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Electrophilic Cleavage of Cyclopropylmethystannanes: An Experimental Comparison of $\sigma-\sigma$ and $\sigma-\pi$ Conjugation†

Andrew J. Lucke and David J. Young*
School of Science, Griffith University, Nathan 4111, Brisbane, Australia
d.young@griffith.edu.au

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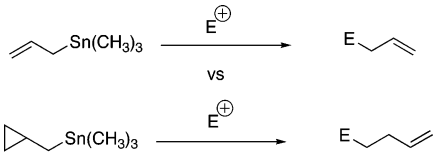
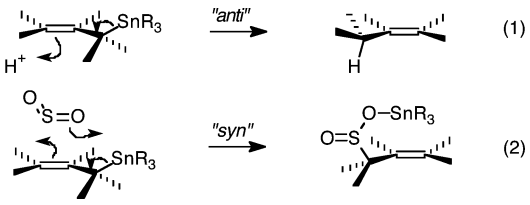


Cyclopropylmethyltrimethylstannanes undergo electrophilic cyclopropane cleavage in chloroform with simple inorganic electrophiles (H^+, SO_2, I_2) in a homologous reaction to the S_E' cleavage of allylic stannanes. The $\sigma-\sigma$ conjugation between the carbon−tin bond and cyclopropane orbitals observed spectroscopically in the parent cyclopropylmethyltrimethylstannane is responsible for a rate enhancement of ca. 10^2 toward iodinolysis, relative to comparable alkyl stannanes. This acceleration is considerably less, however, than the ca. 10^9-fold rate enhancement provided by the corresponding $\sigma-\pi$ conjugation in allylic stannanes. Methanol−tin coordination appears to reduce the activating influence of the metal, promoting methyl cleavage over cyclopropane fission with acid and iodine. Decreased $\sigma-\sigma$ conjugation can also explain the decreased reactivity of cyclopropyltriphenylstannane compared with its trimethyltin counterpart. Cyclopropylmethylstannanes do not undergo the synthetically useful addition of aldehydes under conditions that facilitate the corresponding reaction of allylic stannanes.

Introduction

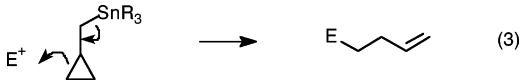
Allylic stannanes are highly reactive toward electrophilic substitution reactions as a result of delocalization of the electron-rich carbon−tin σ bond into the adjacent π system. Substitution occurs at the γ position of the allylic triad with concomitant allylic rearrangement (an S_E' process). The stereochemistry of addition is dependent on the electrophile and the steric environment at the γ carbon. Acidolysis of unhindered allylic stannanes occurs with anti approach of the proton as predicted for a dominating LUMO-HOMO interaction in a concerted S_E2' process (eq 1). The corresponding reaction of electrophiles bearing a nucleophilic appendage (e.g. SO_2), however, proceeds with syn attack as required by an S_Ei' (metalloene) mechanism (eq 2).



† Dedicated to Professors C. J. M. Stirling and W. Kitching.

Most attention has focused on the reaction of allylic stannanes with carbon electrophiles, particularly aldehydes, which provides products with useful functionality for further elaboration. The regio- and stereocourse of these reactions depends very much on the method of promotion, the reaction conditions, and the order of reagent addition. A number of experimental protocols have now been developed which allow a high degree of control over relative and/or absolute stereochemistry and these methodologies have been applied to the synthesis of complex molecules bearing multiple stereogenic centers.

The electrophilic ring fission of cyclopropylmethylstannanes (eq 3) is a logical extension to the corresponding



chemistry of allylic stannanes and would provide access to the homologous products. The reactivity of cyclopropanes toward electrophiles is well-known and should be enhanced by orbital overlap with an adjacent electron-rich carbon−tin bond. Traylor and co-workers, who obtained UV photoelectron spectra of cyclopropylmethyltrimethylstannane and allyltrimethylstannane, provided evidence for strong $\sigma-\sigma$ conjugation of this type.

