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ELECTROPHILICALLY-INDUCED CYCLODESTANNYLATION REACTIONS

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Summary

A variety of cyclopropylcarbinyl compounds has been prepared by cyclodestannylation reactions of alk-3-en-1-yltin compounds. The initial stage of the cyclodestannylation reactions is thought to involve addition of electrophiles to the double bonds of the alk-3-en-1-yltin compounds to form electron deficient carbon atoms γ to tin. These incipient carbonium ions then electrophilically induce heterolytic fragmentations of the carbon—tin σ bonds (electrophilic displacement of R_3Sn^+) with concurrent ring formation. Cyclopropylmethoxy derivatives were similarly obtained from thermal and Lewis acid catalyzed cyclodestannylation reactions of 3,4-epoxybutyltri-n-butyltin.

Introduction

In recent years it has become increasingly apparent that Group IV organometallic compounds having functional groups attached to carbon atoms either β or γ to the metal atoms readily undergo fragmentation reactions. Of particular interest and importance are those reactions involving 1,2- and 1,3-eliminations of R_3MX from compounds of the type $R_3MC—CX$ and $R_3MC—C—CX$, where M is silicon or tin and X is an oxygen-containing moiety or halogen. The 1,2-eliminations can be induced thermally [1], and by acid [2] or base [3] catalysis (eqn.1). Presumably, acids promote 1,2-eliminations by imparting carbonium ion character to the β carbon atom (as illustrated by eqn.2).

$$R_3MC\!<\!C\!<\!X \longrightarrow R_3MX + >C{=}C< \qquad (1)$$

$$R_3SnC(\!-\!)C(\!-\!)OH + H^+ \rightarrow [R_3Sn{-}C(\!-\!)C^+] + H_2O \rightarrow R_3SnOH + >C{=}C< + H^+ \qquad (2)$$

Analogous carbonium ion-induced* 1,3-eliminations are known for both silicon [4] and tin [5,6] compounds. Since it has been reported [5,6] that the organotin reactions occurred readily to give high yields of cyclopropanes, we

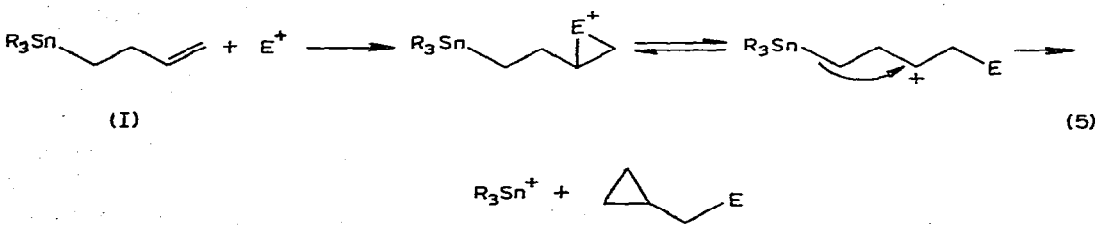
* The classification of these reactions as carbonium ion induced reactions should be regarded as being more formal than real. Indeed, it is possible that the organotin elimination reactions are concerted [5,6] and therefore proceed via transition states possessing little carbonium character.

$$(CH_3)_3SiCH_2CH_2CH_2Br + AlBr_3 \rightarrow (CH_3)_3SiBr + \text{cyclo-}C_3H_6 + AlBr_3 \quad (3)$$

$$(CH_3)_3SnCH_2CH_2CH_2OX \xrightarrow{\Delta} (CH_3)_3SnCH_2CH_2\overset{+}{C}H_2 + {}^{-}OX \quad (4)$$

$$X = CH_3SO_2,\ PCl_2,\ SOCl \qquad (CH_3)_3SnOX + \text{cyclo-}C_3H_6$$

were intrigued by the possibility of modifying this basic elimination reaction so that cyclopropylcarbinyl derivatives, rather than cyclopropanes, would be formed as products of the reaction. Specifically, the initial modification under consideration involved the formation of a substituted carbonium ion γ to the tin atom by the selective addition of electrophiles to 3-butenyltin compounds (eqn.5) [7]. We now report our findings regarding the general utility of this electrophilically-



(I) (5)

induced cyclodestannylation reaction as a method for preparing cyclopropylcarbinyl compounds and some of the chemistry inherent in the process.

Results and discussion

A number of electrophiles have been found to react with I (R = n-C_4H_9) to give moderate to high yields of the desired cyclopropylcarbinyl derivatives (see Table 1). Although the reactivities of the electrophiles employed varied considerably from the highly electrophilic halogens and sulfur trioxide to the mildly electrophilic mercuric chloride and sulfenyl chlorides, all of these reagents preferentially attacked the double bond of the butenyl group of but-3-en-1-yltri-n-butyltin to generate a γ carbonium ion* which initiated cyclopropane formation without significant competitive attack on the carbon—tin bonds. Only reactions of but-3-en-1-yltri-n-butyltin with iodine and mercuric chloride gave rise to small amounts of but-3-en-1-yl and butyl compounds as side products. Selectivity for attack at the double bond was decreased, however, by substituting either methyl or phenyl for the butyl groups on tin. Thus, a reaction of but-3-en-yltrimethyltin with bromine gave 67% cyclopropylcarbinyl bromide accompanied by 17% methyl bromide, while a reaction of bromine with but-3-en-1-yltriphenyltin afforded 66% bromobenzene and none of the desired cyclization product**. Interestingly, an iododestannylation of but-3-en-1-yltrimethyltin in

* It is possible that the immediate precursors to the cyclopropylcarbinyl compounds were $Bu_3SnCH_2CH_2CHYCH_2E$ (Y = nucleophile) rather than $Bu_3SnCH_2CH_2\overset{+}{C}HCH_2E\ Y^{-}$. However, no evidence for the presence of $Bu_3SnCH_2CH_2CHBrCH_2Br$ was obtained by a ^1H NMR spectral analysis of a I—bromine reaction at —65°.

