

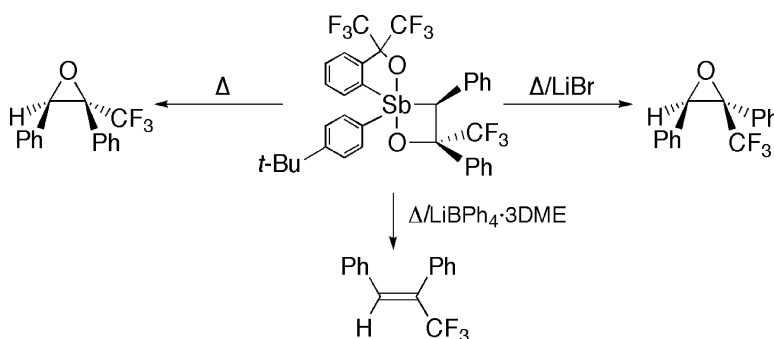
Communication

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Synthesis, Structure, and Thermolysis of a Pentacoordinate 1,2-Oxastibetane

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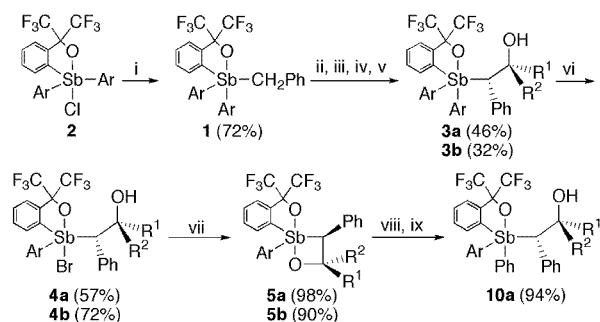
A pentacoordinate 1,2-oxaphosphetane has been widely accepted as the intermediate of the Wittig reaction, which is well-known as a useful method for olefin formation.¹ On the other hand, reactions of stibonium ylides (heavier congeners of phosphonium ylides) with carbonyl compounds afford olefins and oxiranes, depending on the ylide used.² The difference in reactivity between phosphonium and stibonium ylides toward carbonyl compounds has been ascribed to different reaction intermediates. The olefin and the oxirane are believed to be formed from the corresponding oxetane containing a pentacoordinate group 15 element at the position adjacent to the oxygen atom and from the corresponding *anti*-betaine, respectively. Although the reaction of a stibonium ylide with a carbonyl compound has been investigated by theoretical calculations based on the above assumptions,³ there has been no report of the isolation of an intermediate. We herein describe the synthesis and the properties of a pentacoordinate 1,2-oxastibetane, which is an antimony analogue of a pentacoordinate 1,2-oxaphosphetane and a formal [2 + 2] cycloadduct of a stibonium ylide and a carbonyl compound.

Benzylstiborane **1** bearing the Martin ligand,⁴ which was synthesized by the reaction of chlorostiborane **2**⁵ with benzylmagnesium chloride, was allowed to react successively with LiTMP and trifluoroacetophenone in benzene at room temperature to give a mixture of 2-hydroxyalkylstiboranes **3a** and **3b**. After separation by silica gel column chromatography, treatment of **3a** and **3b** with bromine gave bromo(2-hydroxyalkyl)stiboranes **4a** and **4b**, which were allowed to react with NaH to afford the isomeric pentacoordinate 1,2-oxastibetanes **5a** and **5b**, respectively (Scheme 1). Although **5b** was unstable toward moisture and could not be isolated, **5a** was successfully isolated by recrystallization from hexane as colorless crystals.⁶

X-ray crystallographic analysis of **5a**⁷ revealed that it has a distorted trigonal bipyramidal structure with two oxygen atoms at the apical positions and three carbon atoms at the equatorial positions. Moreover, the relative configuration of the phenyl group at the 3-position is *cis* to both the 4-*tert*-butylphenyl group at the 2-position and the phenyl group at the 4-position of the 1,2-oxastibetane ring (Figure 1). The ¹H, ¹³C, and ¹⁹F NMR spectra (CDCl₃) of **5a** were consistent with the crystal structure. At room temperature, **5a** easily undergoes epimerization at the Sb atom by pseudorotation to give the equilibrium mixture of **5a** and its epimer in a ratio 5:1.⁸

Thermolysis of **5a** in *o*-xylene-*d*₁₀ at 220 °C for 17 h gave the corresponding oxirane **6** (90%) with retention of configuration and stibine **7** (89%) along with a small amount of 1,1,1-trifluoro-3,3-diphenyl-2-propanone (5%) and *tert*-butylbenzene (5%), the latter two of which were omitted in Table 1 (entry 1). Similar results were obtained when thermolysis was carried out in CD₃CN (entry 4). In both cases olefin **8** was not detected, which is in marked contrast to the thermolysis of pentacoordinate 1,2-oxaphosphetanes.¹ The formation of **6** with retention of configuration strongly suggests

Scheme 1^a



^a Reaction conditions: Ar = 4-*t*-Bu-C₆H₄, a: R¹ = Ph, R² = CF₃, b: R¹ = CF₃, R² = Ph. i) PhCH₂MgCl (1.2 equiv), Et₂O, 0 °C, 2 h; ii) LiTMP (2.2 equiv), benzene, rt, 12 h; iii) Ph(F₃C)C=O (2.2 equiv), rt, 30 min; iv) H₃O⁺; v) SiO₂ column chromatography; vi) Br₂ (2.0 equiv), CHCl₃, rt, 1 h; vii) NaH (4.0 equiv), THF, rt, 2 h; viii) PhLi, THF, rt, 1 h; ix) H₃O⁺.

