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Retentive Stereospecificity in Deoxygenation of Epoxides with Sn-Al or Si-Al Reagents

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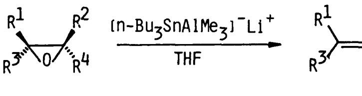
Reaction of epoxides with [n-$Bu_3SnAlMe_3]^-Li^+$ affords β-oxido stannanes which collapse to alkene with overall retention of stereochemistry. The S_N2 type ring opening of epoxides by tributylstannyl anion followed by anti elimination of Bu_3Sn and OAl^-Me_3 groups explains the stereochemical results. The method can be successfully applied to hydroxy epoxides derived from (*E*)-2-nonen-1-ol. The deoxygenation of epoxides with $PhMe_2SiAlEt_2$ also provides olefins of the same geometry as epoxides.

Reagents believed to contain Si–Mg, Si–Al, Sn–Mg, and Sn–Al linkage are obviously reductants in which a Lewis acid center is incorporated. The single bond is weak and the previously reported reaction[1,2] with an acetylenic linkage affords simple and general access to the cis-addition products of the component atoms. In order to examine the nature of these reagents more precisely, we have studied the deoxygenation of epoxides by means of Sn–Al or Si–Al reagents.

The deoxygenation of epoxides to olefins has been widely studied and numerous reagents have been developed. The reduction with strongly reductive metals or metal salts such as chromium(II) ion,[3] tungsten complexes,[4] $TiCl_3/LiAlH_4$,[5] $NbCl_5/NaAlH_4$,[6] and $FeCl_3/n$-BuLi[7] produces olefins nonstereospecifically through a radical intermediate. For instance, treatment of *cis*- or *trans*-5,6-epoxydecane with $TiCl_3/LiAlH_4$ has provided a mixture of (*Z*)- and (*E*)-5-decene in a 21/79 or 18/82 ratio,[5] respectively. In contrast, the reaction with Me_3SiK[8] or $PhMe_2SiLi$[9] has proceeded stereospecifically to give the olefin of geometry opposite to that of the starting epoxide.[10] Here we wish to report that [n-$Bu_3SnAlMe_3]^-Li^+$ (**1**) is effective for the deoxygenation of epoxides to provide olefins of the same geometry as epoxides (Scheme 1).[11]

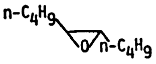
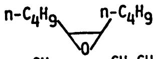
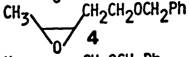
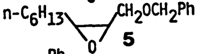
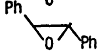
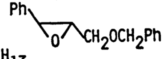
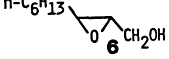
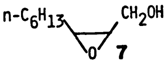
Treatment of (*E*)-5-decene oxide with the reagent **1** derived from n-Bu_3SnLi[12] and Me_3Al at 25 °C gave (*E*)-5-decene exclusively, while (*Z*)-5-decene oxide provided (*Z*)-5-decene as a single product. The results are summarized in Table 1. With some exceptions,[13] the deoxygenation reactions proceeded mostly with high stereospecificities. The deoxygenated product of (*Z*)-stilbene oxide, (*Z*)-stilbene, proved to isomerize partially under the reaction conditions, since treatment of (*Z*)-stilbene with the reagent **1** at 25 °C for 24 h gave a mixture of (*E*)-stilbene and (*Z*)-isomer (*E*/*Z*=40/60).

A priori, the overall retention of configuration can be explained by two ways: (1) S_N2 attack of n-Bu_3Sn anion followed by anti-elimination of Bu_3Sn and OAl^-Me_3 groups, or alternatively (2) retentive C–Sn bond formation under the epoxide ring opening and successive syn elimination of above groups. The stereochemistry of the elimination reaction was studied on the reaction of *erythro*- and *threo*-6-(tributylstannyl)-5-decanols (**2** and **3**) with organoaluminum reagent. Reaction of (*E*)- or (*Z*)-5-decene oxide with tributyltin sodium[14] in 1,2-dimethoxyethane gave the desired erythro- or threo isomer (**2** or **3**), respectively. Exposure of *erythro*-6-(tributylstannyl)-5-decanol **2** to $[Me_4Al]^-Li,^+$ derived from Me_3Al and MeLi, yielded (*E*)-5-decene exclusively, whereas the threo isomer **3** gave (*Z*)-5-decene with high stereoselectivity (Scheme 2).[15] These results proved that the elimination proceeded in anti fashion[16] and therefore

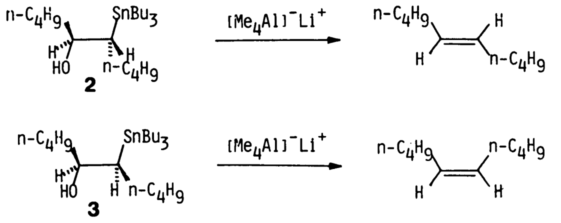


Scheme 1.