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SCHEME 1

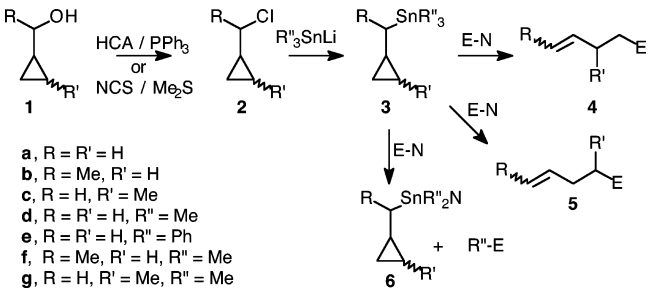

TABLE 1. Electrophilic Cleavage of Cylopropylmethylstannanes, 3

				yield, %		
entry	stannane	E−N	solvent	**4**[a]	**5**	**6**
1	**3d**	SO_2	$CDCl_3$	100		0
2	**3d**	SO_2	CD_3OD	100		0
3	**3e**	SO_2	$CDCl_3$	0		0
4	**3f**	SO_2	$CDCl_3$	100[b]		0
5	**3f**	SO_2	CD_3OD	100[c]		0
6	**3g**	SO_2	$CDCl_3$	80	20	0
7	**3g**	SO_2	CD_3OD	77	23	0
8	**3d**	CF_3COOH	$CDCl_3$	100		0
9	**3d**	CF_3COOH	CD_3OD	0		100
10	**3f**	CF_3COOH	$CDCl_3$	100[d]		0
11	**3f**	CF_3COOH	CD_3OD	0		100
12	**3g**	CF_3COOH	$CDCl_3$	90	10	0
13	**3g**	CF_3COOH	CD_3OD	0	0	100
14	**3d**	I_2	$CDCl_3$	100		0
15	**3d**	I_2	C_6D_5N	0		100
16	**3d**	I_2	CD_3COCD_3	0		100
17	**3d**	I_2	CD_3OD	0		100
18	**3e**	I_2	$CDCl_3$	0		100
19	**3e**	I_2	CD_3OD	0		100
20	**3f**	I_2	$CDCl_3$	100[e]		0
21	**3f**	I_2	CD_3OD	0		100
22	**3g**	I_2	$CDCl_3$	90	10	0
23	**3g**	I_2	CD_3OD	0	0	100

[a] Percent conversion determined by ^1H and ^{13}C NMR spectroscopy. [b] *Z*:*E* = 38:62. [c] *Z*:*E* = 36:65. [d] *Z*:*E* = 73:27. [e] *Z*:*E* = 22:78.

The energy of interaction between the bent cyclopropane orbitals and the polarized C−Sn σ bond of the former was 1.6 eV, which can be compared with 2.2 eV for the corresponding $\sigma-\pi$ interaction in the latter. These researchers predicted that this substantial $\sigma-\sigma$ conjugation might result in some new stereospecific ring-opening reactions. We have previously communicated that cyclopropylmethylstannanes do indeed react with various electrophiles to provide the corresponding ring fission products. We now report on mechanistic and synthetic aspects of these reactions and quantify the reactivity difference between cyclopropylmethylstannanes and allylic stannanes toward electrophilic cleavage.