** However, some addition to the double bond did occur as evidenced by the formation of $(C_6H_5)_3SnCH_2CH_2CHBrCH_2Br$.

TABLE 1

REACTIONS OF ELECTROPHILES WITH $R_3SnCH_2CH_2CH{=}CH_2$

R	Electrophile	Solvent	Temp. (°C)	cyclo-$C_3H_5CH_2E$[a] (%)	RE (%)	C_4H_7E (%)
n-Bu	Cl_2	CH_2Cl_2	—65	72	trace	0
n-Bu	Br_2	CH_2Cl_2	—65	86	0	0
n-Bu	I_2	CH_2Cl_2	0	82	10	trace
n-Bu	SO_3	CH_2Cl_2	—65	84	trace	0
n-Bu	$HgCl_2$	CH_3CN	35	73	6	6
n-Bu	2,4-$(NO_2)_2C_6H_3SCl$	CH_3CO_2H	100	80	0	0
n-Bu	SCl_2	CH_2Cl_2	0	30	0[b]	0[b]
n-Bu	PhSCl	CH_2Cl_2	0	48	0[b]	0[b]
n-Bu	4-ClC_6H_4SCl	CH_2Cl_2	0	80	0	0
Ph	Br_2	CH_2Cl_2	—65	0	66[c]	0
Me	Br_2	CH_2Cl_2	—65	67[c]	17[d]	0

[a] See Experimental Section for characterization or identification of these products. [b] No other volatile products were isolated by TLC or GLC. [c] Distilled yield of bromobenzene. GLC analysis of the reaction mixture gave no evidence of other volatile products. [d] Yield of methyl bromide was estimated by a comparison of its ^1H NMR spectral (at —80°) integral to that of the corresponding integral of cyclopropylcarbinyl bromide in the reaction mixture. The yield of cyclopropylcarbinyl bromide is based on distilled product.

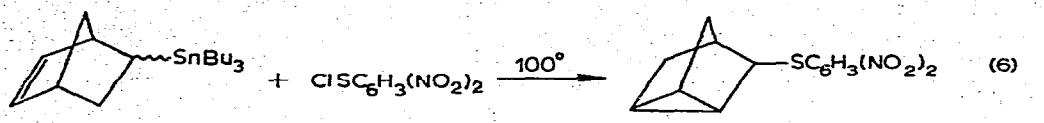
acetonitrile has been reported [8] to proceed with predominant, if not exclusive, methyl group cleavage. It is apparent, therefore, that for the particular solvent—electrophile—substrate combinations investigated for the cyclodestannylation reaction, n-butyl substituents on I are preferred over methyl and phenyl substituents.

From a synthetic point of view, unwanted substituent group cleavages were completely avoided by employing tetra(but-3-enyl)tin as the cyclopropylcarbinyl derivative precursor. Although bromination of this compound afforded pure cyclopropylcarbinyl bromide, the yield of product for some undetermined reason was only 49%.

For the purpose of gaining some insight into the scope of the cyclodestannylation reaction as a method for synthesizing cyclopropylcarbinyl compounds, reactions of other olefinic tri-n-butyltin compounds with bromine and 2,4-dinitrobenzenesulfenyl chloride were investigated. Norborn-2-en-5-yltri-n-butyltin was prepared by a radical addition of tri-n-butyltin hydride to norbornadiene*.

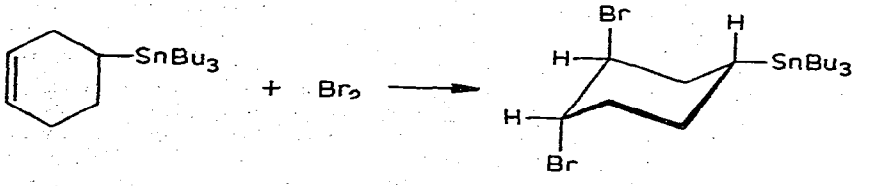
* The carbon-13 NMR spectrum of this material, recorded for the neat liquid with complete proton decoupling, consisted of (1) four intense resonances, of which one appeared as a doublet, assigned to the butyl carbons, with the doublet being the $SnCH_2$ carbon; (2) fourteen smaller resonances, assigned to the seven ring carbons; (3) several much smaller resonances, tentatively assigned to a nortricyclyl isomer and norborn-2-en-7-yltri-n-butyltin. The appearance of two resonances for each ring carbon and for the $SnCH_2$ carbon is attributed to the existence of *exo* and *endo* forms of norborn-2-en-5-yltri-n-butyltin. The above assignments are based on intensities, partially decoupled spectra, and the spectrum of *exo*- and *endo*-5-methyl norborn-2-ene [9]. The ratio of amounts of *endo* to *exo* forms calculated from the carbon-13 NMR line intensities is 0.97 ± 0.03. Trimethyltin hydride also adds thermally or photochemically to norbornadiene to give mixtures of *endo* and *exo* product accompanied by lesser amounts of nortricyclyl isomer and a rearrangement product [10].

This material gave upon reaction with 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid solvent at 100° a 75% yield of nortricyclic product (eqn.6). Although this finding suggests that cyclodestannylation occurred even to form



(6)

a strained ring system, a bromination of cyclohex-3-en-1-yltri-n-butyltin at —65° did not initially give rise to the expected bicyclic compound, but afforded instead a dibromo compound (1-tri-n-butyltin-3-*cis*-bromo-4-*trans*-bromocyclohexane, II) resulting from bromination of the double bond. Heating the dibromo



