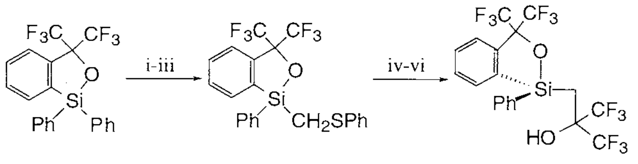


1a



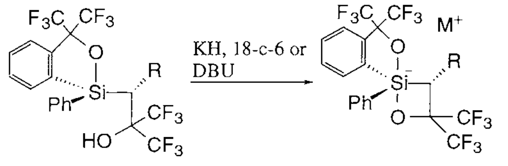
2

We used pentacoordinate 1,2-oxasiletanides bearing the Martin ligand, because of their relatively high stability and their easy derivation. β-Hydroxyalkylsilane **5** was prepared by sequential treatment of **4**, which was obtained by two step reaction from **3**,[6] with lithium naphthalenide (LiNaph), hexafluoroacetone, and then aqueous NH_4Cl (Scheme 1). Pentacoordinate 1,2-oxasiletanides **1a,b** and **7a,b** were synthesized in moderate to high yields by deprotonation of **5** and **6**[3] with KH in the presence of 18-crown-6 (18-c-6) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, respectively (Scheme 2).[7] The ^{29}Si NMR chemical shifts of **1b**, **7a**, and **7b** were −63.87, −76.30, and −64.94, respectively, all of which are close to that of **1a** (−71.83),[3] indicating the formation of pentacoordinate silicates. Other NMR spectral data also support these structures. Very interestingly, **1b** and **7b**, whose counter cation is $[DBU{\cdot}H]^+$, are considerably stable at room temperature in sharp contrast to **2**.[4]



3 **4** (54%) **5** (22%)

Scheme 1. Reagents and conditions: i, $PhSCH_2Li$, THF, 0 °C, 2 h ; ii, aq. NH_4Cl; iii, CH_3CN, 25 °C, 12 h; iv, LiNaph, THF, −78 °C, then −20 °C, 1 h; v, $(CF_3)_2C{=}O$, −78 °C; vi, aq. NH_4Cl.

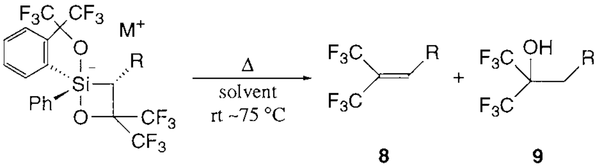


5: R = H
6: R = CH_2-*t*-Bu

1a: R = CH_2-*t*-Bu, $M^+ = K^+$, 18-c-6 (91%)
1b: R = CH_2-*t*-Bu, $M^+ = [DBU{\cdot}H]^+$ (83%)
7a: R = H, $M^+ = K^+$, 18-c-6 (68%)
7b: R = H, $M^+ = [DBU{\cdot}H]^+$ (54%)

Scheme 2.

Table 1. Thermolysis of pentacoordinate 1,2-oxasiletanides

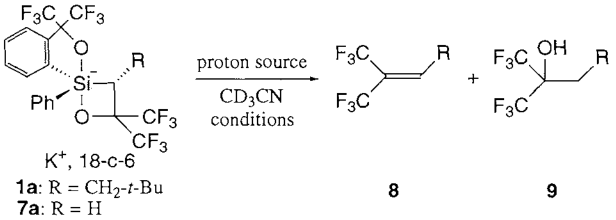


8 **9**

entry	compound	R	M+	solvent	yield[b]	
					8	**9**
1[a]	**1a**	CH_2-*t*-Bu	K^+, 18-c-6	CD_3CN	quant.[c]	–
2	**1b**	CH_2-*t*-Bu	$[DBU{\cdot}H]^+$	$CDCl_3$	57%[c]	–
3	**7a**	H	K^+, 18-c-6	CD_3CN	quant.	–
4	**7b**	H	$[DBU{\cdot}H]^+$	$CDCl_3$	trace	69%