Results and Discussion

Access to the cyclopropylmethylstannanes **3** was possible from the commercially available alcohols **1** (Scheme 1). Cyclopropylmethanols **1a** and **1c** (*Z*:*E* = 15:85) were chlorinated with hexachloroacetone (HCA) and triphenylphosphine without any detectable ring fission. This procedure is also reported to be appropriate for chlorinating the more hindered secondary alcohol **1b**, but requires a large excess of reagents, which can make isolation difficult. To avoid this problem, we investigated an alternative protocol, which used *N*-chlorosuccinimide (NCS) and dimethyl sulfide. This procedure is reported to be selective for allylic and benzylic alcohols, leaving saturated alcohols untouched. Presumably because of the activating influence of the cyclopropane, however, these reagents also proved effective for chlorinating **1b**, albeit over a much longer period of time (96 h) than is required for allylic or benzylic alcohols and with some ring opening (ca. 10%). The ring-opened product, 1-chloro-3-pentene, was removed by careful titration with bromine followed by flash distillation. Conversion to the corresponding cyclopropylmethylstannanes **3** was achieved by treatment with the appropriate triorganotin lithium species in THF. Although chloride **2c** was a 9:1 mixture of *E* and *Z* isomers (reflecting the isomeric composition of the starting alcohols), only the *E* isomer of stannane **3g** was isolated on treatment with Me_3SnLi followed by kügelrohr distillation.

The electrophilic cleavage of **3** was first examined with the inorganic electrophiles sulfur dioxide, trifluoroacetic acid, and iodine in different solvents. Sulfinations were performed by bubbling SO_2 through a solution of **3** in either $CDCl_3$ or CD_3OD at room temperature and then monitoring reaction progress by ^1H and ^{13}C NMR spectroscopy. Only triphenylstannane **3e** was unreactive under these conditions (entry 3). Cyclopropylmethyltrimethylstannanes **3d**, **3f**, and **3g** reacted exclusively with ring fission (entries 1, 2, and 4−7) and reactions were complete within 15 min. The products were identified as trimethyltin *O*-sulfinates **4**, **5** [E = S(O)OSnMe3] rather than the alternative *S*-sulfinates based on the S−O stretching frequency (910−990 cm^{-1}) in the infrared spectrum, the characteristic downfield chemical shift of the CHR′S(O)OSnMe$_3$ ^1H NMR signal (δ 2.1 to 2.5) and ^{13}C NMR signal (δ 59.5 to 67.5) and the large ^1J(^{119}Sn to $^{13}CH_3$) = 484−519 Hz.[2] Isolated yields were ≥93% after evaporation of solvent and triturating with pentane. The α-methyl-substituted substrate **3f** yielded a predominance of *E*-trimethyltin 3-penten-1-sulfinate, **4b**, in both solvents (*E*/*Z* = ca. 1.7, entries 4 and 5). This product ratio did not change throughout the course of these reactions suggesting kinetic control, rather than post-insertion isomerization to the thermodynamically favored *E* isomer. In support of this proposition, sulfur dioxide did not isomerize 3-penten-1-ol (*Z*/*E* = 9.0) over several hours under the same conditions. Sulfur dioxide cleavage of the 2-methyl substrate **3g** also gave very similar results in $CDCl_3$ and CD_3OD, yielding a ca. 4:1 mixture of tin sulfinates **4c** and **5c** (entries 6 and 7), resulting from attack at the less substituted cyclopropane carbon.

Acidolysis of cyclopropyltrimethylstannanes **3d**, **3f**, and **3g** with trifluoroacetic acid in $CDCl_3$ was complete within 5 min at room temperature and proceeded exclusively with ring fission to provide alkenes **4** and **5** (E = H, entries 8, 10, and 12). In contrast to the corresponding sulfinations, however, acidolysis in CD_3OD proceeded exclusively with methyl cleavage to provide cyclopropylmethyldimethyltin trifluoroacetates **6** (entries 9, 11, and 13) and methane. Also in contrast to the corresponding sulfination, acidolysis of **3f** in $CDCl_3$ (entry 10) resulted

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in predominant formation of the *Z* rather than *E* ring fission product **4b** *(E/Z* = 0.37). The regiochemistry of acidolysis of **3g** in $CDCl_3$ (entry 12) favored attack at the less substituted ring carbon (**4c/5c** = 9.0) to a slightly greater extent than was observed for sulfination.

