gave rough cell dimensions. The diffraction symmetry was supported by examination of the axial photographs. Least squares refinement using 15 reflections yielded the cell dimensions given in Table I.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) using measurement parameters listed in Table I. Systematic absences for hkl ($h + k + l \neq 2n$) and $h0l$ ($h, l \neq 2n$) were consistent with space groups $I2/a$ and Ia. The average values of the normalized structure factors suggested the centric choice $I2/a$, which was confirmed by successful refinement of the proposed model.[36] The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change. Absorption corrections were not applied. Seven questionable reflections were deleted; five flooded the counter, and two were poorly centered. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least squares refinement.

The structure was solved using direct methods (SHELXS-86) and unweighted difference Fourier methods. The positions of the oxygen, lithium, and 18 of the carbon atoms were deduced from an E map. Subsequent difference Fourier calculations revealed the positions of the disordered ethyl carbon atoms. The relative site occupancy factor for the disordered ethyl carbon atoms was 0.588 (6) for the "A" sites. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.65/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, a group isotropic thermal parameter was varied for the disordered carbon atoms, while all other non-hydrogen atoms were independently refined with anisotropic thermal coefficients. A group isotropic thermal parameter was varied for the hydrogen atoms which were fixed in "idealized" positions with C-H = 0.95 Å. Successful convergence was indicated by the maximum shift/error of 0.035 in the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features. There were no apparent systematic errors among the final observed and calculated structure factors.

(36) The conventional reduced cell vectors for this I-centered unit cell are $a = 11.723$ Å, $b = 11.732$ Å, $c = 12.967$ Å, $\alpha = 114.36°$, $\beta = 114.34°$, $\gamma = 95.06°$. Axial X-ray diffraction photographs of the data crystal confirmed these reduced cell dimensions. This cell can be transformed into the F-centered pseudoorthorhombic cell $a = 15.837$ Å, $b = 17.301$ Å, $c = 20.538$ Å; however, axial photographs of these axes showed no mirror symmetry for a or b.

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Supplementary Material Available: Tables S1-S3, giving hydrogen atom positions and anisotropic thermal parameters for $LiC_6H_2Ph_3 \cdot 2Et_2O$ (1) (2 pages). Ordering information is given on any current masthead page.

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Stereochemistry of the Thermal Decomposition of (2-(Acyloxy)alkyl)triorganostannanes

Bernard Jousseaume,* Nicolas Noiret, and Michel Pereyre

Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS, Université Bordeaux I, 351, cours de la Libération, F-33405-Talence, France

Jean-Marc Francès

Rhône-Poulenc Recherches, BP 62, F-69192-Saint-Fons, France

Michel Pétraud

Centre d'Etudes Structurales et d'Analyse des Molécules Organiques, Université Bordeaux I, 351, cours de la Libération, F-33405-Talence, France

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Summary: The stereochemical study of the thermal decomposition of (2-(acyloxy)alkyl)triorganostannanes revealed an anti β-elimination of (acyloxy)triorganostannanes. The process is highly stereospecific and not perturbed by the presence of a possible internal chelation favoring syn elimination. It corresponds to an open transition state. Kinetics of β-elimination in cyclohexyl and norbornyl systems showed that the reaction is much more rapid with a 180° dihedral angle between the metal and the ester group than with a 60° angle between the two. Stabilization of the partial positive charge developed during the transition state occurs mainly through hyperconjugation effect.

The β-elimination reaction,[1] which is often an undesirable process because of the induced instability of heterosubstituted organometallic compounds, has been applied to the stereospecific preparation of functional olefins from β-hydroxylated triphenylstannanes.[2] When treated by acids, these alcohols undergo an anti elimination, whereas their thermal decomposition leads to a syn elimination. Similar processes, based on acid- or base-induced eliminations, occur in organosilicon chemistry where their very

(1) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. Kochi, J. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 249.

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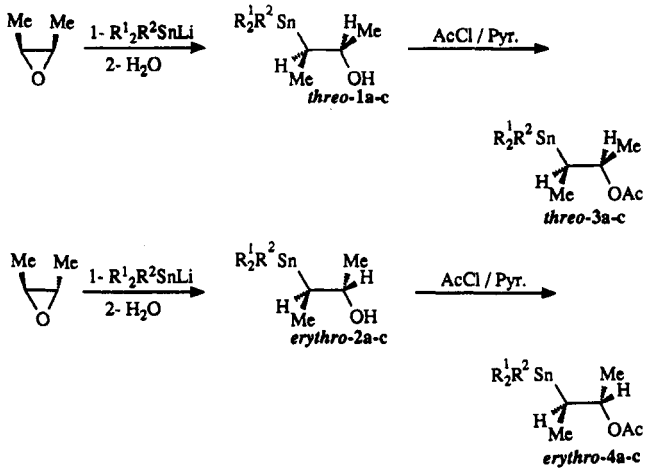
Scheme I



high selectivity makes the Peterson reaction so useful in preparing either an (*E*) or (*Z*) isomer from the same precursor.[3]

The thermal decomposition of bis(2-(acyloxy)alkyl)dialkylstannanes has recently been shown to give dialkyltin dicarboxylates.[4] These organotin compounds can thus be used as latent catalysts for silicon curing and polyurethane preparation. When heated, they liberate the active species in situ, and the mixtures where they have been incorporated are rapidly cured or polymerized.