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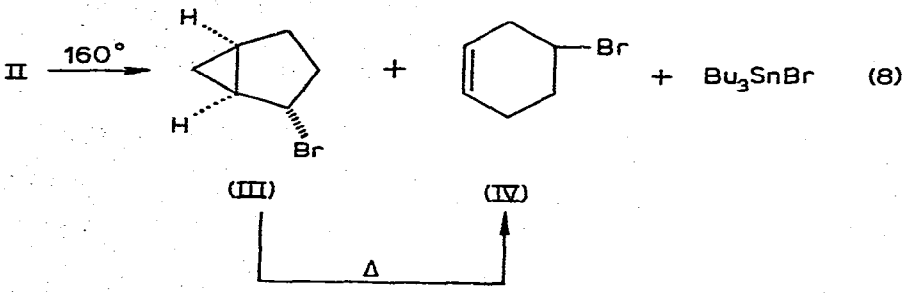
(II)

adduct to ca. 160° in vacuo resulted in its fragmentation to give approximately equal quantities of *trans*-2-bromobicyclo[3.1.0]hexane (III) and 4-bromocyclohexane (IV). Since (IV) was shown not to be present prior to the heating of II,



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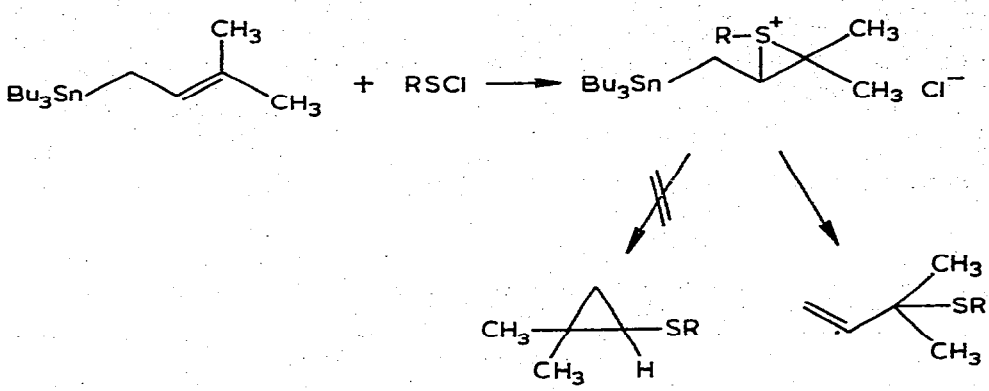
it is likely that it was formed by thermal rearrangement of III. In accord with this conclusion was the finding that IV was the only product which emanated from a column when the mixture of III and IV was subjected to gas phase chromatography (injection temp. of 250°).

Interestingly, an attempt to effect cyclodestannylation of 3-methylbut-2-en-1-yltri-n-butyltin with a sulfenyl chloride failed even though a Markownikoff addition to the double bond would have formed a tertiary carbonium ion γ to the tin. Instead, an S_E2' reaction resulted. Similar acid-catalyzed cleavages of alkyltin compounds are known [11].

Upon considering other possibilities for the cyclodestannylation reaction, it was felt that the OH group of a peroxy compound such as *m*-chloroperbenzoic acid might be sufficiently electrophilic to "trigger" cyclodestannylations of I (eqn.5, $E^+ = OH^+$) to form cyclopropylcarbinol. This proved not to happen as evidenced by the formation of 3,4-epoxybutyltri-n-butyltin (V) in 78% from a



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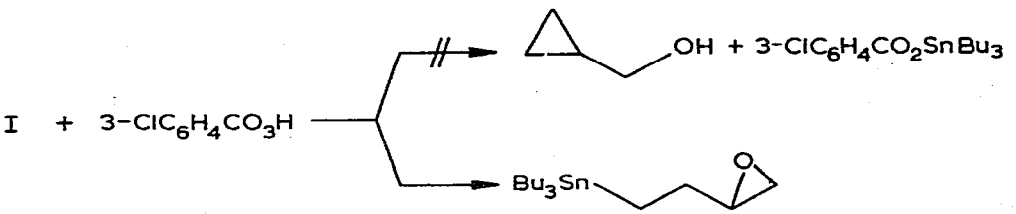
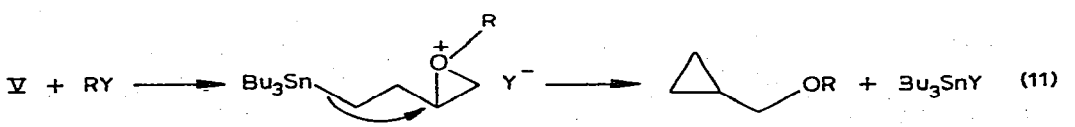
reaction of I with the peracid. However, conversions of V to a variety of onium intermediates (VI) by reactions with hydrogen chloride, picrylsulfonic acid,



(10)

(V)

boron trifluoride etherate, and methyl fluorosulfonate initiated the cyclodestannylation reaction* (eqn.11). Cyclopropylcarbinol was realized from the first three reactions, while cyclopropylcarbinyl methyl ether was obtained from the last reaction (see Table 2).



(11)

(VI)

The low yield of alcohol from the reaction of (V) with hydrogen chloride was accounted for by the tentative identification (by ^{1}H NMR) of some chlorohydrin, $Bu_3SnCH_2CH_2CHClCH_2OH$, in the distillation residue. Apparently, in this reaction, the nucleophilic chloride ion competed with the carbon—tin bond for the incipient carbonium ion.

The absence of but-3-en-1-yl derivatives as products from these reactions of V is of interest since it is known that trialkyltin groups impart significant hydride character to β hydrogens [12], i.e., an elimination of the type shown below (eqn.12) should not be unreasonable. Hydride migration, relative to ring closure,

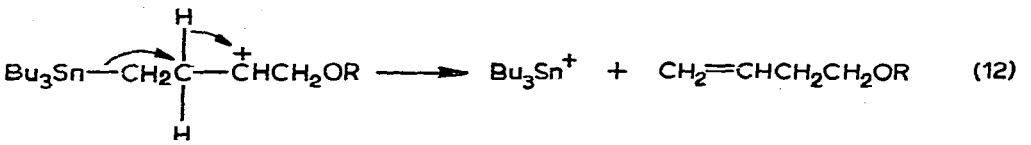
* Precedence for these conversions is found in the work of Kuivila and Scarpa [6] who reported that 3,4-epoxybutyltrimethyltin gave $(cyclo\text{-}C_3H_5CH_2O)_3B$ when treated with boron trifluoride etherate.

