this is in accord with the wide range of variation observed for the estimated $n_{OC}^{\ddagger}$ values.

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Supplementary Material Available: Numerical values of rate constants and examples of fits of observed k_{ψ}'s to eq 2 and of evaluations of k_1^H/k_1^D (3 pages). Ordering information is given on any current masthead page.

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Homolytic Substitution at Carbon: 1,3- and 1,5-Ring Closures in Organotin-Substituted Radicals

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Pivotal to many studies of possible S_H mechanisms at saturated carbon[1] have been reactions involving 1,3-ring closure[2] or cleavage.[3] Remotely functionalized organometallics, particularly organotins,[4] have been shown to undergo facile, stereospecific (inversion),[5] heterolytic 1,3-ring closures; however the scope and mechanisms of the analogous homolytic 1,3-elimination reactions are much less clear. Kaplan and Drury[6] reported that cyclopropane is formed quantitatively by the Ph_3SiH-initiated reaction of γ-haloorganotins:

$$Ph_3SnCH_2CH_2CH_2Cl \xrightarrow[225\ ^\circ C]{3\%\ Ph_3SiH} C_3H_6 + Ph_3SnCl \quad (1)$$

In such cases a dichotomy exists in which bimolecular homolytic substitution (S_H2) at either the metal or the halogen (depending upon the chain carrier) leads to possible cyclopropane-precursor radicals:

$$M\text{-}CH_2CH_2CH_2\text{-}X \xrightarrow{X\cdot} M\text{-}X + \dot{C}H_2CH_2CH_2X \rightarrow C_3H_6 + X\cdot \quad (2)$$

$$M\text{-}CH_2CH_2CH_2\text{-}X \xrightarrow{M\cdot} M\text{-}X + M\text{-}CH_2CH_2\dot{C}H_2 \rightarrow C_3H_6 + M\cdot \quad (3)$$

In this work we demonstrate that not only are S_H2 reactions at tin competitive with remote atom-abstraction reactions but that γ- and ε-trimethyltin-substituted alkyl radicals undergo 1,3- and 1,5-ring closures (S_Hi) efficiently.

The reaction of trimethyl(3-methoxypropyl)tin[7] (**1**), with a variety of photochemically generated H abstractors ($Ph_2CO/h\nu$; $(t\text{-}BuO)_2/h\nu$; $FeCl_3/h\nu$; $PhCOMe/h\nu$) in benzene at 22 °C leads to the formation of cyclopropyl methyl ether, tetrahydrofuran, and methyl propyl ether (Table I). The reaction sequence shown in eq 4-12 accounts for the observed products in terms of competitive H-abstraction reaction (eq 4 and 5) and carbon-tin cleavage (eq 6) followed by product-forming steps. The detailed mechanism of eq 6, in particular, could involve either direct substitution or an initial electron transfer to the ketone triplet, followed by collapse of an organotin cation-ketyl anion radical pair to the intermediates shown. In either case, the net result is a bimolecular radical-induced cleavage of the carbon-tin which we refer to herein as an S_H2 reaction. The similar yields of acyclic and cyclic ethers suggest that the intermolecular substitution reaction at tin and H abstraction from the ether α carbons of **1** are competitive and that subsequent 1,3- or 1,5-ring closure reactions occur with similar facility. The relative yields of cyclopropyl methyl ether and tetrahydrofuran may reflect the greater reactivity of methylene vs. methyl hydrogens toward abstraction and/or the greater reactivity of tetrahydrofuran toward subsequent reactions. Under these conditions neither **1**, **2**, nor **5** give rise to detectable amounts of methyl radical products (methane or dimethylorganotins). This is the only reported homolytic 1,5-ring closure reaction of organotin compounds and shows some analogy to the heterolytic reactions of organotins.[4b]

Table I. Reaction of Trimethyl(3-methoxypropyl)tin with H Abstractors[a]

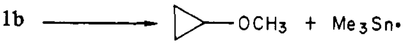
H abstractor	% conversion[b]	rel product distribution		
		MPE[c]	CPME[d]	THF[e]
$Ph_2CO/h\nu$[f]	48	1.0	1.1	1.0
$Ph_2CO/h\nu$	33	1.0	0.33	>0.08
$PhCOMe/h\nu$	49	1.0	0.21	0.30
$(t\text{-}BuO)_2/h\nu$	43[g]	1.0	0.88	0.65
$FeCl_3/h\nu$[h]	37	1.0	0.5	>0.05

[a] In degassed benzene at 0.67 M, 22 °C, 72 h, 200-W medium pressure Hg arc. [b] By difference from recovered 1. Mass balances for other products exceed 70%. [c] MPE = methyl propyl ether. [d] CPME = cyclopropyl methyl ether. [e] THF = tetrahydrofuran. [f] $[Ph_2CO] = 0.67$ M, $[1] = 0.22$ M. Me_6Sn_2 and benzopinacol isolated and identified by NMR spectroscopy and mixed melting point, respectively. Yields >85% in both cases, corrected for conversion. [g] 48 h. [h] Reference 21.