A systematic study has been carried out by varying the substituents R and R′ and measuring the parameters of the thermal decomposition:

$$Bu_2Sn(CH_2CHROCOR')_2 \xrightarrow{\Delta} Bu_2Sn(OCOR')_2 + 2H_2C{=}CHR$$

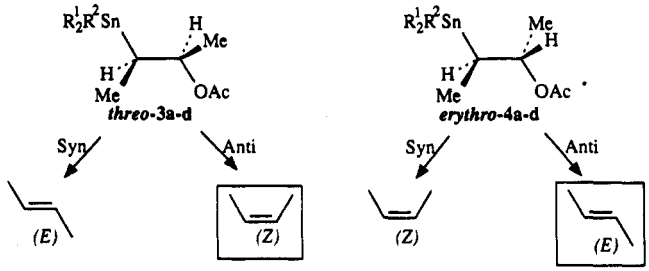
From these data the rate of the reaction was deduced to be a function of the easiness of cleavage of the β-carbon–oxygen bond. As is generally admitted for esters[5] or β-silylated esters,[6] the occurrence of a cyclic six-membered transition state was suggested for the thermolysis of (2-(acyloxy)alkyl)trialkylstannanes. A stereochemical study of the thermal decomposition of (2-(acyloxy)alkyl)triorganostannanes is here reported. The stereochemistry of the reaction was first determined and then the rate of decomposition studied as a function of the Sn–C–C–O dihedral angle.

Requisite *threo*- and *erythro*-(2-(acyloxy)alkyl)triorganostannanes **3a–c** and **4a–c** were prepared by esterification of the corresponding alcohols **1a–c** and **2a–c**, obtained from the reaction of (triorganostannyl)lithiums with the corresponding oxiranes.[7,8] The very high diastereoselectivity of the addition reaction led to alcohols **1a–c** and **2a–c** more than 97% pure (Scheme I). They were found to be stable enough to be distilled, whereas purification by column chromatography on silica proved to be unsatisfactory with immediate decomposition. **1d** and **2d** were respectively prepared by electrophilic cleavage of the phenyl group in **1c** and **2c** by iodine (Table I). All alcohols were then esterified by acyl chlorides in the presence of pyridine.

Table I. Configuration of 2-Butenes Obtained in the Thermolysis of (2-(Acyloxy)but-3-yl)triorganostannanes

compd	R^1	R^2	2-butene
threo-**3a**	Bu	Bu	*Z*
erythro-**4a**	Bu	Bu	*E*
threo-**3b**	Me	Me	*Z*
erythro-**4b**	Me	Me	*E*
threo-**3c**	Bu	Ph	*Z*
erythro-**4c**	Bu	Ph	*E*
threo-**3d**	Bu	I	*Z*
erythro-**4d**	Bu	I	*E*

Scheme II



The stability of acetates **3a–d** and **4a–d** was too low at 30 °C to carry out a full spectroscopic identification. As the stability of (2-(acyloxy)ethyl)tributylstannanes is dependant[4] on the nature of the substituent R′ (the longer and the more branched R′ is, the more stable the stannylated ester is), pivalates **5a–d** and **6a–d** were prepared. They were found stable enough at room temperature to be easily handled for short periods of time, and characterized. Then, acetates **3a–d** and **4a–d**, pure or in solution in carbon tetrachloride, were subjected to thermal decomposition at 50 °C for a few hours, until complete disappearance of the starting material (Scheme II). Reactions were univocal, giving a quantitative yield of 2-butenes and triorganotin acetates (a mixture of diacetoxydibutylstannane, diiododibutylstannane and iodoacetoxydibutylstannane with **3d** and **4d**). The same stereochemistry was recorded with the corresponding pivalates **5a** and **6a**. Results of the thermolysis are given in Table I.

From this data, as the isomeric purity of the 2-alkenes was very high (>97% with 1-butene < 1%) an SE_i mechanism which would lead to a mixture of butenes was ruled out. *threo*- and *erythro*-(2-acetoxybut-3-yl)triorganostannanes gave respectively (*Z*)- and (*E*)-2-butenes, therefore the thermolysis was an anti elimination, occurring through an open transition state, and not a syn elimination with a cyclic six-membered transition state. The nature of the residues linked to the tin atom i.e. methyl, butyl, or mixed butyl and phenyl, did not play a part in the elimination as identical isomeric purities were observed in all cases.

