

ALKYL- AND ACYL-SUBSTITUTED VINYLSTANNANES: SYNTHESIS AND REACTIVITY IN ELECTROPHILIC SUBSTITUTION REACTIONS

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ABSTRACT

Six substituted vinylstannanes have been prepared. (E)- and (Z)-2-trimethylstannyl-2-butene, (**1**) and (**2**), respectively, 2-methyl-1-(trimethylstannyl) propene, (**3**), and 3-methyl-2-trimethylstannyl-2-butene, (**4**), were prepared by coupling the appropriate lithium or Grignard reagent with chlorotrimethylstannane. 3-Trimethylstannyl-3-butene-2-one, (**5**), and (Z)-3-trimethylstannyl-3-hexene-2-one, (**6**), were prepared by palladium(O) catalyzed hydrostannation of the appropriate ynone. This reaction was regiospecific such that the trimethylstannyl and carbonyl groups were bonded at the same vinyl carbon. The reaction was also stereospecific giving *syn* addition in each case. However, isomerization to a

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mixture of isomers was observed for the reaction of (5) with Me_3SnD and complete isomerization of E-(6) to Z-(6). Each compound was characterized by ^1H , ^{13}C , and ^{119}Sn NMR. The reactivity to protodestannylation was determined for each compound by spectrophotometric measurement of second order rate constants. The reactivity of the multimethyl-substituted vinylstannanes was consistent with the reactivity determined previously for monomethyl-substituted vinylstannanes. However, two methyl groups at the remote vinyl carbon exhibited a synergistic activating effect on the protodestannylation reactivity. The acyl group was found to be deactivating for protodestannylation. The stereochemistry of the reaction was found to take place with retention of configuration.

INTRODUCTION

Vinylstannanes have, in recent years, become an increasingly useful component in the synthetic repertoire of the organic chemist. Of central importance has been palladium catalyzed coupling reactions^[1-8] and the newer copper(I) mediated coupling resulting in diene systems.^[9-12] Also, vinylstannanes have been used as intermediates in the production of natural products such as aggregation pheromones,^[13] terpenoids,^[14] antibiotics,^[15,16] and naturally occurring furanones^[17] as well as biologically active compounds such as *anti*-sense oligonucleotides^[18] and radioiodine labeled steroids.^[19] Vinylstannanes have been shown to react with singlet oxygen in photooxygenation reactions^[20] and are precursors of alkyl(phenyl)iodonium salts.²¹ Finally, vinylstannanes undergo electrophilic destannylation with sulfonyl chloride to give vinylsulfonamides.^[22]

This last reaction, electrophilic destannylation has been of interest to us for some time. Vinylstannanes exhibit a broad range of reactivities with electrophiles depending upon the electronic effects of the other three substituents on the carbon-carbon double bond. In 1968, Gielen and co-workers^[23] reported that vinylstannanes, substituted with alkyl groups, undergo iododestannylation with a range of reactivities greater than 10^4 , as a function of the location of the alkyl group relative to tin. Since then we have extensively studied protodestannylation of vinylstannanes as the model for electrophilic substitution in vinyl systems. We find that substituents on the double bond exert a profound effect on the rate of protodestannylation. We have reported a similar range of reactivities, approximately 10^4 , between

the most reactive vinylstannanes, (E)-(trimethylstannyl)propene^[24] and 1,1-diphenyl-2-(trimethylstannyl)ethene^[25] and the least reactive, methyl (Z)-3-(trimethylstannyl)crotonate.^[26] In general, phenyl substituents and alkyl substituents are strongly activating when located on the vinyl carbon remote to tin and weakly deactivating when located on the vinyl carbon proximate to tin. Carbomethoxy substituents act with the opposite effect, strongly deactivating when remote and weakly deactivating when proximate. At the remote carbon, the effect is greater when the substituent is *trans* to tin compared to *cis*. Also, the combined result of two substituents of opposite effect is generally additive. Finally, the stereochemistry of the protodestannylation reaction is generally retention of configuration at the carbon-carbon double bond. However, mixtures of isomers have been observed when an ester carbonyl is located on the vinyl carbon proximate to tin. In these cases the reaction can take an alternate course, probably through an allenol intermediate, which then transfers a proton to either face of the vinyl system.^[27]

In this paper we extend our study of the reactivity of vinylstannanes with the inclusion of multimethyl-substituted vinylstannanes and acyl-substituted vinylstannanes. We report the synthesis, characterization and kinetic results of four vinylstannanes substituted with more than one methyl group on the double bond and two acyl substituted vinylstannanes. Where pertinent, the stereochemistry of the protodestannylation reaction was confirmed.