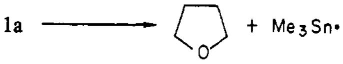
$$1 + Ph_2CO^*(T) \longrightarrow \underset{\mathbf{1a}}{Me_3SnCH_2CH_2CH_2\dot{O}CH_2} + Ph_2\dot{C}OH \quad (4)$$

$$1 + Ph_2CO^*(T) \longrightarrow \underset{\mathbf{1b}}{Me_3SnCH_2CH_2\dot{C}HOCH_3} + Ph_2\dot{C}OH \quad (5)$$

$$1 + Ph_2CO(T)^* \longrightarrow \underset{\mathbf{1c}}{\dot{C}H_2CH_2CH_2OCH_3} + Ph_2\dot{C}OSnMe_3 \quad (6)$$



(7)



(8)

$$1c + solvH\ (or\ 1) \longrightarrow CH_3CH_2CH_2OCH_3 + solv\cdot\ (or\ 1a,1b) \quad (9)$$

$$Me_3SnO\dot{C}Ph_2 \rightleftharpoons Me_3Sn\cdot + Ph_2CO\ (ref\ 8) \quad (10)$$

$$2Me_3Sn\cdot \longrightarrow (Me_3Sn)_2 \quad (11)$$

$$2Ph\dot{C}OH \longrightarrow (Ph_2COH)_2 \quad (12)$$

Reports on the mechanism of trichloromethyl abstractions from 2-(trimethylstannyl)butane,[9] the rate constant for *tert*-butoxy abstraction from the α position of tetraethyltin,[10] the absolute rate constants for benzophenone triplet and *tert*-butoxy abstractions

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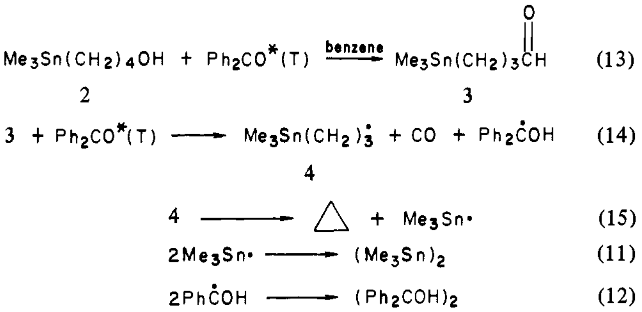
from *tert*-butyl methyl ether,[11] and thermochemical data on stabilities of α-silyl radicals[12] are generally consistent with a greater ease of abstraction α to the ether linkage. The competitive substitution observed here is unusual in that the *tert*-butoxy radical/tetraethyltin reaction[10] gave no evidence of ethyl displacement and only a trace of methyl-radical products was observed in the trichloromethyl/2-(trimethylstannyl)butane system.[9] The relatively facile displacement on **1** may suggest a strong steric influence on the course of these substitutions.[13]

That 1,3-ring closure is a general reaction of γ-organotin radicals is demonstrated by the benzophenone-induced photooxidation/decarbonylation[14] sequence shown by trimethyl(4-hydroxybutyl)tin (**2**). Chromatographic analysis of a reaction mixture of **2** and benzophenone at varying conversions clearly shows the buildup of **3** as a precursor of the ultimate products of cyclopropane and CO. The photooxidation of trimethyl(3-hydroxypropyl)tin (**5**) also shows the initial conversion to the aldehyde, trimethyl(3-oxopropyl)tin (**6**), and the subsequent decarbonylation of **6** to ethylene and CO. Hexamethylditin and benzopinacol are formed in both photooxidation/decarbonylation sequences in benzene; however, if the reaction is carried out carbon tetrachloride, trimethyltin chloride is the organotin product. Ethylene arises from the facile elimination of Me_3Sn from the (β-trimethyltin) ethyl radical[15] formed by decarbonylation of **6**. Since the ω-trimethyltin-substituted aldehydes[16] are readily available and easily decarbonylated, this reaction may offer a general route to (ω-trimethyltin) alkyl radicals. Interestingly, the benzophenone-induced photooxidation of **5** gave *propanal* as a major product, but **2** showed no butanal! Propanal could arise by an S_H2 reaction of ketone triplet on **5** (or **6**) but since the expected analogous reaction toward **2** (or **3**) did not occur, the more likely source of propanal is the 1,3-ring closure of the intermediate radical, $Me_3SnCH_2CH_2\dot{C}HOH$, to cyclopropanol. Not surprisingly, cyclopropanol was not detected since it undergoes a rapid ketone triplet induced ring opening to form propanal.[17] Thus the formation of propanal from **2** but not butanal from **5** suggests that 1,3-ring closures of the radical $Me_3SnCH_2CH_2\dot{C}HOH$ to yield cyclopropanol and eventually propanal are much faster the 1,4-ring closure of $Me_3SnCH_2CH_2CH_2\dot{C}HOH$.