TABLE 2

REACTIONS OF 3,4-EPOXYBUTYLTRI-n-BUTYLTIN WITH ELECTROPHILES

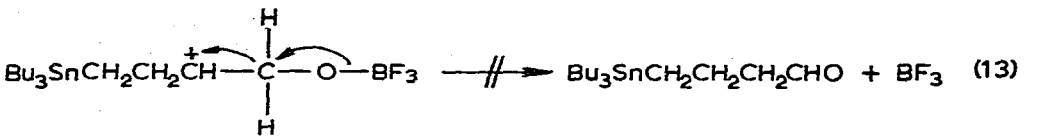
Reactant	Solvent	Temp. (°C)	cyclo-$C_3H_5CH_2OR$[a] (%)
$BF_3 \cdot Et_2O$	Et_2O	−65	90[b]
$2,4,6\text{-}(NO_2)_3C_6H_2SO_3H$	$Et_2O \cdot CH_2Cl_2$	0	65[c]
HCl(anhyd.)	CH_2Cl_2	0	29
CH_3OSO_2F	CH_2Cl_2	20	86[d]

[a] R = H for first three entries; R = CH_3 for last entry. [b] Reaction mixture hydrolyzed prior to the isolation of cyclopropylcarbinol by distillation at reduced pressure. [c] Excess acid was neutralized with dilute aq. base before allowing the reaction mixture to warm to room temperature. [d] Yield a combination of cyclopropylcarbinyl methyl ether (42%) and cyclobutyl methyl ether (44%) and cyclobutyl methyl ether (42%). A trace of but-3-en-1-yl methyl ether was also formed. In other runs, differing ratios of products were obtained. The cyclobutyl methyl ether and but-3-en-1-yl methyl ether most probably result from a secondary reaction of the cyclopropylcarbinyl methyl ether with the methylating agent.



$$Bu_3Sn\text{—}CH_2\overset{H}{\underset{H}{C}}\text{—}\overset{+}{C}HCH_2OR \longrightarrow Bu_3Sn^+ + CH_2{=}CHCH_2CH_2OR \qquad (12)$$

was also of no consequence in the decomposition of the intermediate in the boron trifluoride reaction with V as indicated by the absence of 4-tri-n-butylstannylbutanal as a product.



$$Bu_3SnCH_2CH_2\overset{+}{C}H\text{—}\overset{H}{\underset{H}{C}}\text{—}O\text{—}BF_3 \not\longrightarrow Bu_3SnCH_2CH_2CH_2CHO + BF_3 \qquad (13)$$

A cyclodestannylation of V was also found to occur thermally; i.e. (cyclopropylmethoxy)tributyltin was the major product (ca. 75% of total peak areas) emanating from gas chromatography of V on a 5ft. 10% SE-30 GLC (column temp. 150°, injection temp. 250°). The compound thus collected was identical to an authentic sample prepared in 83% yield from the reaction of (*N,N*-dimethylamino)tri-n-butyltin with cyclopropylcarbinol.

$$V \xrightarrow{\Delta} \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!CHCH_2OSnBu_3 \qquad (14)$$

Experimental

General

All reactions and manipulations involving organometallic compounds were performed under an atmosphere of oxygen-free argon. The organotin compounds

were stored under argon in glass ampoules fitted with ground glass stopcocks.

Proton NMR measurements were made at 100 MHz on a Varian HA-100 spectrometer. Spectra were recorded in the field sweep mode using a sulfuric acid capillary for the field-frequency stabilization signal. Chemical shifts are reported in ppm downfield (δ scale) from internal tetramethylsilane (TMS). Carbon-13 NMR spectra were recorded on a Bruker HX-90 pulsed Fourier transform spectrometer, operating at 22.6 MHz using 10 mm diameter sample tubes, with a Nicolet 1083 data system. Carbon-13 chemical shifts are measured in ppm downfield from internal TMS.

But-3-en-1-yltri-n-butyltin [13], -trimethyltin [14], and -triphenyltin [15] were prepared by reactions of but-3-en-1-ylmagnesium bromide with the corresponding trialkyltin halides [7]. Since the reactions of the halogens, as well as the reactions of the sulfenyl chlorides, with but-3-en-1-yltri-n-butyltin (I) were quite similar, only experiments typifying these reactions are described in detail. The essential experimental differences in the reactions of the electrophilic analogs with I are footnoted in Table 1. The experimental description of reactions of 3,4-epoxybutyltri-n-butyltin with the Lewis acids was treated in a similar manner (see Table 2).

Cyclopropylcarbinyl chloride [16], bromide [17], and iodide[18], and cyclopropylcarbinol* [19], cyclopropylcarbinyl methyl ether [20] and cyclobutyl methyl ether [21] were identified by comparisons of their boiling points and spectral data with those reported in the literature for authentic compounds. The ^{1}H NMR spectra of these compounds, in particular, afforded convincing evidence in support of their assigned structures owing to the highly characteristic resonances exhibited by their cyclopropyl and carbinyl protons [19]. The previously unreported sulfides were further identified as follows.

Bis(cyclopropylcarbinyl) sulfide. (Found: C, 68.1; H, 9.9. $C_8H_{14}S$ calcd.: C, 67.6; H, 9,9%.) A mass spectrum of the compound was comprised, in part, of intense fragment peaks at *m/e* 55 (C_4H_7-base peak), 86 (C_4H_6S), 101 (C_4H_7-SCH_2), 142 (parent ion), and 142.0816 (by peak matching; molecular weight calcd.: 142.0818). A ^{13}C NMR spectrum of the compound in carbon disulfide was comprised of signals at 37.7 (carbinyl carbons), 11.4 (methine carbons), and 5.4 ppm (ring methylene carbons).