The halogenolysis of carbon−tin bonds has been extensively investigated as an archetypal electrophilic substitution. Iodinolysis of organostannanes can proceed via an electrophilic or radical-chain mechanism with the latter becoming competitive for slow reactions in nonpolar solvents on irradiation with visible light. The iodinolyses of cyclopropylmethylstannanes **3** were performed in the dark and in solvents for which electrophilic substitution has been reported to be the exclusive reaction pathway. The regiochemistry of cleavage was as observed for acidolysis, i.e., ring fission to yield iodides **4** and **5** (E = I) in $CDCl_3$ (entries 14, 20, and 22) and with substitution at the less substituted carbon (**4c/5c** = 9.0), but exclusive methyl cleavage in coordinating solvents (entries 15−17, 21, and 23) to provide cyclopropylmethyldimethyltin iodides **6** and iodomethane. Iodinolysis of triphenylstannane **3e** in either $CDCl_3$ or CD_3OD (entries 18 and 19) proceeded exclusively with phenyl cleavage to yield **6c** and iodobenzene. While the regiochemistry of iodinolysis was similar to that of acidolysis, the stereochemistry of reaction of **3f** in $CDCl_3$ (entry 20) resembled that of sulfination, providing a 3.5:1 ratio of the isomeric iodides **4b** in favor of the *E* isomer. Again, this ratio was constant throughout the reaction, suggesting a kinetically determined product ratio. Treatment of predominantly *Z*-**4b** (*Z/E* = 9.0, prepared by treatment of **1b** with MgI_2) with excess iodine in chloroform under the same conditions did not result in any observable isomerization over 4 days.

A second-order rate constant was measured for the iodinolysis of **3d** at 25.0 ± 0.3 °C in dichloromethane by monitoring the disappearance of iodine at 502 nm. Reactions were relatively rapid and required the use of a stop-flow apparatus. The concentration of iodine after mixing was 1.395×10^{-3} M while the concentration of stannane was between 9.274×10^{-3} and 2.899×10^{-2} M (i.e., 6.6 to 20.8 equiv). At least five pseudo-first-order rate constants were measured at each of five concentrations over this range. The rate equation for the disappearance of iodine is satisfactorily described by $-d[I_2]/dt = k[CPMSn(Me)_3][I_2]$ and the plot of observed rate constant versus stannane concentration was linear within experimental error (Figure 1) and yielded the second-order rate constant, $k = 4.6 \pm 0.8 \times 10^{-1}$ M^{-1} s^{-1}.

An attempt was made to measure the rate constant for the corresponding iodinolysis of allyltrimethylstannane. The reaction was too rapid, however, being complete in less than 0.01 s at millimolar concentrations of stannane and iodine (1:1) in dichloromethane. Thus, the second-order rate constant is > ca. 10^8 M^{-1} s^{-1} (approaching diffusion control), which is consistent with the value of ca. 3×10^7 M^{-1} s^{-1} determined for the corresponding reaction of tetraallyltin with iodine in acetone.[9a] A comparison of rate constants for the iodinolysis of **3d** relative to a number of other tetraorganostannanes is presented in Table 2.

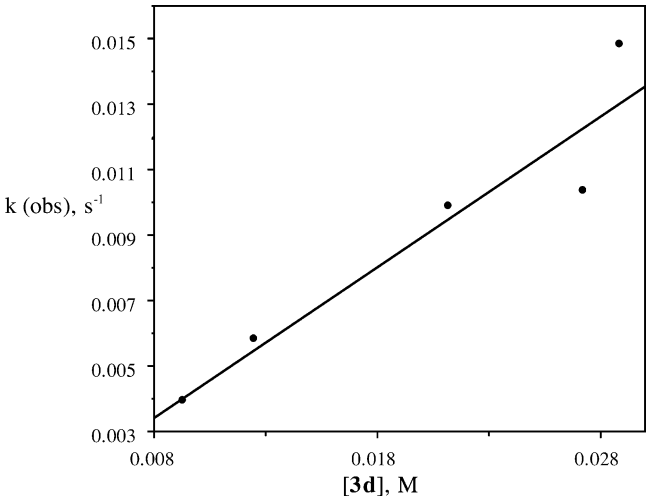

FIGURE 1. Pseudo-first-order rate constants as a function of stannane concentration for the iodinolysis of **3d** in dichloromethane (25 °C).