$$Me_3Sn(CH_2)_4OH + Ph_2CO^*(T) \xrightarrow{\text{benzene}} Me_3Sn(CH_2)_3\overset{O}{\overset{\|}{C}}H \quad (13)$$

2 3

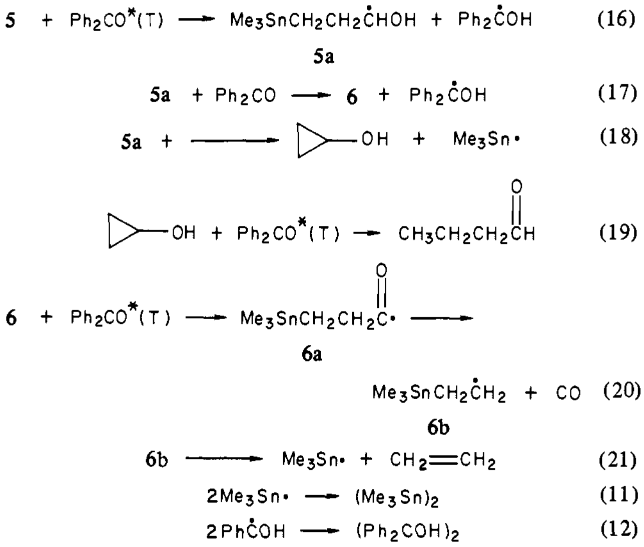
$$3 + Ph_2CO^*(T) \longrightarrow Me_3Sn(CH_2)_3^{\bullet} + CO + Ph_2\dot{C}OH \quad (14)$$

4

$$4 \longrightarrow \triangle + Me_3Sn\cdot \quad (15)$$

$$2Me_3Sn\cdot \longrightarrow (Me_3Sn)_2 \quad (11)$$

$$2Ph\dot{C}OH \longrightarrow (Ph_2COH)_2 \quad (12)$$



$$5 + Ph_2CO^*(T) \longrightarrow Me_3SnCH_2CH_2\dot{C}HOH + Ph_2\dot{C}OH \quad (16)$$

5a

$$5a + Ph_2CO \longrightarrow 6 + Ph_2\dot{C}OH \quad (17)$$

$$5a + \longrightarrow \triangleright\!\!-OH + Me_3Sn\cdot \quad (18)$$

$$\triangleright\!\!-OH + Ph_2CO^*(T) \longrightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H \quad (19)$$

$$6 + Ph_2CO^*(T) \longrightarrow Me_3SnCH_2CH_2\overset{O}{\overset{\|}{C}}\cdot \longrightarrow Me_3SnCH_2\dot{C}H_2 + CO \quad (20)$$

6a 6b

$$6b \longrightarrow Me_3Sn\cdot + CH_2{=}CH_2 \quad (21)$$

$$2Me_3Sn\cdot \longrightarrow (Me_3Sn)_2 \quad (11)$$

$$2Ph\dot{C}OH \longrightarrow (Ph_2COH)_2 \quad (12)$$

The lack of strong evidence for the generality of radical adducts of group 4 organometallics[10c] as compared to the corresponding group 3 or 5 elements,[18] the expected large ring strain in stannacyclobutanes,[19] the strain-accelerated ring-opening reactions of stannacyclopentanes,[20] the facile 1,3- and 1,5-ring closures, and the apparent lack of 1,4-ring closure suggest that these reactions are occurring through 3- or 5-membered cyclic transition states involving homolytic substitution at the carbon atom in the carbon–metal bond.

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^{17}O ENDOR of Horseradish Peroxidase Compound I

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Hydrogen peroxide treatment of peroxidases and catalase produces an enzymic intermediate, called compound I, which is oxidized by 2 equiv above the ferriheme resting state.[1-3] Recently we employed electron nuclear double reasonance (ENDOR)[4] to prove that one oxidizing equivalent of horseradish peroxidase compound I (HRPI) exists as the porphyrin π-cation radical,[5] as proposed.[3] We now report the observation of ^{17}O ENDOR from HRPI prepared with $H_2{}^{17}O_2$. This result proves that one oxygen atom from the oxidant remains with the intermediate and therefore

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