Cyclopropylcarbinyl phenyl sulfide. (Found: C, 72.9; H, 7.3. $C_{10}H_{12}S$ calcd.: C, 73.2; H, 7.3%.) A mass spectral analysis of the compound supported the structure assignment with major fragments at *m/e* 55 (C_4H_7), 86 (C_4H_6S), 123 ($C_6H_5SCH_2$-base peak), and 164 (parent ion).

4-Chlorophenyl cyclopropylcarbinyl sulfide. (Found: C, 60.9, H, 5.6. $C_{10}H_{11}ClS$ calcd.: C, 60.5; H, 5.5%.)

Characterization of trans-2-bromobicyclo[3.1.0]hexane and 4-bromocyclohexene

The products (III and IV) of the fragmentation reaction (eqn.8) were identified by ^{1}H NMR spectral analysis. Multiplets at δ 0 to 0.34 and 0.4 to 0.7 were assigned to the cyclopropyl methylene protons of III, multiplets at δ 1.2 to 2.8 were assigned to protons on C-1, C-3, C-4 and C-5 of III, and the doublet (J 4.5 Hz) at δ 4.39 was assigned to the *cis*-2-proton of III. Assignment of III as the

* The ^{1}H NMR spectrum of cyclopropylcarbinol is contained in the Sadtler Compilation, No.2561 M.

trans-2-bromo compound was based on the results of Freeman, Raymond and Grostic [21] on *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexane, in which: (1) the upfield cyclopropyl methylene multiplet at δ 0 to 0.33 was found only for the *trans* compound; (2) the tertiary proton α to chloride appeared as a doublet at δ 4.29 (J 4.3 Hz) in the *trans* material (due to dihedral angles close to 90° between this and the adjacent *trans* protons on C-1 and C-3) [22] and as a complex multiplet centered at δ 4.35 in the *cis*-chloro compound. Multiplets centered at δ 2.15, 2.59, 4.29, and 5.59 were assigned to protons on C-5 and 6, C-3, C-4 and C-1 and 2 of IV, respectively, from the work of Jensen and Bushweller [23].

There was some overlap between the doublet at δ 4.39 assigned to the *cis*-2 proton of III and the multiplet centered at 4.29, due to IV. To confirm these assignments double-decoupling experiments were performed, in which: (1) multiplets due to protons on C-5 (δ 2.15) and C-3 (δ 2.59) of IV were simultaneously irradiated, with resulting collapse of the multiplet at δ 4.29, to a singlet, leaving a clean doublet centered at δ 4.39; (2) multiplets in the region 1.7 and 2.1 [due to III] were simultaneously irradiated, resulting in collapse of the doublet at δ 4.39 to a singlet. These results confirm the origin of this doublet as the *cis* proton of III.

Characterization of 1-tri-n-butyltin-3-cis-bromo-4-trans-bromocyclohexane

Based on the following ^{13}C NMR spectral analysis, II is assigned the structure of 1-tri-n-butyltin-3-*cis*-bromo-4-*trans*-bromocyclohexane.

The ^{13}C NMR spectrum of II in chloroform was recorded at 30° C with complete proton decoupling. Resonances were observed at 9.3, 14.8, 18.6, 26.3, 28.6, 30.5, 31.6, 34.5, 55.7, and 56.4 ppm from internal TMS. The resonances at 9.3, 14.8, 28.6, and 30.5 were assigned to the $SnBu_3$ carbons on the basis of intensities, the ~ 320 Hz Sn—C coupling for the $SnCH_2$ carbon resonance, and the spectrum of cyclohexyltri-n-butyltin. On the basis of a spectrum recorded under off-resonance decoupling conditions, and calculations based on chemical shift substituent parameters derived from ^{13}C NMR spectra of cyclohexane, bromocyclohexane, n-butyl bromide, and cyclohexyltri-n-butyltin, the following assignments were made: C-1 (18.6), C-6 (26.3), C-5 (31.6), C-2 (34.5), C-3, C-4 (55.7, 56.4).

The tri-n-butyltin group was assigned an equatorial position on the basis of the closeness of the chemical shift of the bromine-substituted carbons (C-3, C-4), whose separation is only 0.7 ppm. In methylcyclohexane, a large γ effect (—5.4 ppm, downfield) was found for axial methyl substitution, and zero γ effect for equatorial methyl substitution [24]. Since the δ effect of either axial or equatorial methyl substitution is only —0.1 to —0.2 ppm, this suggests that the resonances due to C-3 and C-4 would be separated by at least 5 ppm in II, were the tri-n-butyltin group located axially. Using the substituent parameters for axial and equatorial methyl substitution in cyclohexane [24] and the substituent parameters for replacement of a methyl group with bromine and tri-n-butyltin, spectra were calculated for II, assuming equatorial tin substitution, with both diaxial and diequatorial bromide conformations. The results of these calculations are shown in Table 3, for comparison with the observed chemical shifts. The agreement between the observed shifts and those calculated for the diaxial bromide conformation is good except for C-1; in particular, the shifts of C-3 and

TABLE 3

CONFORMATIONAL ANALYSIS OF 3,4-DIBROMOCYCLOHEXYLTRI-n-BUTYLTIN[a]

Carbon	Chemical shift[b]		
	Calculated		Observed
	Diaxial Br	Diequatorial Br	
C-1	13.9	19.1	18.6
C-2	35.1	44.2	34.5
C-3	57.6	65.8	55.7, 56.4
C-4	57.3	65.5	
C-5	29.9	39.0	31.6
C-6	26.7	31.7	26.3

[a] Carbon-13 NMR chemical shifts observed and calculated for 3,4-dibromocyclohexyltri-n-butyltin, assuming equatorial $SnBu_3$ and diaxial and diequatorial bromides. [b] Shifts are in ppm from internal TMS.

C-4, which would be most sensitive to the bromide configuration, agree quite well. Agreement between the observed shifts and those calculated for the diequatorial bromide conformation is quite poor, particularly for C-3 and C-4.