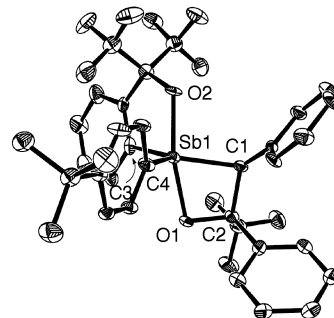
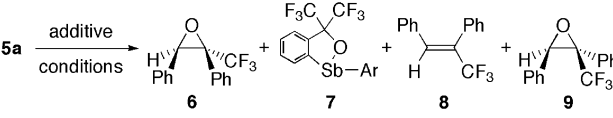


Figure 1. ORTEP drawing of **5a** with thermal ellipsoids plotted at 50% probability. Selected bond lengths (Å) and angles (deg): Sb1–O1, 2.054(7); Sb1–O2, 2.038(7); Sb1–C1, 2.144(9); Sb1–C3, 2.103(10); Sb1–C4, 2.106(10); C1–C2, 1.575(13); O1–C2, 1.440(11); O1–Sb1–O2, 165.4(3); O1–Sb1–C1, 69.7(3); Sb1–O1–C2, 96.2(5); Sb1–C1–C2, 88.7(5); C1–C2–O1, 105.4(7). One of the independent molecules of **5a** and the hydrogen atoms are omitted for clarity.

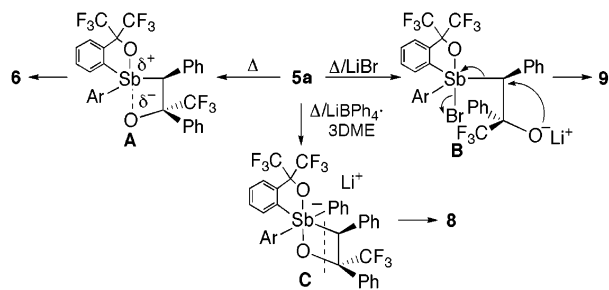
that the reaction occurs via apical–equatorial ligand coupling.⁹ Although the mode of such ligand coupling is thermally forbidden according to the Woodward–Hoffmann rules, Morokuma et al. reported that this process is thermally favored over other symmetry-allowed ligand coupling processes in the case of BiH₃, which involves a zwitterionic transition state.^{8,10} Since a polar transition state was strongly supported by the solvent effect (entries 2 and 3), it is most likely that the formation of **6** proceeds via apical–equatorial ligand coupling through polar transition state **A** (Scheme 2).

Thermolysis of **5a** in the presence of LiBr or LiI in CD₃CN at 140 °C provided a mixture of **6**, **7**, and **9** (entries 5 and 6). The formation of **6** and **9** contrasts the reaction without the salts which affords only **6** (entry 4). Taking into consideration the results of the thermolyses with LiI and (*n*-Bu)₄NBr (entries 6 and 7), it is concluded that both lithium cation and bromide ion play an important role in the formation of **9**, which requires the interaction

Table 1. Thermolyses of **5a** in the Presence of Salts^{a,b}


entry	solvent	time (h)	additive	yields ^c (%)				
				5a	6	7	8	9
1	<i>o</i> -xylene- <i>d</i> ₁₀	17	none	5	90	89	0	0
2	<i>o</i> -xylene- <i>d</i> ₁₀	48	none	98	2	2	0	0
3	CD ₃ CN	48	none	52	46	48	0	0
4	CD ₃ CN	112.5	none	19	80	80	0	0
5	CD ₃ CN	10	LiBr	12	10	88	0	71
6	CD ₃ CN	10	LiI	56	18	44	0	19
7	CD ₃ CN	10	(<i>n</i> -Bu) ₄ NBr	68	13	32	2	18
8	CD ₃ CN	10	LiBPh ₄ ·3DME	10	<1	<1	85	<1
9	PhCN	6	PhLi	0	0	0	74	0

^a Thermolyses were carried out at 220 °C for entry 1 and 140 °C for entries 2–9. ^b Rearranged ketone and *tert*-butylbenzene were omitted for clarity in Table 1. ^c Yields were calculated on the basis of the molar ratios with respect to **5a**. Unreacted starting material **5a** was recovered.

