this is in accord with the wide range of variation observed for the estimated n_{OC} [‡] values.

Acknowledgment. Portions of this work were supported by the National Science Foundation (CHE 76-21052).

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

(28) Gold, V.; Grist, S. J. Chem. Soc. B 1971, 1665-1670.

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 Received October 27, 1980

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 Ph₃SiH-initiated reaction of γ -haloorganotins:

$$Ph_{3}SnCH_{2}CH_{2}CH_{2}Cl \xrightarrow{3\% Ph_{3}SiH}_{225 °C} C_{3}H_{6} + Ph_{3}SnCl (1)$$

In such cases a dichotomy exists in which bimolecular homolytic substitution $(S_H 2)$ at either the metal or the halogen (depending upon the chain carrier) leads to possible cyclopropane-precursor radicals:

...

$$\begin{array}{c} \text{M-CH}_2\text{CH}_2\text{CH}_2\text{-X} \xrightarrow{X^{\cdot}} \text{M-X} + \dot{\text{CH}}_2\text{CH}_2\text{CH}_2\text{X} \xrightarrow{} \\ \text{C}_3\text{H}_6 + \text{X}^{\cdot} (2) \end{array}$$
$$\begin{array}{c} \text{M-CH}_2\text{CH}_2\text{CH}_2\text{-X} \xrightarrow{M^{\cdot}} \text{M-X} + \text{M-CH}_2\text{CH}_2\dot{\text{CH}}_2 \xrightarrow{} \\ \text{C}_3\text{H}_6 + \text{M}^{\cdot} (3) \end{array}$$

In this work we demonstrate that not only are S_H^2 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 ($Ph_2CO/h\nu$;

(2) (a) Kaplan, L. J. Am. Chem. Soc. 1967, 39, 1953. (b) Druy, K. F.;
Kaplan, L. J. Am. Chem. Soc. 1973, 95, 2217; 1972, 94, 3982. (c) Kaplan,
L. Chem. Commun. 1968, 754.
(3) (a) Maynes, G. G.; Applequist, D. E. J. Am. Chem. Soc. 1973, 95, 856.
(b) Hoffman, J. M.; Graham, K. J.; Rowell, C. F. J. Org. Chem. 1975, 46, 3005. (c) Shea, K. J.; Skell, P. S. J. Am. Chem. Soc. 1973, 95, 6728.
(4) (a) Davis, D. D.; Chambers, R. L.; Johnson, H. T. J. Organomet.
Chem. 1970, 25, C13. Davis, D. D.; Black, R. D. H. Ibid. 1974, 82, C30. (b) Kuivila, H. G.; Scarpa, N. M. J. Am. Chem. Soc. 1970, 92, 6990. McWil-liam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. Ibid. 1978, 100, 6407. (c) Peterson, D. J.; Robbins, M. D.; Hansen, J. R. J. Organomet. Chem. 1974, ŻŻ, 237

 (5) Davis, D. D.; Johnson, H. T. J. Am. Chem. Soc. 1974, 96, 7576.
 (6) Kaplan, L.; Drury, R. Abstract 5.19, Joint Meeting of the Chemical Society and the Royal Institute of Chemistry, Edinburgh, 1970. Kaplan, L., private communication.

(7) Prepared by the addition of Me₃SnH to allyl methyl ether; 2 and 5 are prepared by addition of Me₃SnH to the 1-alkenois. The physical and spectral properties of these compounds are consistent with previously reported values.

(8) Newman, W. P.; Schroeder, B.; Ziebarth, M. Liebigs Ann. Chem. 1975, 2279.