These results provide evidence for, but do not unequivocally prove, the structure 1-tri-n-butyltin-3-*cis*-bromo-4-*trans*-bromocyclohexane for II. To check the possibility that the observed chemical shifts might be the result of exchange between II and some other conformer, spectra were recorded at low temperatures. At the lowest temperature attained before loss of II from acetone solution, which occurred at —80°C, no spectral changes were evident. This result does not exclude the possibility that a small amount of some conformer other than II may exist in solution, but may only mean that a temperature low enough to sufficiently slow the possible exchange between forms was not reached.

In accord with the structure assignment is the known tendency of conformationally biased 4-substituted cyclohexanes to undergo *trans*-(diaxial)-brominations [25].

Reaction of but-3-en-1-yltri-n-butyltin (I) with bromine

To a solution of 13.8 g (0.04 mole) of I in 50 ml of methylene chloride at —65° there was added dropwise a solution of 2 ml of bromine contained in 10 ml of methylene chloride. The reaction, which was spontaneous, was monitored by GLC. Subsequent to the complete addition, the solvent was removed by careful distillation and the residue was fractionated under a moderate vacuum (~ 20 mm) into a cold trap to give 4.6 g (86%) of cyclopropylcarbinyl bromide. The product, at atmospheric pressure, boiled at 102—104° (lit. [17] b.p. 101.5—102°).

The distillation residue, which was shown to be tri-n-butyltin bromide by GLC and ^{1}H NMR spectral analyses, was discarded.

Reaction of but-3-en-1-yltri-n-butyltin (I) with 2,4-dinitrobenzenesulfenyl chloride

To 1.38 g (0.004 mole) of I there was added 0.94 g (0.004 mole) of 2,4-dinitrobenzenesulfenyl chloride in 20 ml of glacial acetic acid. The mixture was

heated on a steam bath for 20 min, cooled to room temperature, and poured into ice water. The precipitate present was removed by filtration and recrystallized from ethanol to yield 0.80 g of cyclopropylcarbinyl-2,4-dinitrophenyl sulfide, m.p. 80—81°. (Found: C, 46.9; H, 4.0. $C_{10}H_{10}N_2O_4S$ calcd.: C, 47.2; H, 4.0%.) The compound exhibited NMR ($CDCl_3$/TMS) peaks centered at δ 9.1 (d, J 2 Hz, 1H), 8.5 (2d, J 2 Hz, and 8 Hz, 1H), 7.7 (d, J 8 Hz, 1H), 3.1 (d, J 7 Hz, 2H) and 1.5 to 0.3 (m, 5H); and IR absorptions at (KBr) 1580 s, 1340 s, 1050 m, 910 m, 830 m, and 740 m.

Reaction of but-3-en-1-yltri-n-butyltin with sulfur trioxide

To 3.44 g (0.01 mole) of I in 200 ml of dichloromethane at —65° there was added by means of a syringe 0.90 g (0.01 mole) of sulfur trioxide. The mixture was allowed to warm to room temperature and the solvent was removed by means of a rotary evaporator at room temperature. Then 0.5 g of water was added to the residue and after stirring for 0.5 h, 50 ml of acetone was added and stirring continued for 0.5 h. Ethereal diazomethane was added until no more bubbles were evolved and a faint yellow color remained. The solvent was removed on a rotary evaporator, the residue taken up in ether, dried over $CaCl_2$ and again concentrated on a rotary evaporator. The residue was then distilled to yield 1.46 g (84%) of a colorless oil, b.p. 68—72° (2 mm). GLC analysis of the distillate on an SE-30 column showed that only trace quantities of (< 1%) dimethyl sulfate and methyl butanesulfonate accompanied the methyl cyclopropylcarbinylsulfonate. (Found: C, 39.8; H, 6.7; S, 21.1. $C_5H_{10}O_3S$ calcd.: C, 40.0; H, 6.7; S, 21.4%.) NMR ($CDCl_3$/TMS) δ 4.0 (s, 3H), 3.2 (d, J 7 Hz, 2H) and 1.6—0.3 (m, 5H); IR (film) 1340 s, 1160 s, 990 s, and 800 s.

Reaction of 3-methylbut-2-en-1-yltri-n-butyltin with 2,4-dinitrobenzenesulfenyl chloride

To 0.36 g (0.001 mole) 3-methylbut-2-en-1-yltri-n-butyltin in 100 ml of acetic acid there was added 0.24 g (0.001 mole) of 2,4-dinitrobenzenesulfenyl chloride and the mixture was heated on the steam bath for 1 h. After cooling, the mixture was poured into ice water and the crystals present were collected by filtration. A recrystallization of this material from ethanol yielded 0.43 g (73%) of 1,1-dimethylprop-2-en-1-yl-2,4-dinitrophenyl sulfide, m.p. 76—78°. (Found: C, 48.9; H, 4.5; N, 10.4. $C_{11}H_{10}N_2O_4S$ calcd.: C, 49.2; H, 4.5; N, 10.4%.) NMR ($CDCl_3$/TMS) δ 9.1 (d, J 2Hz, 1H), 8.6 (2d, J 2 Hz and 8 Hz, 2H), 7.7 (d, J 8 Hz, 1H), 6.0 (m, 1H), 5.3 (m, 2H), 1.6 (s, 6H); IR (film) 1640 w, 1610 s, and 1360 s.