Table 1. Deoxygenation of epoxides with [n-$Bu_3SnAlMe_3]^-Li^+$ [a)]

Run	Epoxide	Reaction Time (h)	Olefin	
			Y/%	*E*/*Z*
1		18	80	99% *E*
2		24	67	99% *Z*
3	 **4**	16	63	99% *Z*
4	 **5**	40	70	99% *Z*
5		3	98	99% *E*
6		24[b)]	100	99% *E*
7		6	88	34/66
8		17	88	99% *E*
9	 **6**	18	75	99% *E*
10	 **7**	40	65	99% *Z*

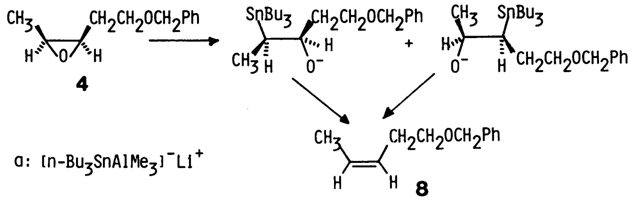
a) The reactions were performed in THF at 25 °C. b) [n-$Bu_3SnAlEt_3]^-Li^+$ was used instead of [n-$Bu_3SnAlMe_3]^-Li^+$.



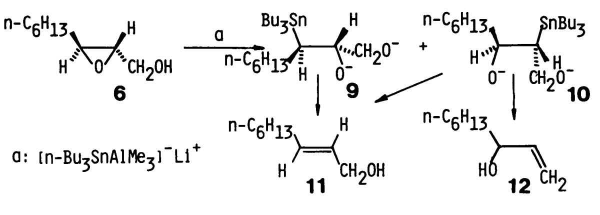
Scheme 2.

the epoxide ring opening must have proceeded with inversion of its stereochemistry at the carbon bearing oxygen. Moreover, both processes are stereospecific.

The intermediate alkoxy stannanes have not been characterized in the deoxygenation reaction with the reagent **1** and we assume that two positional isomers are present, derived from either mode of S_N2 epoxide opening in the case of unsymmetrical epoxides such as **4**, **5**, **6**, and **7**. This complication in no way impairs conversion to olefins in the case of **4** and **5**, since elimination of *n*-Bu$_3$Sn and oxide group from each pair of intermediates provides the same (*Z*)-alkene **8** (Scheme 3). Situation is more complicated in the case of epoxides **6** and **7** derived from (*E*)- and (*Z*)-2-nonen-1-ol. The S_N2 type ring opening of the (*E*)-epoxide **6** could afford two isomeric *β*-oxido stannanes **9** and **10**. The former *β*-oxido stannane **9** would provide (*E*)-2-nonen-1-ol **11** by anti elimination, whereas the latter isomer **10** would produce 1-nonen-3-ol (**12**) in addition to starting allylic alcohol **11**. The absence of the compound **12** in the reaction mixture implies that a single isomer **9** is produced by epoxide ring opening. We are tempted to assume the following reaction scheme. The hydroxyl group is converted into aluminum alkoxide with the first stannyl reagent. The epoxide-oxygen coordinates to the aluminum and this coordination plays the important role in the product determining ring opening step. The epoxide carbon (C$_3$)-oxygen bond is cleaved by the attack of the stannyl anion liberated from the second molecule **1** (Scheme 4)[17]

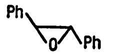
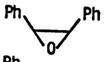
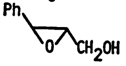
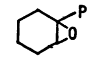
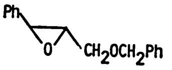


Scheme 3.



Scheme 4.

TABLE 2. DEOXYGENATION OF EPOXIDES WITH Si-Al REAGENTS

Epoxide	Reagent	Conditions Temp	Conditions Time	Olefin	
		°C	h	Y/%	*E*/*Z*
	A[a)]	25	4	71	*E* only
	A	25	5	75	7/3
	A[b)]	25	3	40	*E* only
	A	25	4	54	—
	B[c)]	25	18	72	*Z* only

a) PhMe$_2$SiAlEt$_2$ in hexane. b) PhMe$_2$SiAlEt$_2$ in ClCH$_2$CH$_2$Cl. c) [PhMe$_2$SiAlMe$_3$]$^-$Li$^+$ in THF.

Another stannylalanate reagent, [*n*-Bu$_3$SnAlEt$_3$]$^-$-Li$^+$ derived from *n*-Bu$_3$SnLi and Et$_3$Al was as effective as the reagent **1** for the reduction of epoxides, although the prolonged reaction time was needed for the completion (run 5 and 6 in Table 1). A stannylaluminum, *n*-Bu$_3$SnAlEt$_2$ prepared from *n*-Bu$_3$SnLi and Et$_2$AlCl was not effective for the transformation. The starting epoxides were recovered unchanged after heating the reaction mixture in CH$_2$ClCH$_2$Cl or THF. High nucleophilicity of tributylstannyl anion of the ate complex **1** could explain the facile epoxide ring opening in S_N2 fashion.