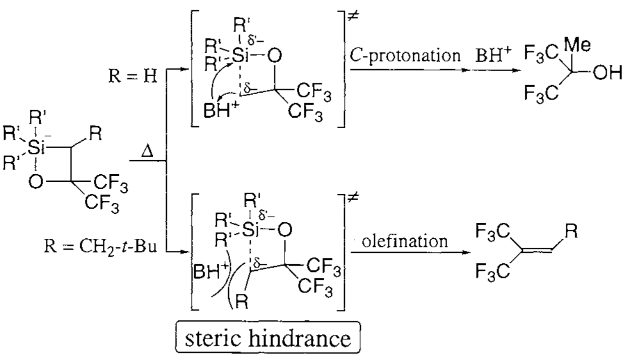
[a] Ref 3. [b] Estimated by ^{19}F NMR spectroscopy. [c] This olefin was partly isomerized to its double-bond-shifted isomer. The yield is shown as the sum of those of two isomers.

Table 2. Thermolysis of pentacoordinate 1,2-oxasiletanides in the pressence of a proton source



entry	compound	proton source	conditions	yield[c] 8	yield[c] 9
1	**1a**	CH_3OH[a]	75 °C, 10 h	–[d]	–
2	**1a**	CF_3CH_2OH[a]	60 °C, 24 h	–[d]	–
3	**1a**	CH_3COOH[b]	60 °C, 5 h; 80 °C, 4 h	quant.	–
4	**7a**	CH_3OH[a]	75 °C, 18 h	–[d]	–
5	**7a**	CF_3CH_2OH[a]	60 °C, 8 h	2%	98%
6	**7a**	CH_3COOH[b]	rt, 27 h	–	quant.

[a] 50 equiv. of proton source was used. [b] 10 equiv. of proton source was used. [c] Estimated by ^{19}F NMR spectroscopy. [d] The yield could not be estimated because of secondary decomposition of **8**, although **8** was a sole product in the early stage of the reaction.



Scheme 3. Decomposition route of pentacoordinate 1,2-oxasiletanides in the presence of an effective proton source.

The thermolysis of **1** bearing a neopentyl group at the 3-position afforded the corresponding olefin and its double-bond-shifted isomer t-BuCH=CHCH$(CF_3)_2$, but t-BuCH$_2$CH$_2$C$(CF_3)_2$OH was not observed at all even when the counter cation is [DBU·H]$^+$ (entry 2). On the other hand, the thermolysis of **7** without a neopentyl group gave olefin **8** as a sole product when the counter cation is K$^+$, 18-c-6 (entry 3), but the corresponding alcohol **9** was mainly obtained when the counter cation is [DBU·H]$^+$ (entry 4) (Table 1).

For the purpose of clarifying the effect of a proton source, we also investigated the thermolysis of **1a** and **7a** in the presence of methanol, 2,2,2-trifluoroethanol or acetic acid (Table 2). In the case of **7a**, the corresponding alcohol was a major product in the reactions with the latter two proton sources, although thermolysis in the presence of methanol mainly gave the corresponding olefin. But, the thermolysis of **1a** gave only the olefin even in the presence of 2,2,2-trifluoroethanol or acetic acid.[8]

In summary, alcohol **9** was formed only in the reaction of unsubstituted oxasiletanide **7** in the presence of a proton source of relatively high acidity, while olefin **8** was formed when the protonation of negatively charged carbon, which would be generated by elongation of the Si-C bond in the oxasiletanide ring of **7**, was encumbered by the bulky neopentyl group (Scheme 3).[9] These results clearly indicate that two modes (Peterson reaction and homo-Brook rearrangement) in the reaction of β-hydroxyalkylsilanes with bases proceed via an identical intermediate, a pentacoordinate 1,2-oxasiletanide.

Further study on the reactions of these pentacoordinate 1,2-oxasiletanides with various electrophiles other than proton is underway.