TABLE 2. Relative Second-Order Rate Constants for the Iodinolysis of Various Organostannanes at 25.0 °C

entry	stannane	k_{rel}[a]	ref
1	Me_4Sn	1	9b
2	*i*-Pr_4Sn	0.38	9b
3	3d	79	*b*
4	$allylSnPh_3$	3.5×10^7 [c]	9a
5	$(allyl)_4Sn$	ca. 5×10^9 [c]	9a
6	$allylSnMe_3$	$>10^{10}$	*b*

[a] In dichloromethane, unless otherwise stated. [b] This work. [c] In acetone.

We next turned our attention to the potentially more useful cleavage reactions involving aldehydes (Scheme 2). The corresponding reactions of allylic stannanes generally require heat, high pressure, or Lewis acid

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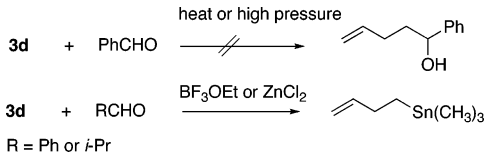
SCHEME 2



promotion.[3] We investigated the application of a number of these experimental protocols to the reactions of **3d** with benzaldehyde or isobutyraldehyde. Neither heat (145 °C, 24 h) nor high pressure (15 kbar, 80 °C, 6 d) promoted the addition of benzaldehyde to **3d**. No reaction was observed with 1.0 equiv of $BF_3{\cdot}OEt_2$ and benzaldehyde (CH_2Cl_2, −78 to 0 °C), but isomerization to 3-butenyltrimethylstannane was observed with 2.0 equiv of Lewis acid or with 1.0 equiv of $BF_3{\cdot}OEt_2$ in the absence of aldehyde. Isomerization was also observed for the attempted $ZnCl_2$ promoted addition of isobutyraldehyde to **3d** (CH_2Cl_2, 25 °C, 7 d) and the combination of benzaldehyde, $MgBr_2{\cdot}OEt_2$ (1 equiv), and pressure (CH_2Cl_2, 17 kbar, 30 °C, 2 d). A variety of other Lewis acids were also examined, but none promoted homoallylation of the aldehyde.

The above results confirm the prediction of Traylor and co-workers that $\sigma-\sigma$ conjugation would result in enhanced reactivity of cyclopropylmethyltrimethylstannanes toward electrophilic ring cleavage.[4] Sulfur dioxide is a relatively mild electrophile, yet quantitatively reacts with **3d**, **3f**, and **3g** in under 15 min at room temperature. By comparison, insertion into inactivated tin−alkyl bonds can take up to several days in liquid SO_2 while allylic stannanes react with dissolved SO_2 in a matter of seconds. This latter reaction (eq 1) proceeds with syn stereoselectivity in chloroform, consistent with a six-member cyclic transition state. In methanol, however, this stereoselectivity is lost, suggesting disruption of internal O−Sn coordination. It was somewhat of a surprise, therefore, when the reaction of sulfur dioxide with α-methylcyclopropylmethylstannane **3f** yielded the same ratio of alkenyl sulfinates **4b**, favoring the *E* isomer, in both a coordinating and noncoordinating solvent. A predominance of the *E* isomer was also observed for iodinolysis of this substrate in chloroform, while acidolysis under the same conditions yielded a predominance of the *Z* cleavage product. It is tempting to suggest that this dependence of stereoselectivity on electrophile reflects the outcome of a cyclic versus an acyclic mechanism of addition. It seems reasonable that sulfination or iodination in chloroform should involve internal O−Sn or I−Sn coordination, respectively, while the stereochemistry of acidolysis might be controlled by steric and/or stereoelectronic factors in an acylic transition state as is observed for the corresponding reaction of allylic stannanes.[2] This explanation requires, however, that sulfination in methanol also occurs via a cyclic addition mechanism. If this is the case, then it could also account for the quite different regiochemical outcomes observed for reactions of the different electrophiles in methanol. While acidolysis and iodinolysis in this solvent proceeded with exclusive methyl cleavage, sulfination in the same solvent proceeded with ring fission. We suggest that methanol−tin coordination reduces $\sigma-\sigma$ conjugation in cyclopropylmethyltrimethylstannanes promoting the statistically and sterically favored methyl cleavage with acid and iodine, but that the preferred reaction pathway for sulfination is via a six-member cyclic transition state even in this coordinating solvent.