Finally, the reaction of epoxides with silyl-metal reagents such as [PhMe$_2$SiAlMe$_3$]$^-$Li$^+$ and PhMe$_2$Si-AlEt$_2$ were examined. These reagents have proven to be less reactive for the deoxygenation of epoxides than the above mentioned stannyl reagents. Highly reactive epoxides bearing a phenyl substituent only gave the corresponding olefins in moderate yields (Table 2). Other purely aliphatic epoxides such as 5-decene oxide and 1-dodecene oxide gave the complex mixture containing the desired olefins as a minor component (<20%) after prolonged heating in CH$_2$ClCH$_2$Cl or benzene.

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer, the mass spectra on a Hitachi M-80 machine, and the proton NMR spectra on a Varian EM-390 spectrometer, and the ^{119}Sn NMR spectra on a JEOL JNM-FX 90Q spectrometer. The chemical shifts of the proton NMR are given in δ with TMS as an internal standard, and those of the ^{119}Sn NMR are given in δ with tetramethylstannane as an internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Purificaton of products was performed by column chromatography on silica-gel (Wakogel C-100) or preparative thin-layer chromatography (TLC). Analytical GLPC was performed with a Yanagimoto GCG-550-F and a Shimadzu GC-4CPT.

General Procedure for the Deoxygenation of Epoxide with $[n\text{-}Bu_3SnAlMe_3]^-Li^+$. Transformation of (*E*)-5-decene oxide into (*E*)-5-decene is representative. Butyllithium (1.7 M* hexane solution, 3.5 ml, 6.0 mmol) was added dropwise to a suspension of anhydrous $SnCl_2$ (0.38 g, 2.0 mmol) in THF (5.0 ml) at 0 °C under an argon atmosphere. The solution turned to reddish brown immediately. After stirring for 10 min, a hexane solution of Me_3Al (1.0 M, 2.0 ml, 2.0 mmol) was added. The resulting mixture was stirred for another 10 min, then a solution of epoxide (0.16 g, 1.0 mmol) in THF (2.0 ml) was added. The whole was stirred for 24 h at 25 °C and the reaction mixture was poured into 1 M HCl and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give 5-decene which was purified by silica-gel column chromatography. In order to check the *cis*:*trans* ratio of the product, the olefin was transformed into epoxide upon treatment with 86% *m*-chloroperbenzoic acid (0.60 g, 3.0 mmol) in CH_2Cl_2. Workup and purification by silica-gel column chromatography gave (*E*)-5-decene oxide exclusively (0.12 g, 80% overall yield): bp 95 °C/15 Torr** (bath temp); NMR (CCl_4) δ=1.83 (t, *J*=6 Hz, 6H), 1.16—1.46 (m, 12H), 2.30—2.55 (m, 2H). GLPC examination of the epoxide showed only one peak at t_r=4.0 min (Silicone OV-17 3% on Uniport HP, 2 m, 100 °C). The peak at t_r=4.6 min corresponding to (*Z*)-5-decene oxide (NMR (CCl_4) δ 1.83 (t, *J*=6 Hz, 6H), 1.10—1.46 (m, 12H), 2.30—2.55 (m, 2H)) was not observed.

erythro-*6-(Tributylstannyl)-5-decanol (2).* The title compound was obtained according to the reported procedure[14] using *n*-Bu_3SnCl instead of Ph_3SnCl. A solution of tributyltin chloride (4.1 g, 12.5 mmol) in DME (4.0 ml) was added slowly to a DME solution (10 ml) of sodium naphthalene prepared from sodium metal (0.58 g, 0.025 g-atom) and naphthalene (0.26 g, 21 mmol) to maintain a green color at all times. After complete addition, the solution was stirred for 2 h and then cooled in an ice bath and a solution of *trans*-5-decene epoxide (0.78 g, 5.0 mmol) in DME (2.0 ml) was added dropwise. The resulting solution was stirred for another 1.5 h. Workup and purification by silica-gel column chromatography gave stannyl compound **2** as a colorless oil: bp 140 °C (dec. 0.1 Torr, bath temp); IR (neat) 3350, 2900, 1460, 1385, 1060, 1000 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.71—1.05 (m, 21H), 1.10—1.75 (m, 26H), 3.73—3.95 (m, 1H), ^{119}Sn-NMR ($CDCl_3$) δ=−15.7. Found: *m/z* 389.2045. $C_{18}H_{39}O^{119}Sn$: $M-C_4H_9$ 389.2019.

threo-*6-(Tributylstannyl)-5-decanol (3)*: Bp 140 °C (dec. 0.1 Torr, bath temp); IR (neat) 3400, 2900, 1460, 1378, 1070, 1000 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 0.75—1.10 (m, 21H), 1.15—1.75 (m, 26H), 3.70—3.95 (m, 1H), ^{119}Sn-NMR ($CDCl_3$) δ=−19.3. Found: *m/z* 389.1997. Calcd for $C_{18}H_{39}O^{119}Sn$: $M-C_4H_9$ 389.2019.