Reaction of but-3-en-1-yltri-n-butyltin with mercuric chloride

To 0.69 g (0.002 mole) of but-3-en-1-yltri-n-butyltin in 25 ml acetonitrile at 55°C was added slowly and dropwise 0.54 g (0.002 mole) of mercuric chloride in 25 ml of acetonitrile over 10 min. The mixture was stirred for 1 h and then the solvent was removed by means of a rotary evaporator at room temperature. The liquid was taken up in chloroform and the solid ($HgCl_2$) was removed by filtration. 50 ml of pentane was added to the filtrate and the solution was cooled in a Dry Ice/acetone bath to yield 0.59 g of white crystals (89% conversion). The NMR spectrum ($CDCl_3$/TMS) of the crude cyclopropylcarbinylmercuric chloride had peaks at δ 5.5 (m, 3 units), 3.7 (m, 2.5 units), 2.3 (m, 4 units), 2.1

(d, J 7 Hz, 18 units), and 0.8 (m, 57 units) indicating the presence of n-butyl- and 3-butenyl-mercuric chloride impurities. Careful TLC on silica gel using 50/50 pentane/chloroform removed some, but not all of the impurities. The white crystals so obtained were estimated by ^{1}H NMR spectral analysis to be cyclopropylcarbinylmercuric chloride of approximately 95% purity. (Found: C, 16.4; H, 2.4. C_4H_7ClHg calcd.: C, 16.4; H, 2.4%.) NMR ($CDCl_3$/TMS) δ 2.05 (d, J 7 Hz, 2H) and 1.5—0.0 (m, 5H); IR (KBr) 3180 w, 2925 w, 1440 w, 1240 w, 1130 w, 970 w; ^{13}C NMR ($CHCl_3$/TMS) 38.7 (t, $J \cong 140$ Hz), 10.6 (d, $J \cong 160$ Hz) [n-butylmercuric chloride shows peaks at 33.1, 30.6, 27.7 and 13.5 ppm from TMS].

On standing for six days, the cyclopropylcarbinylmercuric chloride partially (> 75%) rearranged to but-3-en-1-ylmercuric chloride as evidenced by ^{1}H NMR spectral analysis.

Preparation of tetra(but-3-en-1-yl)tin

To 500 ml of a chilled (0°) solution of but-3-en-1-ylmagnesium bromide in tetrahydrofuran (THF), prepared from the reaction of 75 g (0.55 mole) of but-3-en-1-yl bromide with excess magnesium (24.3 g, 1.0 g atom), there was added cautiously 32.6 g (0.125 mole) of stannic chloride which resulted in a very vigorous reaction. Subsequent to the complete addition, the reaction mixture was allowed to warm to room temperature during 0.5 h, and was then hydrolyzed with 10% hydrochloric acid. The organic phase was extracted with ether and dried over sodium sulfate. Removal of the solvent left an oil that was distilled to give 32 g (76%) of product, b.p. 78—82° (0.04 mm). (Found: C, 56.5; H, 8.4. $C_{16}H_{28}Sn$ calcd.: C, 56.7; H, 8.4%.) The structure assignment was confirmed by ^{1}H (typical but-3-en-1-yl absorption pattern) and IR spectral analyses. Also, the compound was further characterized by its reaction with bromine (see following experiment).

Reaction of tetra(but-3-en-1-yl)tin with bromine

To a solution of 3.4 g (0.01 mole) of tetra(but-3-en-1-yl)tin in 15 ml of methylene chloride cooled by means of a Dry Ice/acetone bath to —65° there was added dropwise 6.4 g (0.04 mole) of bromine contained in 15 ml of methylene chloride. After the addition, which required 0.25 h, the reaction mixture was allowed to warm to room temperature and the solids present were removed by filtration and discarded. The filtrate was then carefully distilled under vacuum (~ 20 mm) into a cold trap. The distillate was comprised of methylene chloride and cyclopropylcarbinyl bromide. A redistillation separated the components; 2.65 g (49%) of cyclopropylcarbinyl bromide, b.p. 103—108°, was obtained. The product was free of any but-3-en-1-yl bromide.

Reaction of norborn-2-en-5-yltri-n-butyltin with 2,4-dinitrobenzenesulfenyl chloride

To 0.8 g (0.002 mole) of the organotin compound in 10 ml of glacial acetic acid there was added 0.5 g of 2,4-dinitrobenzenesulfenyl chloride (0.002 mole) and the mixture was heated on the steam bath for 0.75 h. The reaction mixture was then poured into ice water and allowed to stand for 1 h. The crystals present were filtered and washed with pentane to yield 0.52 g of 2,4-dinitro-

phenyl sulfide. A recrystallization of the product from ethanol gave tricyclo-[2.2.1.$0^{2,6}$]hept-3-yl 2,4-dinitrophenyl sulfide having a m.p. of 131—133°. (Found: C, 53.4; H, 4.4; N, 9.4. $C_{13}H_{11}N_2O_4$ calcd.: C, 53.4; H, 4.1; N, 9.6%.) The compound had NMR peaks ($CDCl_3$/TMS) at δ 9.0 (d, *J* 2 Hz, 1H), 8.3 (2d, *J* 2 Hz and 8 Hz, 1H), 7.7 (d, *J* 8 Hz, 1H), 3.3 (m, 1H), 2.3 (m, 1H), 1.2 (m, 7H). The tricyclo[2.2.1.$0^{2,6}$]heptane portion of the spectra was similar to those of authentic samples containing that hydrocarbon residue; e.g., tricyclo-[2.2.1.$0^{2,6}$]heptane-3-carbamic acid, ethyl ester, No.3787 in Sadtler Standard Spectra (1967).

Preparation of cyclohex-3-en-1-yltri-n-butyltin

A solution of 11.3 g (0.097 mole) of cyclohex-3-en-1-yl chloride dissolved in 80 ml of THF was added dropwise to a rapidly stirred suspension of 4.9 g (0.2 g atom) of magnesium turnings in 20 ml of THF. The Grignard formation was initiated by warming to ~ 50°. The temperature was maintained throughout the addition of the chloride by the application of moderate external heating. Subsequently, the reaction mixture was stirred for 1 h at room temperature, the excess magnesium was removed by filtration, and the Grignard solution was treated with 28 g (0.08 mole) of tri-n-butyltin chloride which was added dropwise. After it had been stirred for an additional hour, the reaction mixture was poured into chilled aqueous ammonium chloride. The product was extracted into ether and isolated by distillation; 24.3 g (82%), b.p. 103—119° (0.05 mm). The structure assignment was confirmed by ^1H [vinyl protons (multiplet) centered at 5.65 ppm] and ^{13}C [resonances for the ring carbon atoms at 128.8 and 130.7 (C-3 and C-4), 31.6 (C-2), 29.2 (C-6), 28.8 (C-5), and 23.2 (C-1) ppm] NMR spectral analyses and by its derivatization with bromine (see following experiment). (Found: C, 58.0; H, 9.3. $C_{18}H_{36}Sn$ calcd.: C, 58.2; H, 9.7%.)