In the thermal decomposition of bis(2-(acyloxy)alkyl)-diorganostannanes, the first step permitted neither isolation nor detection of (acyloxy)(2-(acyloxy)alkyl)dialkylstannane intermediates,[9] which would have shown an in-

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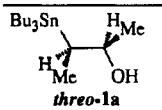
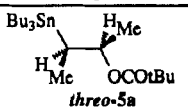
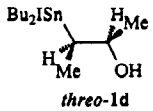
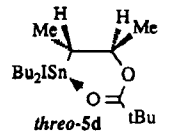
(7) Mordini, A.; Taddei, M.; Seconi, G. *Gazz. Chim. Ital.* **1986**, *116*, 239.

(8) Davis, D. D.; Gray, C. F. *J. Org. Chem.* **1970**, *35*, 1303.

Table II. ^{13}C-^{119}Sn Coupling Constants

compd	$^1J_{C-Sn}$ (Hz)	compd	$^1J_{C-Sn}$ (Hz)
 *threo*-**1a**	319	 *threo*-**5a**	319
 *threo*-**1d**	401	 *threo*-**5d**	449

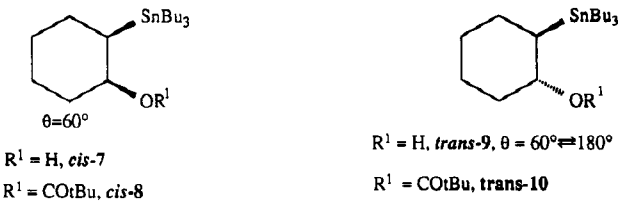
tramolecular chelation of the tin by the oxygen of the carbonyl, giving a six-membered ring. Although such an internal complexation has never been firmly demonstrated by a crystal structure in a triorganostannane[11] with a carbonyl as ligand in δ position, the presence of a carbonyl in δ position has a strong effect on the reactivity of the corresponding stannane.[12] Internal coordination has also been recently demonstrated in cases where a five-membered ring can be formed intramolecularly with an ester as ligand.[13] Evidence for such an intramolecular coordination in **3d** and **4d** comes from ^{119}Sn and ^{13}C NMR data (ref 14 and 15, respectively). In ^{119}Sn NMR, for (2-acetoxyethyl)dibutylacetoxystannane or (2-acetoxyethyl)dibutylchlorostannane an upfield shift of ~60 ppm was measured from tributylacetoxystannane or tributylchlorostannane values. An upfield shift of ~100 ppm has already been recorded in the case of an established coordination.[13] Unfortunately, the high instability of **5d** and **6d** prevented the recording of their ^{119}Sn NMR spectrum. The $^1J(^{13}C-^{119}Sn)$ value is a function of the tin coordination. For a tetracoordinated tin atom it is lower than 390 Hz, whereas for a pentacoordinated tin it is higher than 450 Hz.[15] For **5a** and **6a**, recorded values were the same as for **1a** and **2a**, 319 Hz, indicating no more coordination in an ester than in an alcohol. In the corresponding iodo compounds, this value is 401 Hz for **1d** and **2d** and 449 Hz for **5d** and **6d**, indicating a higher coordination in the iodo ester (see Table II).

This probable internal chelation could have decreased or even reversed the selectivity observed for (2-(acyloxy)alkyl)triorganostannanes. In fact, when **3d** was thermally decomposed, it gave (*Z*)-2-butene, whereas **4d** gave (*E*)-2-butene. Indeed an anti elimination was observed here, the stereochemical behavior of the reaction being the same as when a chelating group is not present in the molecule.

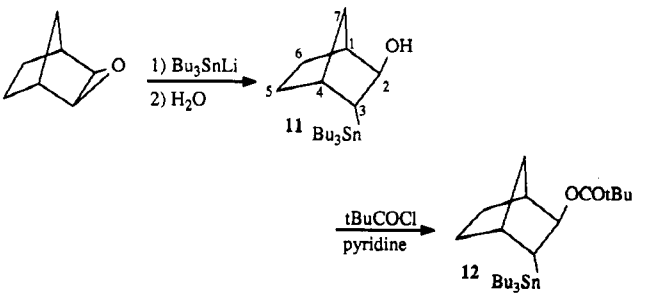
Results of these eliminations are quite analogous to those reported for the solvolysis of β-stannylated[8] or β-silylated alcohols,[13] or for the abstraction of a β-hydrogen by trityl cation in tetraorganostannanes.[16] For these reactions stereochemical studies demonstrate an antiperiplanar geometry of the metal and of the leaving group, in the transition state. However, our thermolyses were conducted in a neutral medium when more polar conditions were used for the solvolysis of β-metalated alcohols[3,8] or for the abstraction of a β-hydrogen.[16] Thus, in our experiments, even if development of charge is reasonably postulated as being lower than in polar media, the stabilizing effect and its geometrical requirement are still very high. This remarkable stereochemistry has been explained by the very strong metal-stabilizing effect of a positive charge developed on a β-carbon, at a maximum for an antiperiplanar geometry and at a minimum for an orthogonal conformation.[17] To get a deeper insight into the mechanism of charge stabilization, a kinetic study of thermolysis of esters with rigid frameworks was undertaken.

cis- and *trans*-2-(tributylstannyl)cyclohexanols (**7** and **9**, respectively) were prepared using procedures described for trimethylstannyl derivatives[18] and esterified (Scheme III).