A decreased activating influence of the carbon−tin bond on cyclopropane fission was also noted on changing from methyl to phenyl substituents on tin. Sulfur dioxide did not react with triphenyltin derivative **3e** under the relatively mild conditions employed while iodinolysis in chloroform resulted in exclusive phenyl cleavage in preference to ring fission. The lower electron donating ability of triphenyltin relative to a trialkyltin moiety has been reported to result in a 10^2-fold decrease in reactivity for the electrophilic cleavage of allylic stannanes with acid or diarylcarbenium ions.

Iodinolysis in dichloromethane proved to be a convenient reaction for quantifying the effect of $\sigma-\sigma$ conjugation on reactivity. A comparison of the second-order rate constants for iodinolysis of **3d** and tetramethyltin (Table 2) reveals a 79-fold difference in reactivity which, while significant, is well short of the $>10^9$ rate enhancement provided by $\sigma-\pi$ conjugation in the corresponding reaction of allylic trialkylstannanes. It was perhaps not surprising, therefore, that the reaction of **3d** with aldehydes under various conditions did not mimic the corresponding allylic tin chemistry. Heat or pressure in excess of that required to promote addition of aldehydes to allylic stannanes was insufficient to mediate reaction of **3d**. Likewise, a range of quite different Lewis acids that catalyze the former reaction did not catalyze the latter, which were complicated by isomerization and/or transmetalation. While these processes also occur in the Lewis acid mediated addition of aldehydes to allylic stannanes, the isomerized or transmetalated allylic metal intermediates are still reactive and add to the aldehyde.

Finally, the electrophilic cleavage of cyclopropylmethylsilanes with a variety of electrophiles has been reported and, while no rate data are available, a qualitative comparison of reaction conditions and yields indicates that the corresponding stannanes are (not surprisingly) substantially more reactive. Ring fission for both *(E)*-2-methylstannane **3g** and various ring-substituted silanes occurs predominantly at the less congested unsubstituted carbon for all electrophiles examined.

Experimental Section

1-Chloro-1-cyclopropylmethane (2a). To a flask containing 67 g (253 mmol) of hexachloroacetone at 0 °C was added 12.4 g (47 mmol) of triphenylphosphine and the suspension was stirred for 5 min. To this solution was added 3.02 g (42 mmol) of 1-cyclopropylmethanol (**1a**) over 15 min, maintaining the temperature between 0 and 10 °C. The mixture was warmed to ambient temperature and stirred for 3 h before flash distillation (0.1 Torr) to collect all volatile products. Fractionally distillation provided 3.9 g (95%) of **2a**: bp 87 °C (lit.[6] bp 86−88 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.40 (d, 2H, $J = 7.4$ Hz), 1.97 (m, 1H), 0.65−0.31 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.8 MHz) δ 50.5, 13.7, 5.6.