Elimination of erythro- *and* threo-*6-(Tributylstannyl)-5-decanol to* (E)- *and (Z)-5-decene.* A solution of *erythro* β-hydroxy stannane **2** (0.67 g, 1.5 mmol) in THF (3.0 ml) was added to a solution of $[Me_4Al]^-Li^+$ derived from Me_3Al (1.0 M hexane solution, 3.0 ml, 3.0 mmol) and MeLi (1.5 M ether solution, 2.0 ml, 3.0 mmol) at 0 °C. The mixture was stirred for 40 h at 25 °C. Workup (1 M HCl, ether) and purification by silica-gel column chromatography gave (*E*)-5-decene (0.14 g, 65% yield) which was oxidized into 5-decene oxide upon treatment with *m*CPBA. The purity of the resulting epoxide was found to be >99% (*E*) by the GLPC examination. Starting from *threo* isomer **3** (0.67 g, 1.5 mmol), (*Z*)-5-decene (0.12 g, 57% yield) was obtained as a single isomer (>99% (*Z*)).

Conversion of trans-*2,3-epoxy-1-nonanol (6) into* (E)-*2-nonen-1-ol.* A solution of $[n\text{-}Bu_3SnAlMe_3]^-Li^+$ (5.08 mmol) was prepared from *n*-Bu_3SnLi[18] and Me_3Al according to the procedure described above. A THF solution of epoxide **6** (0.20 g, 1.27 mmol) was added and the whole was stirred for 18 h at 25 °C. Extractive workup (1 M HCl, ether) and purification by preparative thin-layer chromatography on silica-gel gave (*E*)-allylic alcohol (0.11 g, 75% yield) as a colorless oil. The alcohol was treated with *m*CPBA to give epoxy alcohol whose purity (>99% (*E*)) was determined by GLPC (t_r=6.0 min, Silicone OV-17 3% on Uniport HP, 2 m, 120 °C). The epoxy alcohol derived from (*Z*)-2-nonen-1-ol had a longer retention time (t_r=7.0 min).

General Procedure for the Deoxygenation of Epoxides by Means of $PhMe_2SiAlEt_2$. Reduction of (*E*)-stilbene oxide to (*E*)-stilbene is representative. A THF solution of $PhMe_2SiLi$[19] (0.65 M, 3.0 ml, 2.0 mmol) was added to a hexane solution of diethylaluminium chloride (1.0 M, 2.0 ml, 2.0 mmol) at 0 °C under an argon atmosphere. After stirring for 20 min at 25 °C, the solvent was evaporated *in vacuo* and hexane (8 ml) was introduced to the residue. Then a hexane solution of (*E*)-stilbene oxide (0.20 g, 1.0 mmol) was added and the resulting mixture was stirred at 25 °C for 4 h. The mixture was diluted with AcOEt and poured into 1 M HCl. Organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The remaining semisolid was submitted to preparative thin-layer chromatography on silica-gel to give (*E*)-stilbene (0.13 g, 71% yield) as crystals which was identical with an authentic sample. The purity of the compound was checked by NMR and GLPC (t_r=8.0 min, Silicone OV-17 3% on Uniport HP, 2 m, 140 °C). (*Z*)-stilbene had a longer retention time (t_r=11.0 min).

Deoxygenation of Epoxide derived from Cinnamyl Alcohol Benzyl Ether by Means of $[PhMe_2SiAlMe_3]^-Li^+$. A hexane solution of Me_3Al (1.0 M, 2.0 ml, 2.0 mmol) was added dropwise to a THF solution of $PhMe_2SiLi$ (0.3 M, 6.5 ml, 2.0 mmol) at 0 °C. After stirring for 10 min, a THF solution of epoxide (0.24 g, 1.0 mmol) was added and the reaction mixture was warmed to room temperature, the whole was stirred for 18 h. The mixture was poured into water and extracted with ether. Purification by silica-gel column chromatography gave cinnamyl alcohol as a colorless oil. GLPC analysis proved that the purity of the alcohol was >97% (*Z*) (t_r=11.5 min, Silicone OV-17 3% on Uniport HP, 2 m, 180 °C). Retention time of (*E*)-isomer was 18.0 min.

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* 1 M=1 mol dm^{-3}.

** 1 Torr=133.322 Pa.

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