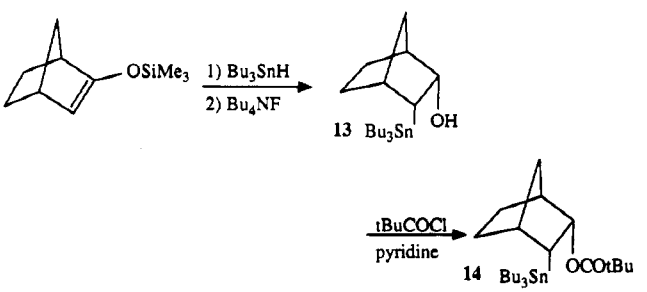
Scheme III



Scheme IV



Scheme V



Ring opening of *exo*-2,3-epoxynorbornane by (tributylstannyl)lithium gave *endo*-3-(tributylstannyl)-*exo*-2-norborneol (**11**) in good yield (Scheme IV). Its stereochemistry was confirmed by (1) the small $^3J(H_2-H_3)$ (4 Hz), indicating a trans relationship,[19] (2) the large $^3J(^{119}Sn-^{13}C_7)$ (51.1 Hz) characteristic of an endo position for the tin (not detected for an *exo*-tin), (3) the small $^3J(^{119}Sn-^{13}C_5)$ in *endo*-2-(tributylstannyl)norbornane (31.1–32.2 Hz) and in

(9) The higher instability of **3d** and **4d** with respect to **3a** and **4a** can be explained by the higher stabilizing[10] effect of a positive charge on the tin by a heteroatom than by a butyl group.

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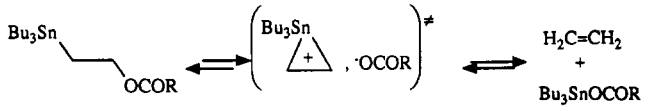
(17) For a comprehensive discussion on β-effect in organosilicon chemistry see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(18) Lambert, J. B.; Wang, G.-t. *Tetrahedron Lett.* **1988**, *29*, 2551. Lambert, J. B.; Wang, G.-t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422.

(19) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie Int.: Deerfield Beech, FL, 1982; p 112.

Scheme VI



exo-2-(tributylstannyl)norbornane (61.8 Hz),[20] and (4) the very small $^3J(^{119}Sn–H_4)$ (not detected) in *endo*-2-(tributylstannyl)norborane (2.4 Hz) and in *exo*-2-(tributylstannyl)norbornane (31.5 Hz).

Addition of tributyltin hydride to 2-((trimethylsilyl)oxy)-2-norbornene gave an adduct, easily hydrolyzed into the corresponding alcohol (Scheme V). Unexpectedly *endo*-3-(tributylstannyl)-*endo*-2-norborneol (**13**) was obtained, whereas *exo*-3-(tributylstannyl)-*exo*-2-((trimethylsilyl)oxy)-5-norbonene has been isolated from 2-((trimethylsilyl)oxy)-2,5-norbornadiene,[21] and *exo*-2-(trimethylstannyl)norbornane has been produced from norbornene.[22] Configuration assignment was based on the large $^3J(H_2–H_3)$ (10.3 Hz), indicating a cis relationship,[19] the large $^3J(^{119}Sn–^{13}C_7)$ (62.7 Hz), the small $^3J(^{119}Sn–^{13}C_5)$ (28.7 Hz),[20] and the very small $^3J(^{119}Sn–H_4)$ (not detected).

As already observed for the trifluoroacetate or the acetate,[18] pivalate of *trans*-2-(tributylstannyl)cyclohexanol (**9**) could not be isolated even below 0 °C. The trans relationship between tin and the acyloxyl group (possibility of 180° dihedral angle) provides a too efficient stabilization of the positive charge developed during the decomposition. *cis*-2-(Tributylstannyl)cyclohexyl pivalate (**7**), where the dihedral angle is about 60°, was found much more stable. Kinetic of the decomposition of **7** has been followed by NMR and gave a rate constant of 5.3×10^{-5} s^{-1}.