Scheme 2

of a lithium cation and an oxygen atom of **5a**, and the nucleophilic attack of bromide ion on the antimony atom. Oxirane **9** can be obtained by the backside attack of the oxide anion of the *anti*-betaine type intermediate **B** (Scheme 2).

Interestingly, thermolysis of **5a** in the presence of lithium tetraphenylborate·3dimethoxyethane (LiBPh₄·3DME) gave olefin **8** (85%) selectively, together with **5a** (10%) and trace amounts of **6**, **7**, and **9** (entry 8). Other products containing antimony and the Martin ligand were obtained as a complex mixture, and they could not be identified by ¹H and ¹⁹F NMR spectroscopy, but FAB-MS of the reaction mixture showed a peak at *m/z* 573, which could be assigned to the *tert*-butylphenyl(phenyl)benzoxastibonium ion. It is expected that formation of **8** involves the migration of a phenyl group from the boron atom of tetraphenylborate to the antimony atom of **5a**, followed by thermal decomposition of the hexacoordinate 1,2-oxastibetanide **C** (Scheme 2).¹¹ Actually, **C** (which was alternatively generated by the reaction of **5a** with PhLi in THF at 0 °C) gave **8** (74%) upon heating at 140 °C after changing the solvent from THF to benzonitrile (entry 9). Hydrolysis of **C** provided 2-hydroxyalkylstiborane **10a** (94%) (Scheme 1), and the reaction of **10a** with LiH gave **C** at room temperature quantitatively. These results suggest that hexacoordinate 1,2-oxastibetanide **C** is an intermediate in the olefin formation reaction from **5a** in the presence of LiBPh₄·3DME.

We have found that thermolyses of a pentacoordinate 1,2-oxastibetanide under suitable conditions give the corresponding

oxirane, with both retention and inversion of configuration, and the corresponding olefin. It is interesting that three different products can be selectively obtained from a single compound by appropriately tuning the conditions.

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Supporting Information Available: Experimental procedures and spectral data for **1**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, and **10a** (PDF), and data for the X-ray crystallographic analysis of **5a** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) **5a**: colorless crystals from hexane; mp 189–190 °C dec; ¹H NMR (500 MHz, CDCl₃) δ 1.30 (s, 9H), 6.09 (s, 1H), 6.65 (d, ³J_{HH} = 7.5 Hz, 2H), 6.94 (t, ³J_{HH} = 7.4 Hz, 2H), 7.04 (t, ³J_{HH} = 7.5 Hz, 1H), 7.16–7.19 (m, 5H), 7.30 (br d, ³J_{HH} = 6.4 Hz, 2H), 7.55 (d, ³J_{HH} = 8.4 Hz, 2H), 7.68 (t, ³J_{HH} = 7.9 Hz, 1H), 7.74 (t, ³J_{HH} = 7.1 Hz, 1H), 7.87 (br d, ³J_{HH} = 7.3 Hz, 1H), 8.19 (d, ³J_{HH} = 7.4 Hz, 1H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 31.1 (s, CH₃), 35.1 (s), 78.7 (s, CH), 81.7 (q, ²J_{CF} = 28 Hz), 82.1 (sept, ²J_{CF} = 30 Hz), 123.38 (q, ¹J_{CF} = 288 Hz), 123.41 (q, ¹J_{CF} = 288 Hz), 124.5 (q, ¹J_{CF} = 288 Hz), 126.2 (s), 126.4 (s), 127.1 (s), 127.3 (s), 127.4 (s), 127.8 (s), 128.2 (s), 128.3 (s), 128.5 (s), 130.1 (s), 131.3 (s), 132.3 (s), 132.4 (s), 133.5 (s), 134.1 (s), 136.5 (s), 137.2 (s), 156.4 (s); ¹⁹F NMR (470 MHz, CDCl₃) δ –79.3 (s, 3F), –76.8 (q, ⁴J_{FF} = 8.2 Hz, 3F), –74.3 (q, ⁴J_{FF} = 8.2 Hz, 3F); MS (FAB) *m/z* 761 (M + H⁺), 691 (M⁺ – CF₃), 648, 586, 513, 496, 481, 427, 335, 273, 185, 115, 57; Anal. Calcd for C₃₄H₂₈F₉O₂Sb: C, 53.64; H, 3.71. Found C, 53.68; H, 3.89.
- (7) Crystal data for **5a**: C₃₄H₂₈F₉O₂Sb, *FW* = 761.31, triclinic, space group *P*-1, *a* = 9.733(2) Å, *b* = 10.284(5) Å, *c* = 36.391(7) Å, α = 97.523(6)°, β = 90.015(13)°, γ = 118.133(7)°, *V* = 3176.6(17) Å³, *Z* = 4, *D_c* = 1.592 g cm^{–3}. The final cycle of full-matrix least-squares refinement was based on 10995 observed reflections and 835 variable parameters and converged at R1 = 0.0988 (*I* > 2σ(*I*)) and wR2 (all data) = 0.1917 with a GOF = 1.382.
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