

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

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Supplementary Material Available: Numerical values of rate constants and examples of fits of observed k_p '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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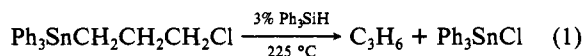
Homolytic Substitution at Carbon: 1,3- and 1,5-Ring Closures in Organotin-Substituted Radicals

Dennis D. Davis* and Fahim U. Ahmed

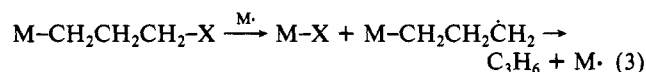
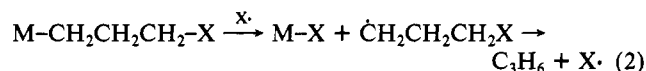
Department of Chemistry, New Mexico State University
Las Cruces, New Mexico 88003

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Pivotal to many studies of possible S_H mechanisms at saturated carbon¹ have been reactions involving 1,3-ring closure² 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 Drury⁶ reported that cyclopropane is formed quantitatively by the Ph_3SiH -initiated reaction of γ -haloorganotins:



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:



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.

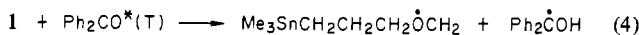
The reaction of trimethyl(3-methoxypropyl)tin⁷ (**1**), with a variety of photochemically generated H abstractors ($Ph_2CO/h\nu$;

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

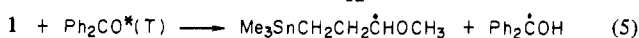
H abstractor	% conversion ^b	rel product distribution		
		MPE ^c	CPME ^d	THF ^e
$Ph_2CO/h\nu^f$	48	1.0	1.1	1.0
$Ph_2CO/h\nu$	33	1.0	0.33	>0.08
$PhCOMe/h\nu$	49	1.0	0.21	0.30
$(t-BuO)_2/h\nu$	43 ^g	1.0	0.88	0.65
$FeCl_3/h\nu^h$	37	1.0	0.5	>0.05

^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, $[I] = 0.22$ M. Me_3Sn_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.

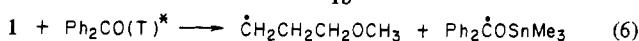
$(t-BuO)_2/h\nu$; $FeCl_3/h\nu$; $PhCOMe/h\nu$) in benzene at 22 °C leads to the formation of cyclopropyl methyl ether, tetrahydrofuran, and methyl propyl ether (Table I). The reaction sequence shown in eq 4-12 accounts for the observed products in terms of competitive H-abstraction reaction (eq 4 and 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



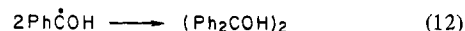
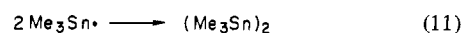
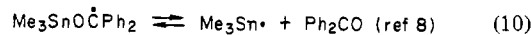
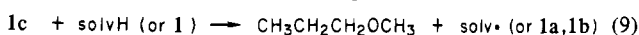
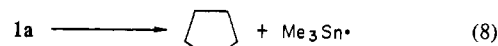
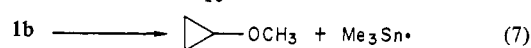
1a



1b



1c



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}

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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(7) Prepared by the addition of Me_3SnH to allyl methyl ether; **2** and **5** are prepared by addition of Me_3SnH to the 1-alkenols. The physical and spectral properties of these compounds are consistent with previously reported values.^{4a,b}

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