Decomposition of *endo*-3-(tributylstannyl)-*endo*-2-norbornyl pivalate and *endo*-3-(tributylstannyl)-*exo*-2-norbornyl pivalate (**12** and **14**, respectively) were also followed by NMR. Rate constants were found to be 4.6×10^{-4} s^{-1} for the endo–endo isomer (dihedral angle, 0°) and 8.6×10^{-4} s^{-1} for the endo–exo isomer (dihedral angle, 120°). Surprisingly these values do not fit what could be expected for the stabilization of a carbocation center by hyperconjugation. One could expect a rate constant being higher for the endo–endo isomer than for the endo–exo isomer, as the stabilization effect by an hyperconjugative model depends on the cosine squared of the dihedral angle of the Sn–C–C–OCOtBu fragment. A similar effect has been encountered for acid-catalyzed elimination in *endo*-3-(trimethylsilyl) *endo*-2-norborneol and exo-3-(trimethylsilyl)-endo-2-norborneol where the exo-endo isomer is more reactive than the endo–endo isomer.[23]

To explain the β-effect of tin in the studied thermolysis, another stabilizing mechanism might thus be taken in account (Scheme VI). Calculations have shown that the inductive effect is not significant in systems[24] where the carbocation and the stabilizing group are located on secondary carbons, and experimental results have indicated its low participation for the stabilization of a β-carbocation.[25] Involvement of a bridging intermediate seems possible. It has been deduced from calculations that in silicon or tin models a bridged transition state cannot be ruled out, as its energy stabilization is equivalent to or greater than the energy of an opened transition state depending on the substituants.[26]

An experiment was thus carried out to detect such an intermediate. Analysis of recovered starting material in the thermolysis of (2-(acetoxy)ethyl)tributylstannane-2-*d* (**15**) after 80% decomposition did not reveal the presence of (2-(acetoxy)ethyl)tributylstannane-1-*d* (**16**). This compound should be formed if the reaction involves a symmetrical intermediate[27] (Scheme VII). However, a negative result is not conclusive as a low reversibility factor in the thermolysis can simply explain this result.

In conclusion, thermal decomposition of (2-(acyloxy)-alkyl)triorganostannanes was clearly shown to proceed via an anti elimination with open-chain alkyls, in contrast to what has been postulated for equivalent silicon derivatives or esters where a syn elimination is usually proposed. In cyclohexanyl models, when an angle of 180° can be formed between the carbon–tin bond and the carbon–oxygen bond, elimination was very fast. With an angle of 60°, the decomposition is considerably slower.

In norbornenyl models, the elimination was faster with a dihedral angle of 120° than with 0°. Thus, in this case, either hyperconjugation is not the only mechanism of stabilization of an adjacent positive charge by a tin atom and a bridged intermediate contributes to the stabilization or hyperconjugative stabilization for a dihedral angle of 0° is overweight.[28] The possible assistance to the leaving group in **12** by a nonclassical carbocation delocalization[29] could also falsify the results.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl prior use. $CHCl_3$ was passed through a short basic alumina column before use. *cis*- and *trans*-epoxy-2,3-butane, 1,2-epoxycyclohexane, and *exo*-2,3-epoxynorbornane were used as received. 2-((Trimethylsilyl)oxy)-2-norbornene,[30] 1-bromocyclohexene,[31] trimethyltin hydride,[32] tributyltin hydride, and dibutylphenyltin hydride[33] were prepared following standard procedures. Diisopropylamine was distilled on KOH before use. Acetyl chloride and pivaloyl chloride were distilled before use. ^{1}H NMR spectra were recorded on a Perkin-Elmer-Hitachi R 24A or a Bruker AC-250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si), ^{13}C NMR spectra were taken on a Bruker AC-250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si), ^{119}Sn NMR spectra were recorded on a Bruker AC-200 spectrometer (solvent C_6D_6, internal reference Me_4Sn).

(2-(Acyloxy)alkyl)triorganostannanes. To a cooled solution (0 °C) of (triorganostannyl)lithium,[34] prepared from the corresponding triorganostannane (20 mmol), diisopropylamine (22 mmol, 2.2 g), and butyllithium (22 mmol) in THF (30 mL), was added a solution of epoxide (25 mmol) in 10 mL of THF. After

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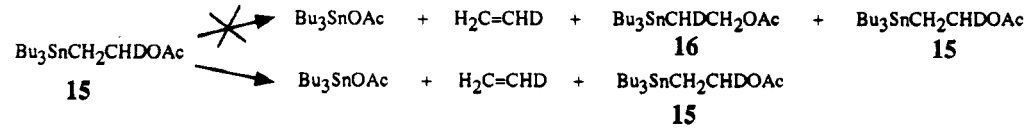
Scheme VII