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

$\frac{\text{H abstractor version}^b \text{ MPE}^c \text{ CPME}^d \text{ THF}^e}{\text{Ph}_2 \text{CO}/h\nu^f} 48 1.0 1.1 1.0$		% con-	rel pi	oduct distr	ibution	
	H abstractor		MPE ^c	CPME ^d	THF ^e	
	 $Ph_{2}CO/hv^{f}$	48	1.0	1.1	1.0	
$11300/n\nu$ 33 1.0 $0.33 > 0.08$	$Ph, CO/h\nu$	33	1.0	0.33	>0.08	
PhCOMe/ $h\nu$ 49 1.0 0.21 0.30		49	1.0	0.21	0.30	
	$(t-BuO), /h\nu$	43 ^g	1.0	0.88		
$(t-\text{BuO})_2/h\nu$ 43 ^g 1.0 0.88 0.65 FeCl ₃ /h ν ^h 37 1.0 0.5 >0.05	$FeCl_3/h\nu^h$	37				

^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 [Ph₂CO] = 0.67 M, [1] = 0.22 M. Me₆Sn₂ and benzopinacol isolated and identified by NMR spectroscopy and mixed melting point, respectively. Yields >85% in both cases, corrected for conversion. f 48 h. h Reference 21.

 $(t-BuO)_2/h\nu$; FeCl₃/h ν ; PhCOMe/h ν) 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

$$1 + Ph_2CO^*(T) \longrightarrow Me_3SnCH_2CH_2\dot{O}CH_2 + Ph_2\dot{O}CH (4)$$

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

$$1 + Ph_2CO(T)^* \longrightarrow \dot{C}H_2CH_2CH_2OCH_3 + Ph_2\dot{C}OSnMe_3 \qquad (6)$$

$$1c$$

$$1b \longrightarrow OCH_3 + Me_3Sn \cdot (7)$$

$$1a \longrightarrow \sqrt{0} + Me_3 Sn \cdot$$
(8)

1c + solvH (or 1) \rightarrow CH₃CH₂CH₂OCH₃ + solv (or 1a,1b) (9)

Me3SnOCPh2 == Me3Sn. + Ph2CO (ref 8) (10)

$$2 \operatorname{Me}_{3} \operatorname{Sn}_{2} \qquad (\operatorname{Me}_{3} \operatorname{Sn})_{2} \qquad (11)$$

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

Ingold, K. U.; Roberts., B. P. "Free Radical Substitution Reactions";
 Wiley-Interscience: New York, 1971; pp 72-109.
 (2) (a) Kaplan, L. J. Am. Chem. Soc. 1967, 89, 1953. (b) Drury, R. F.;

⁽⁹⁾ Stark, T. J.; Nelson, N. T.; Jensen, F. R. J. Org. Chem. 1980, 45, 420.
(10) (a) Davies, A. G.; Scaiano, J. C. J. Organomet. Chem. 1972, 39, C55.
(b) Krusic, P. J.; Kochi, J. K. J. Am. Chem. Soc. 1969, 91, 5151. (c) Davies, A. G. In "Organotin Compounds: New Chemistry and Applications"; Zuckerman, J. S., Ed.; American Chemical Society: Washington, DC, 1976; Adv. Chem. Soc. New Stephenet Chemical Society: Mashington, DC, 1976; Adv. Chem. Ser. No. 157, pp 26-40 and references therein.

from tert-butyl methyl ether,¹¹ and thermochemical data on stabilities of α -silvl radicals¹² 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 reaction¹⁰ 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/decarbonylation¹⁴ sequence shown by trimethyl(4hydroxybutyl)tin (2). Chromatographic analysis of a reaction

$$Me_{3}Sn(CH_{2})_{4}OH + Ph_{2}CO^{*}(T) \xrightarrow{benzene} Me_{3}Sn(CH_{2})_{3}CH$$
(13)

$$3 + Ph_2CO^*(T) \longrightarrow Me_3Sn(CH_2)_3^* + CO + Ph_2CO^*(T)$$
 (14)
4

$$4 - - - + Me_3Sn \cdot (15)$$

$$2Me_3Sn \cdot - - - (Me_3Sn)_2$$
 (11)

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(3hydroxypropyl)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 Me₃Sn from the (β -trimethyltin) ethyl radical¹⁵ formed by decarbonylation of **6**. Since the ω -trimethyltin-substituted aldehydes¹⁶ 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, Me₃SnCH₂CH₂CHOH, 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 Me₃SnCH₂CH₂ĊHOH to yield cyclopropanol and eventually propanal are much faster the 1,4-ring closure of Me₃SnCH₂CH₂CH₂ĊHOH.

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 stan-

(18) Krusic, P. J.; Kochi, J. K. J. Am. Chem. Soc. 1969, 91, 3942, 3944.