Bromination of cyclohex-3-en-1-yltri-n-butyltin

To a solution of 7.4 g (0.02 mole) of cyclohex-3-en-1-yltri-n-butyltin dissolved in 10 ml of methylene chloride at —65° there was added dropwise 1.05 ml (0.02 mole) of bromine contained in 10 ml of methylene chloride. The reaction was spontaneous as evidenced by the rapid disappearance of the bromine color. Also, at the end of the addition, the starting organotin compound was shown by GLC to have been consumed. The solvent was then removed by evaporation. The residue was identified as 1-tri-n-butyltin-3-*cis*-bromo-4-*trans*-bromocyclohexane (II) by ^1H and ^{13}C NMR spectral analyses (see General portion of Experimental Section for spectral details).

Compound II was then heated in a distillation apparatus under moderate vacuum. At a bath temperature of approximately 160°, 1.3 g of a liquid, b.p. ~ 65—79°, collected in a receiver that was immersed in a Dry Ice/acetone bath. Analysis of the distillate by ^1H and ^{13}C NMR analyses revealed it to be comprised of ca. equal amounts of *trans*-1-bromo[3.1.0]bicyclohexane (III) and cyclohex-3-en-1-yl bromide (IV) accompanied by a small amount of n-butyl bromide (see General portion of Experimental Section for spectral details). Only one major peak was evident upon gas phase chromatography of the distillate. The compound which comprised this peak was collected and identified as IV by ^1H NMR spectral analysis. Based on the logical assumption that IV was

formed from thermal isomerization of III, the yield of III from the fragmentation reaction was 41%.

The distillation residue was identified as tri-n-butyltin bromide by GLC and ^{1}H NMR spectral analyses.

A repetition of the above reaction afforded roughly the same yield of volatile components, but the ratio of III to IV was lower.

Preparation of 3,4-epoxybutyltri-n-butyltin (V)

To a chilled solution (0°) of 34.5 g (0.1 mole) of but-3-en-1-yltri-n-butyltin in 150 ml of methylene chloride, 22.4 g (0.11 mole) of *m*-chloroperbenzoic acid was added portionwise during ca. 10 min. After the addition, the reaction mixture was stirred for one h at 0°, warmed to room temperature and the *m*-chlorobenzoic acid was removed by washings with cold dilute sodium carbonate. The organic phase was concentrated by means of a rotary evaporator and the residue was distilled to give 28.1 g (78%) of epoxide, b.p. 111—114° (0.03 mm). (Found: C, 53.4; H, 9.3. $C_{16}H_{34}OSn$ calcd.: C, 53.2; H, 9.4%.) A ^{1}H NMR spectrum of V in $CDCl_3$ showed the characteristic pattern for —CH—CH_2—O at δ 2.2—2.85 relative to TMS.

A typical reaction of 3,4-epoxybutyltri-n-butyltin with an electrophile (methyl fluorosulfonate)

To a chilled solution (0°) of 14.4 g (0.04 mole) of V in 40 ml of methylene chloride there was added dropwise 4.6 g (0.04 mole) of freshly distilled methyl fluorosulfonate. The cooling bath was then removed and stirring was continued for ca. 1 h during which time V was consumed (as determined by GLC analysis). The reaction mixture was then treated with gaseous trimethylamine to remove any excess methyl fluorosulfonate. The solid which formed was removed by filatration. The filtrate was distilled under moderate vacuum (ca. 20 mm) into a cold trap; three fractions were obtained and found to contain by GLC and ^{1}H NMR analyses: (1) methylene chloride; (2) methylene chloride, 1.45 g (42%) of cyclopropylcarbinyl methyl ether and 0.97 g (28.2%) of cyclobutyl methyl ether and (3) methylene chloride, 0.55 g (16%) cyclobutyl methyl ether, and a trace of but en-1-yl methyl ether. These products were identified by comparison of their ^{1}H NMR spectra with those of authentic compounds (see General part of Experimental Section for references to these compounds).

Preparation of (cyclopropylmethoxy)tri-n-butyltin

To a flask containing 5.1 g (0.015 mole) of (*N*,*N*-dimethylamino)tri-n-butyltin (under an atmosphere of argon) there was added dropwise 1.1 g (0.015 mole) of cyclopropylcarbinol which resulted in the evolution of a gas (dimethylamine). After 0.15 h, the reaction was complete as shown by GLC. The reaction mixture was then subjected to a slight vacuum to remove any residual dimethylamine and the residue was then distilled under vacuum to give 4.5 g (83%) of (cyclopropylmethoxy)tri-n-butyltin, b.p. 90—93° (0.03 mm), and 0.7 g of tri-n-butyltin oxide. The (cyclopropylmethoxy)tri-n-butyltin was identified by its ^{1}H NMR spectrum which exhibited signals relative to TMS for carbinyl protons δ 3.55 (J(CH—CH_2) 6 Hz, J(^{117}Sn—CH_2) 22 Hz, J(^{119}Sn—CH_2) 34 Hz), and methylene ring protons at ~ 0.1—0.7 ppm; and by its ^{13}C NMR spectrum with signals rela-

tive to TMS at 69.9 ppm for the carbinyl carbon, 15.2 ppm for the methine carbon, and 2.3 ppm for the ring methylene carbons. Interestingly, the Sn—^{13}C signal at 14.0 ppm, was accompanied by two distinct doublets arising from ^{13}C—^{117,119}Sn interaction with J's of 350 and 365 Hz, respectively [26]. Treatment of V with water gave cyclopropylcarbinol and tri-n-butyltin oxide as evidenced by GLC and ^{1}H NMR analytical determinations.

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