3 h at room temperature, petroleum ether (50 mL) was added and the mixture washed three times with a saturated solution of NH_4Cl. After drying and evaporation of solvents, the alcohol was isolated by distillation in a Kugelrohr apparatus and stored in a freezer. Centesimal analysis accuracy for alcohols: C ± 0.50, H ± 0.30. No satisfactory analysis could be obtained for pivalates. Compound, bath temperature, yield: **1a**, 130 °C (10^{-4} mm), 50% [^{1}H NMR δ 0.8–1.9 (m, 35 H), 3.20 (bs, 1 H), 3.85 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); ^{119}Sn NMR δ −15.9]; **2a**, 130 °C (10^{-4} mm), 71% [^{1}H NMR δ 0.8–1.9 (m, 35 H), 3.0 (bs, 1 H), 3.87 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); ^{119}Sn NMR δ −15.2]; **1b**, 55 °C (0.4 mm), 52% [^{1}H NMR δ 0.0 (s, 9 H), 0.6 (m, 1 H), 1.05 (d, 3 H, $^2J_{H-H}$ = 4 Hz), 1.15 (d, 3 H, $^2J_{H-H}$ = 5 Hz), 2.25 (bs, 1 H), 3.8 (m, 1 H); ^{119}Sn NMR δ −1.6]; **2b**, 65 °C (0.4 mm), 67% [^{1}H NMR δ 0.0 (s, 9 H), 0.6 (m, 1 H), 1.05 (m, 6 H), 3.1 (bs, 1 H), 3.82 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); ^{119}Sn NMR δ −0.4]; **1c**, 150 °C (10^{-3} mm), 45% [^{1}H NMR δ 0.6–1.9 (m, 25 H), 2.7 (bs, 1 H), 3.7 (qt, 1 H, $^2J_{H-H}$ = 6 Hz), 7.2 (m, 5 H); ^{119}Sn NMR δ −47.5]; **2c**, 150 °C (10^{-3} mm), 71% [^{1}H NMR δ 0.6–1.9 (m, 25 H), 3.25 (bs, 1 H), 3.8 (qt, 1 H, $^2J_{H-H}$ = 6 Hz), 7.2 (m, 5 H); ^{119}Sn NMR δ −46.7]; *trans*-**9**, 140 °C (10^{-4} mm), 45% [^{1}H NMR δ 0.9–2.1 (m, 37 H), 4.0 (m, 1 H); ^{119}Sn NMR δ −21.2]; **11**, 165 °C (6 × 10^{-4} mm), 62% [^{1}H NMR δ 0.85 (m, 6 $H_{1\,butyl}$), 0.89 (t, 9 $H_{4\,butyl}$), 1.31 (m, 6 $H_{3\,butyl}$), 1.49 (m, 6 $H_{2\,butyl}$), 0.94 (m, 1 H_5, $^2J_{H-H}$ = 11.5 Hz), 0.96 (m, 1 H_6, $^2J_{H-H}$ = 11.9 Hz), 1.08 (m, 1 H_3, $^3J_{H-H}$ = 4.0 Hz, $^2J_{Sn-H}$ = 49.5 Hz), 1.21 (m, 1 H_{7a}, $^2J_{H-H}$ = 9.50 Hz, $^4J_{Sn-H}$ = 7.90 Hz), 1.43 (m, 1 H_5, $^2J_{H-H}$ = 12.5 Hz), 1.49 (m, 1 H_6, $^2J_{H-H}$ = 11.9 Hz), 1.49 (m, 1 H_{7s}, $^2J_{H-H}$ = 9.5 Hz, $^4J_{Sn-H}$ = 7.9 Hz), 2.17 (m, 1 H_1), 2.33 (m, 1 H_4), 3.35 (bs, 1 H), 3.76 (m, 1 H_3, $^3J_{H-H}$ = 4.0 Hz, $^3J_{Sn-H}$ = 45.6); ^{13}C NMR δ 9.19 ($C_{1\,butyl}$), 13.70 ($C_{4\,butyl}$), 27.55 ($C_{3\,butyl}$), 29.33 ($C_{2\,butyl}$), 24.72 (C_6), 29.53 (C_5, $^3J_{Sn-C}$ = 28.7 Hz), 36.14 (C_7, $^3J_{Sn-C}$ = 51 Hz), 39.90 (C_4, $^2J_{Sn-C}$ = 7.7 Hz), 41.24 (C_3, $^1J_{Sn-C}$ = 325 Hz), 44.67 (C_1, $^3J_{Sn-C}$ = 25.7 Hz), 79.21 (C_3, $^2J_{Sn-C}$ = 8.5 Hz); ^{119}Sn NMR δ − 16.0]. To a solution of alcohol (10 mmol) and pyridine (10 mmol, 1.6 g) in 10 mL of diethyl ether at 0 °C was added a solution of acid chloride (acetyl chloride or pivaloyl chloride) (10 mmol) in 10 mL of diethyl ether. After 1 h at 0 °C, the mixture was filtered and the organics were washed with 2 × 20 mL of a cooled saturated $CuSO_4$ solution (1 N) and 2 × 20 mL of cooled $NaHCO_3$ (1 N). Esters were isolated after drying and evaporation of the solvent below room temperature. They were used as soon as prepared. Compound, yield, ^{1}H NMR, δ: **5a**, 72%, 1.24 (s, 9 H), 0.8–1.8 (m, 34 H), 3.80 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **6a**, 83%, 1.23 (s, 9 H), 0.8–1.80 (m, 34 H), 3.70 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **5b**, 85%, 0.0 (s, 9 H), 0.6 (m, 1 H), 1.05 (d, 3 H, $^2J_{H-H}$ = 4 Hz), 1.15 (d, 3 H, $^2J_{H-H}$ = 6 Hz), 1.25 (s, 9 H), 3.85 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **6b**, 77%, 0.0 (s, 9 H), 0.6 (m, 1 H), 1.05 (m, 6 H), 1.24 (s, 9 H), 3.75 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **5c**, 58%, 1.25 (s, 9 H), 0.8–1.8 (m, 34 H), 3.80 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **6c**, 60%, 1.22 (s, 9 H), 0.4–1.7 (m, 26 H), 3.90 (qt, 1 H, $^2J_{H-H}$ = 6 Hz); **12**, 79%, 0.8–1.8 (m, 34 H), 2.20 (m, 2 H), 3.80 (m, 1 H).