Chloro(2-methylcyclopropyl)methane (2c). 2c was prepared in a manner similar to that described above and was identified by ^{1}H and ^{13}C NMR; see the Supporting Information for details.

1-Chloro-1-cyclopropylethane (2b). To an ice-cold solution of 2.55 g (19 mmol) of *N*-chlorosuccinimide in 80 mL of anhydrous CH_2Cl_2 was added 1.3 g (21 mmol) of dimethyl sulfide dropwise. 1-Cyclopropylethanol (1.5 g, 17 mmol) was

then slowly added, maintaining the temperature between 5 and 10 °C for 1 h. The reaction mixture was then warmed to ambient temperature, stirred for 62 h, and quenched with water. The aqueous layer was extracted with ether and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. ^{1}H NMR spectroscopy of the crude product indicated ca. 5% ring-opened material, which was carefully titrated with bromine. Subsequent fractional distillation provided 1.1 g (61%) of **2b**: bp 101 °C (lit.[6] bp 100−102 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.38 (m, 1H), 1.57 (d, 3H, J = 6.4 Hz), 1.14 (m, 1H), 0.62−0.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.8 MHz) δ 63.9, 24.9, 20.4, 5.6, 5.2.

General Stannylation Procedure of 1-Chlorocyclopropylmethyl Derivatives 2. To a solution of trimethyltin chloride (39.7 mmol) in THF (40 mL) was added freshly cut lithium pieces (397 mmol). Formation of a deep green color indicated the presence of the trimethyltin lithium. Excess lithium was removed by filtration and the solution was cooled in ice before drop-wise addition of **2** (33.1 mmol). The mixture was warmed to ambient temperature, stirred for 3 h, and then quenched with KF (10%, 15 mL). The aqueous layer was extracted with Et_2O and the combined organic extracts were washed with saturated NH_4Cl, dried ($MgSO_4$), and concentrated. Short-path distillation provided products **3**, which were identified by ^{1}H and ^{13}C NMR; see the Supporting Information for details.

General Procedure for the Reaction of Sulfur Dioxide and (Cyclopropylmethyl)stannane Derivatives, 3. Sulfur dioxide was slowly bubbled through a solution of **3** (1.0 mmol) in $CHCl_3$ (0.5 mL) for 15 min. The solvent was evaporated and the product triturated with pentane and dried under high vacuum to provide products that were identified by ^{1}H and ^{13}C NMR and microanalysis; see the Supporting Information for details.

General Procedure for the Trifluoroacetolysis of (Cyclopropylmethyl)stannane Derivatives, 3. To an NMR tube containing 0.50 mmol of **3** in 0.5 mL of solvent ($CDCl_3$ or CD_3OD) was added 0.060 g (0.52 mmol) of TFA. The NMR tube was stoppered, shaken, and monitored by ^{1}H NMR spectroscopy until the reaction was complete (ca. 30 min). Products were identified by ^{1}H and ^{13}C NMR; see the Supporting Information for details.

General Procedure for the Iodinolysis of (Cyclopropylmethyl)stannane Derivatives, 3. A solution of 0.5 mmol of the (cyclopropylmethyl)stannane in 0.2 mL of solvent was added to a clean dry 5 mm NMR tube wrapped in aluminum foil to exclude light. To the mixture was added 0.3 mL of iodine solution (1.6 M) in the deuterated solvent. The NMR tube was stoppered, shaken, and monitored by ^{1}H NMR spectroscopy until the reaction was complete. Products were identified by ^{1}H and ^{13}C NMR and GCMS (if required); see the Supporting Information for details.

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Supporting Information Available: Full experimental and characterization data for all compounds and ^{13}C NMR spectra of a mixture of (*Z*) and (*E*) trimethylstannane 3-pentenylsulfinate and a mixture of trimethylstannane 2-methyl-3-butenylsulfinate and trimethylstannane 1-methyl-3-butenylsulfinate. This material is available free of charge via the Internet at http://pubs.acs.org.

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