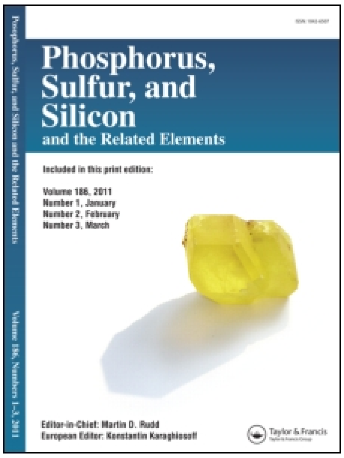

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SYNTHESIS, STRUCTURE AND THERMOLYSIS OF PENTACOORDINATE 1,2-OXASTIBETANES

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SYNTHESIS, STRUCTURE AND THERMOLYSIS OF PENTACOORDINATE 1,2-OXASTIBETANES

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Pentacoordinate 1,2-oxastibetanes have been synthesized and characterized by x-ray crystallographic analysis and NMR spectroscopy. Thermolyses of a pentacoordinate 1,2-oxastibetane were carried out under various conditions to give the corresponding oxirane with retention of configuration, the oxirane with inversion of configuration and the olefin respectively.

Keywords: Ligand coupling; oxirane formation; pentacoordinate 1,2-oxastibetane; thermolysis; x-ray crystallographic analysis

Although the Wittig reaction of a phosphorus ylide with a carbonyl compound gives the corresponding olefin via a pentacoordinate 1,2-oxaphosphetane,[1] the similar reactions of stibonium ylides give either the corresponding olefins or the oxiranes depending on the ylides.[2] On the other hand, in the course of our study on heteracyclobutanes containing highly coordinate main group elements, we have reported that oxetanes containing pentacoordinate phosphorus, silicon, germanium, and tin undergo Wittig-type reactions to give the corresponding olefins upon heating, whereas some of group 16 element analogs gave the corresponding oxiranes with retention of configuration.[3,4] We report here the synthesis, crystal structure and thermolysis of pentacoordinate 1,2-oxastibetanes, formal [2 + 2] adduct of stibonium ylides with carbonyl compounds.

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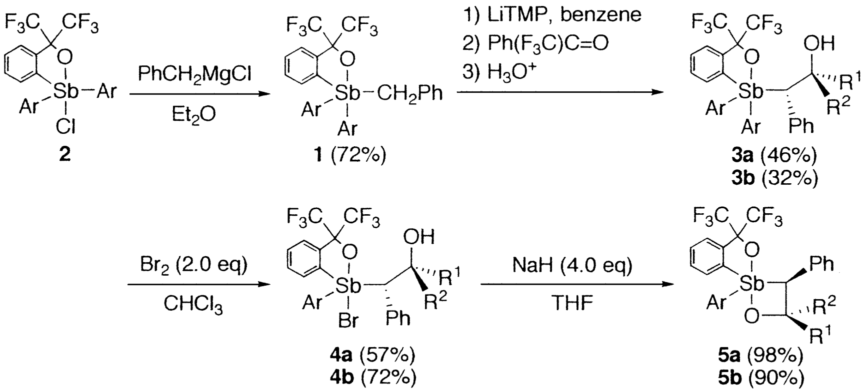
RESULTS AND DISCUSSION

Benzylstiborane **1**, which was prepared by the reaction of chlorostiborane **2**[5] with benzylmagnesium chloride, was allowed to react successively with LiTMP in benzene at room temperature, trifluoroacetophenone, and aqueous NH_4Cl 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 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.



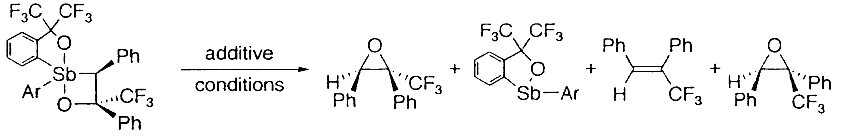
Ar = 4-*t*-Bu-C_6H_4, **a**: R^1 = Ph, R^2 = CF_3, **b**: R^1 = CF_3, R^2 = Ph

SCHEME 1

X-ray crystallographic analysis of **5a** revealed that **5a** has a distorted trigonal bipyramidal structure with two oxygen atoms at the apical positions and three carbon atoms at the equatorial positions, respectively, and that the relative configuration of the phenyl group at the 3-position is *cis* to both the 4-*t*-butylphenyl group at the 2-position and the phenyl group at the 4-position of 1,2-oxastibetane ring. The ^1H, ^{13}C, and ^{19}F NMR spectra of **5a** were consistent with the crystal structure, but **5a** immediately epimerized at the antimony atom to give the equilibrium mixture (5:1) with its epimer at room temperature.

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 *t*-butylbenzene (5%), which were omitted in Table I.

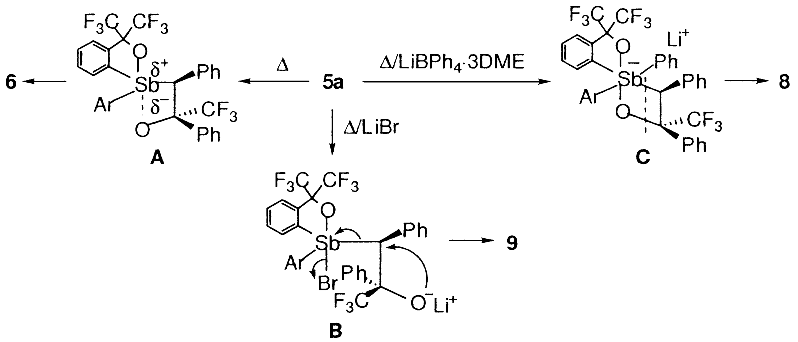
TABLE I Thermolysis of **5a**



	5a	**6**	**7**	**8**	**9**
o-xylene-d_{10}, 220°C, 17 h[a]		90%	89%	0%	0%
LiBr, CD_3CN, 140°C, 10 h[b,c]		10%	88%	0%	71%
$LiBPh_4 3DME$, CD_3CN, 140°C, 10 h[c,d]		<1%	<1%	85%	<1%

[a] Recovery was 5%.
[b] Recovery was 12%.
[c] Additives (6.5 eqiv) were used.
[d] Recovery was 10%.

Use of CD_3CN instead of *o*-xylene-d_{10} as a solvent accelerated the reaction. Olefin **8** was not detected at all on the thermolyses of **5a** in marked contrast to the thermolysis of pentacoordinate 1,2-oxaphosphetanes.[1] The formation of **6** with retention of configuration and the solvent effect strongly suggest that the formation of **6** proceeds via apical–equatorial ligand coupling with polar transition state A (Scheme 2).[4]



SCHEME 2

On the other hand, thermolysis of **5a** in the presence of LiBr in CD_3CN at 140°C provided a mixture of **6**, **7**, and **9**. Oxirane **9** would be obtained by the backside attack of the oxide anion of *anti*-betaine type intermediate **B** (Scheme 2).

Interestingly, thermolysis of **5a** in the presence of lithium tetraphenylborate·3dimethoxyethane (DME) gave the olefin **8** (85%)

selectively, together with **5a** (10%) and trace amounts of **6**, **7**, and **9**. Since FAB—MS of the reaction mixture showed the peak at m/z 573 which was attributable to *t*-butylphenyl(phenyl)benzoxastibonium ion, it is expected that a phenyl group migrated at the initial step from the boron atom of tetraphenylborate to the antimony atom of **5a** affording a hexacoordinate 1,2-oxastibetanide C and it gave **8** upon thermolysis (Scheme 2).[6]

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