***threo*- and *erythro*-(2-(Pivaloyloxy)but-3-yl)iododibutylstannane (5d, 6d).** To a solution of **1c** (or **2c**) (1 mmol, 0.38 g) in 5 mL of CCl_4 at 0 °C was added a solution of iodine (1 mmol, 0.26 g) in 20 mL of CCl_4. Iodobenzene was removed by evaporation under high vacuum. Compound, yield, NMR: **1d**, 85%, ^{1}H NMR δ 0.8–2.2 (m, 25 H), 3.85 (m, 1 H); ^{119}Sn NMR δ 67.3; **2d** 92%, ^{1}H NMR δ 0.8–2.2 (m, 25 H), 3.80 (m, 1 H), ^{119}Sn NMR δ 71.9. **1d** and **2d** were esterified as described for other alcohols. Compound, yield, NMR: **5d**, 85%, ^{1}H NMR δ 1.20 (s, 9 H), 0.7–2.0 (m, 25 H), 3.80 (qd, 1 H, $^2J_{H-H}$ = 6 Hz); **6d**, 89%, ^{1}H NMR δ 1.22 (s, 9 H), 0.7–2.0 (m, 25 H), 3.80 (qd, 1 H, $^2J_{H-H}$ = 6 Hz).

***cis*-2-(Tributylstannyl)cyclohexanol (7).** Tributyltin chloride (40 mmol, 13 g) was added at room temperature to a solution of 1-cyclohexenylmagnesium bromide, prepared from 1-bromocyclohexene (55 mmol, 4.45 g) magnesium (60 mmol, 1.44 g) in 20 mL of THF. The mixture was refluxed for 2 h, cooled at 0 °C, and 20 mL of petroleum ether was added, followed by 50 mL of saturated NH_4Cl solution. After separation and drying, the solvents were removed and the product distilled: yield 71%; bp 150 °C (10^{-4} mm); ^{1}H NMR δ 0.8–2.3 (m, 35 H), 5.58 (m, 1 H). A solution of 1-(tributylstannyl)cyclohexene (28 mmol, 10.5 g) in 50 mL of $CHCl_3$ was added dropwise to a solution of *m*-chloroperbenzoic acid (28 mmol, 5.9 g) in 200 mL of $CHCl_3$ at 0 °C. The mixture was stirred for 14 h and the solids filtered. The filtrate was washed with a 10% $NaHCO_3$ solution and dried. After evaporation of the solvent and distillation, the desired epoxide was recovered: yield 45%; bp 160 °C (10^{-4} mm); ^{1}H NMR δ 0.8–1.8 (m, 29 H), 1.8–2.1 (m, 6 H), 2.82 (m, 1 H); ^{119}Sn NMR, δ −30.1 ppm. The stannylated epoxide (3.9 g, 10 mmol) in 10 mL of diethyl ether was added to a slurry of $LiAlH_4$ (1.6 g, 42 mmol) in diethyl ether (50 mL) at 0 °C. After two days of stirring at room temperature, the mixture was carefully hydrolyzed with 10 mL of saturated NH_4Cl, the solids filtered, and the filtrate dried and evaporated. The alcohol was recovered by distillation: yield 45%; bp 140 °C (10^{-4} mm); ^{1}H NMR δ 0.9–2.1 (m, 37 H), 2.90 (bs, 1 H), 3.80 (m, 1 H); ^{13}C NMR δ 8.88 ($C_{1\,butyl}$), 13.88 ($C_{4\,butyl}$), 27.78 ($C_{3\,butyl}$), 29.54 ($C_{2\,butyl}$), 25.23, 29.86, 27.68, 35.60 (C_2, $^1J_{Sn-C}$ = 328), 38.52 (C_6, $^3J_{Sn-C}$ = 43 Hz), 74.58 (C_1, $^2J_{Sn-C}$ = 23 Hz); ^{119}Sn NMR δ −21.2. It was esterified as described for other alcohols. **8**: yield 85%; ^{1}H NMR, δ 0.9–1.9 (m, 37 H), 1.20 (s, 9 H), 3.88 (m, 1 H).