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

$$5a + Ph_2CO \longrightarrow 6 + Ph_2COH$$
 (17)

$$\rightarrow$$
 OH + Ph₂CO^{*}(T) - CH₃CH₂CH₂CH (19)

$$6 + Ph_2CO^*(T) \longrightarrow Me_3SnCH_2CH_2C \cdot - 6a$$

6b

2

$$Me_3SnCH_2CH_2 + CO$$
 (20)

O)

$$----- Me_3Sn \cdot + CH_2 = CH_2$$
(21)

$$Me_3Sn \cdot - (Me_3Sn)_2 \tag{11}$$

$$2PhCOH \longrightarrow (Ph_2COH)_2$$
(12)

nacyclobutanes,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.

(21) Possible ionic contributions for the Fe(III)-promoted reactions are detailed in: Walling, C.; Humphreys, R. W. R. J. Org. Chem. 1981, 46, 1260.

¹⁷O ENDOR of Horseradish Peroxidase Compound I

James E. Roberts and Brian M. Hoffman*

Department of Chemistry, Northwestern University Evanston, Illinois 60201

Rick Rutter and Lowell P. Hager

Department of Biochemistry, University of Illinois Urbana, Illinois 61801 Received July 27, 1981

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 ¹⁷O 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

^{(11) (}a) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. J. Am. Chem. Soc. 1978, 100, 4520.
(b) Wong, S. K. Ibid. 1979, 101, 1235.
(12) Doncaster, A. M.; Walsh, R. J. Chem. Soc., Faraday Trans. 1 1976,

^{72, 2908}

⁽¹³⁾ The S_H2 displacement at Me₃SnR by ketone triplets provides additional detail to the "energy transfer" mechanism proposed for the direct photocleavage of Me₃Sn(CH₂)_nCOCH₃ reported in: Kuivila, H. G.; Maxfield, P. L.; Tsai, K.-H.; Dixon, J. E. J. Am. Chem. Soc. 1976, 98, 104. Kuivila, H. G.; Tsai, K.-H.; Maxfield, P. L. Ibid. 1970, 92, 6696.
(14) Berman, J. D.; Stanley, J. H.; Sherman, W. V.; Cohen, S. G. J. Am. Chem. Soc. 1963, 85, 4010.

Chem. Soc. 1963, 85, 4010.

⁽¹⁵⁾ Nugent, W. A.; Kochi, J. K. J. Organomet. Chem. 1977, 124, 371.

 ⁽¹⁶⁾ Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka,
 T. M.; Tsai, K.-H.; Warsthorn, K. R. J. Organomet. Chem. 1975, 86, 89.

⁽¹⁷⁾ DePuy, C. H.; Jones, H. L.; Moore, W. M. J. Am. Chem. Soc. 1973, 05 477

⁽¹⁹⁾ Damrauer, R. Organomet. Chem. Rev., Sect. A 1972, 8, 67. Yoder, C. H.; Zuckerman, J. J. Prep. Inorg. React. 1971, 6, 81. Pant, B. C. J. Organomet. Chem. 1974, 66, 321.

⁽²⁰⁾ Davies, A. G.; Parry, G. R.; Roberts, B. P.; Tse, M.-W. J. Organomet. Chem. 1976, 110, C33.

⁽¹⁾ Hewson, W. D.; Hager, L. P. In "The Porphyrins"; Dolphin, D., Ed; Academic Press: New York, 1979; Vol. 7, pp 295-332. (2) (a) Schonbaum, G. R.; Chance, B. Enzymes, 3rd Ed. 1976, 13,

^{363-408. (}b) Dunford, H. B.; Stillman, J. S. Coord. Chem. Rev. 1976, 19, 187-251.

^{(3) (}a) Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. Proc. Natl. Acad. Sci. U.S.A. 1971, 68, 614-618. (b) Dolphin, D.; Felton, R. H. Acc. Chem. Res. 1974, 7, 26-32.

⁽⁴⁾ Abbreviations: ENDOR, electron nuclear double resonance; HRPI, compound I of horseradish peroxidase; EPR, electron paramagnetic resonance. (5) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. J. Biol. Chem. 1981, 256, 2118-2121.