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5 This ligand, [α,α-bis(trifluoromethyl)benzenemethanolato(2–)-C^2,*O*], (-*o*-$C_6H_4C(CF_3)_2O$-), was developed by Martin for stabilizing hypervalent species: E. F. Perozzi, R. S. Michalak, G. D. Figuly, W. H. Stevenson III, W. H. Dess, M. R. Ross, and J. C. Martin, *J. Org. Chem.*, **46**, 1049 (1981).

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7 Physical and spectral data of **7b** shown as a typical example; **7b**: colorless crystals; mp 50.9 -56.8 °C (decomp.); ^{1}H NMR (CD_3CN, 500 MHz) δ 1.62-1.75 (m, 6H, [DBU·H]$^+$), 1.90-1.97 (m, 2H, [DBU·H]$^+$), 2.04 (d, ^2J = 15.3 Hz, 1H, SiC*H*H'), 2.28 (d, ^2J = 15.3 Hz, 1H, SiCH*H'*), 2.52-2.57 (m, 2H, [DBU·H]$^+$), 3.21 (t, ^3J = 5.6 Hz, 2H, [DBU·H]$^+$), 3.42 (t, ^3J = 6.0 Hz, 2H, [DBU·H]$^+$), 3.48-3.52 (m, 2H, [DBU·H]$^+$), 4.07 (br s, 1H, HN of [DBU·H]$^+$), 7.10-7.19 (m, 3H), 7.33 (td, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1H), 7.41 (td, ^3J = 7.2 Hz, ^4J = 1.0 Hz, 1H), 7.47 (d, ^3J = 7.5 Hz, 1H), 7.81 (d, ^3J = 7.6 Hz, 2H), 8.01 (d, ^3J = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) δ 19.89 (s), 24.35 (s), 26.94 (s), 29.19 (s), 29.42 (s), 33.92 (s), 39.16 (s), 49.35 (s), 55.24 (s), 75.08 (sept, $^2J_{CF}$ = 29.5 Hz, *C*$(CF_3)_2$), 83.23 (sept, $^2J_{CF}$ = 29.0 Hz, *C*$(CF_3)_2$), 124.40 (s), 125.31 (q, $^1J_{CF}$ = 287.9 Hz, CF_3), 125.42 (q, $^1J_{CF}$ = 287.9 Hz, CF_3), 126.51 (q, $^1J_{CF}$ = 286.9 Hz, CF_3x2), 127.22 (s), 127.89 (s), 129.51 (s), 129.66 (s), 136.60 (s), 136.65 (s), 141.00 (s), 146.00 (s), 146.51 (s), 167.05 (s, C=N of [DBU·H]$^+$).; ^{19}F NMR (254 MHz, CD_3CN) δ –79.04 (q, $^4J_{FF}$ = 9.8 Hz, 3F), –77.72 (q, $^4J_{FF}$ = 9.6 Hz, 3F), –76.87 (q, $^4J_{FF}$ = 9.4 Hz, 3F), –74.81 (q, $^4J_{FF}$ = 9.4 Hz, 3F).; ^{29}Si NMR (54 MHz, THF) δ –64.94 (s). Anal. Found: C, 43.15; H, 3.65; N, 3.63%. Calcd for $C_{28}H_{28}N_2F_{12}O_2Si \cdot CHCl_3$: C, 43.54; H, 3.65; N, 3.50%.

8 No reaction took place when **1a** was treated with 10 equiv. of acetic acid, but **6** was quantitatively recovered by quenching the $CDCl_3$ solution of **1a** with 100 equiv. of acetic acid at room temperature. See Ref 3.

9 The thermolysis of pentacoordinate 1,2-oxasiletanides bearing a *n*-propyl group, which is not as bulky as neopentyl group, at the 3-position in the presence of acetic acid (10 equiv.) gave the corresponding olefin (94%) and alcohol (6%). This result clearly indicates that the steric factor is important for the determination of the reaction modes.