***endo*-3-(Tributylstannyl)-*endo*-2-norborneol (13).** A mixture of tributyltin hydride (3.5 g, 12 mmol), 2-((trimethylsilyl)oxy)-2-norbornene (1.8 g, 10 mmol) and AIBN (10 mg) was heated at 110 °C for 48 h. The adduct was purified by column chromatography (florisil, petroleum ether/ether acetate 95/5), yield 38%. The ether (2.18 g, 3.8 mmol) was hydrolyzed by treatment with Bu_4NF (5 mL of a 1 N solution in THF, room temperature, 2 h) and distilled: yield 79%; bp 140 °C (10^{-4} mm); ^{1}H NMR δ 0.85 (m, 6 $H_{1\,butyl}$), 0.89 (t, 9 $H_{4\,butyl}$), 1.31 (m, 6 $H_{3\,butyl}$), 1.48 (m, 6 $H_{2\,butyl}$), 1.26 (m, 1 H_5, $^2J_{H-H}$ = 11.3 Hz), 1.34 (m, 1 H_6, $^2J_{H-H}$ = 12.2 Hz), 1.43 (m, 2 H_7), 1.56 (m, 1 H_5, $^2J_{H-H}$ = 11.3 Hz), 1.84 (m, 1 H_6, $^2J_{H-H}$ = 12.2 Hz), 1.96 (m, 1 H_3, $^2J_{Sn-H}$ = 53.5 Hz), 2.17 (m, 1 H_1), 2.27 (m, 1 H_4), 4.46 (m, 1 H_2, $^3J_{Sn-H}$ = 27.7 Hz); ^{13}C NMR δ 10.64 ($C_{1\,butyl}$), 13.76 ($C_{4\,butyl}$), 19.88 (C_6), 27.59 ($C_{3\,butyl}$), 29.50 ($C_{2\,butyl}$), 30.66 (C_5, $^3J_{Sn-C}$ = 31.1 Hz), 41.05 (C_3, $^1J_{Sn-C}$ = 348.0 Hz), 41.78 (C_1, $^3J_{Sn-C}$ = 13.3 Hz), 43.49 (C_4, $^2J_{Sn-C}$ = 6.3 Hz); ^{119}Sn NMR δ −30.0. It was esterified as described for other alcohols. **14**: yield 81% ^{1}H NMR δ 0.9–1.9 (m, 34 H) 1.22 (s, 9 H) 2.20 (m, 2 H), 3.88 (m, 1 H).

(2-Acetoxyethyl)tributylstannane-2-*d* (15). A solution of tributylstannane-*d* (20 mmol, 5.80 g) and vinyl acetate (60 mmol, 5.16 g) in 30 mL of dry deaerated cyclohexane under nitrogen was irradiated (Pyrex flask, Philips HPK 125 UV lamp) for 6 h at 30 °C. After evaporation of solvent and excess vinyl acetate, the product was recovered: ^{1}H NMR, δ 0.91 (m, 15 H), 1.34 (m, 6 H), 1.51 (m, 6 H), 1.91 (m, 2 H), 2.04 (s, 3 H), 4.28 (m, 1 H); ^{13}C NMR, δ 8.89 ($C_{1\,butyl}$) 9.22 (C_1), 13.56 ($C_{4\,butyl}$), 21.08 (CH_3), 27.24 ($C_{3\,butyl}$), 29.05 ($C_{2\,butyl}$), 64.45 (C_2, t, J_{C-D} = 22.6 Hz), 170.94 (C=O); ^{119}Sn NMR δ −16.0. After 1 h at 110 °C, the product was analyzed by ^{13}C NMR. A spectrum identical to that of the starting material was recorded.

Thermolysis Experiments. A sample of pure acetate (for linear compounds) or pivalate (for cyclic compounds) was placed in a flask and heated at 50 °C. When **3a–d** and **4a–d** were used, butenes were recovered in a gas burette. They were analyzed by gas chromatography and identified by simultaneous injection of the pyrolysis products and a sample of authentic butenes.

Kinetics. A sample of pure pivalate was placed in the probe of an NMR spectrometer at 32 °C. After a 15-min equilibration period, spectra were recorded every 10 min. Both decrease of the signal of C*H*O and increase of the olefinic signal were followed. Rates are the average of at least four runs.

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