RESULTS AND DISCUSSION

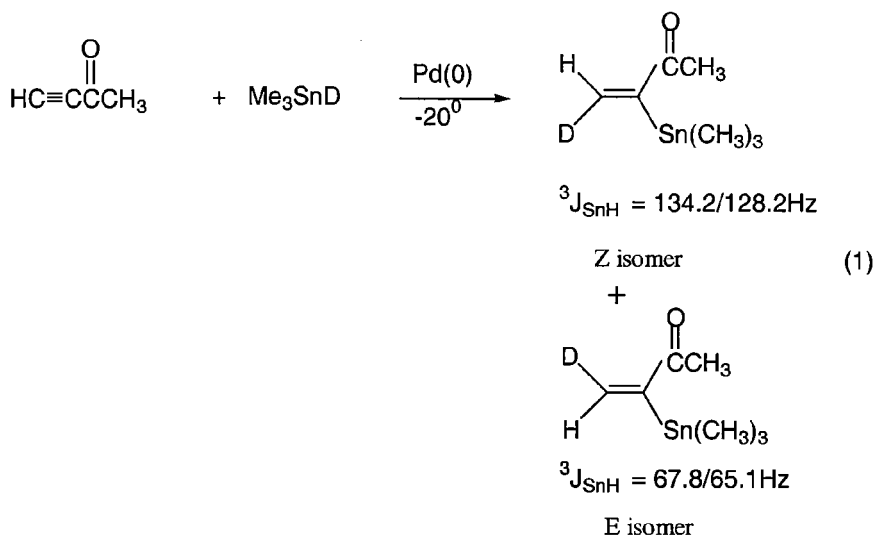
Synthesis

While hydrostannylation of 2-butyne is the most direct method for the syntheses of (E)-2-(trimethylstannyl)-2-butene (**1**) and (Z)-2-(trimethylstannyl)-2-butene (**2**), the palladium(0) catalyzed process^[28-30] with trimethylstannane gave only hexamethyldistannane, indicating that the alkyne is very unreactive. Free radical catalysis, with AIBN,^[31,32] led to a mixture of E and Z isomers that could not be separated by either gas or column chromatography. Thus, we took the longer route of *anti* addition of bromine to (E)- and (Z)-2-butene followed by *anti* elimination of hydrogen bromide to give, in each case, (E)- and (Z)-2-bromo-2-butene. Conversion of the bromides to the lithium compound (E isomer) or the Grignard reagent (Z isomer) and then coupling with chlorotrimethylstannane resulted in isomerically pure (**1**) and (**2**). 2-Methyl-1-(trimethylstannyl) propene (**3**) and 3-methyl-2-(trimethylstannyl)-2-butene (**4**) were

prepared directly from the available vinyl bromides *via* coupling of the Grignard reagent (3) or the lithium derivative (4) with chlorotrimethylstannane.

The syntheses of 3-trimethylstannyl-3-butene-2-one (5) and (Z)-3-trimethylstannyl-3-hexene-2-one (6) were accomplished by palladium(0) catalyzed hydrostannation of the corresponding conjugated ynones. Compound (5) has been reported as a product of oxidation of the corresponding alcohol with dioxirane.^[33] Both hydrostannation reactions led to single regioisomers with the trimethyltin group and carbonyl bonded to the same vinyl carbon. Surprisingly, however, hydrostannation of 3-hexyne-2-one gave only the Z isomer. It is well known that the stereochemistry of palladium(0) catalyzed hydrostannation is predominantly, if not exclusively, *syn* addition.^[28-30]

The stereochemistry of this reaction was probed using trimethylstannane- d_1 and the reaction was followed by NMR. At -20°C deuterostannation of 3-butyne-2-one gave two vinyl hydrogen peaks with an area ratio of 8:1 (Eq. 1). The major peak appeared at 6.62 ppm with $^3J_{\text{SnH}} = 134.2/128.2\text{ Hz}$. In this structure the proton is *trans* to tin and this is the product of *syn* addition and is the Z isomer. The other peak occurred at 6.14 ppm with $^3J_{\text{SnH}} = 67.8/65.1\text{ Hz}$. This structure is the E isomer. When the same reaction is run at 20°C , the ratio of vinylic-proton peaks is changed to 4:1 indicating a greater portion of the E isomer. Upon standing at room temperature the isomeric ratio approached 1:1.



To further explore palladium catalyzed hydrostannation of conjugated ynones, we carried out the hydrostannation of 3-hexyne-2-one at $-20\text{ }^{\circ}\text{C}$ and again followed the reaction by NMR. Early in the reaction, a triplet appeared at 5.92 ppm with $^3J_{\text{SnH}} = 72\text{ Hz}$. This peak is attributed to a proton *cis* to tin, and the structure resulting from the expected *syn* addition of tin and hydrogen to the triple bond. As the reaction continued and the sample allowed to warm to room temperature, the peak at 5.92 ppm disappeared and a new triplet appeared at 7.17 ppm with $^3J_{\text{SnH}} = 127.2/121.5\text{ Hz}$. This structure is the *Z* isomer (**6**) and is the result of isomerization from the *E* isomer, the initial product of *syn* addition. MM2 calculations, using tin parameters of Horner and Newcomb,^[34] indicate that that *Z* isomer is approximately 19 kJ more stable than the *E* isomer. It is not known whether the palladium is involved in the isomerization reaction, however, the NMR experiments demonstrate that the rate of isomerization is only slightly less than the rate of *syn* hydrostannation of the triple bond. The syntheses of compounds (**1**)–(**6**) are shown in Fig. 1.

Characterization by ^1H , ^{13}C , and ^{119}Sn NMR

Compounds (**1**)–(**6**) were characterized by ^1H , ^{13}C and ^{119}Sn NMR. Although there have not been extensive studies of the NMR spectra of vinylstannanes, Maire and coworkers^[35] showed that configurational geometry can be assigned from the relative magnitude of the tin-hydrogen coupling constants where $J_{\text{Sn-H}}(\textit{trans}) > J_{\text{Sn-H}}(\textit{gem}) > J_{\text{Sn-H}}(\textit{cis})$ (*vide supra*). Our previous work, with stannylcrotonates^[26] and phenyl-substituted vinylstannanes^[25] showed that the trend in magnitude can be extended to tin-carbon coupling constants where $J_{\text{Sn-C}}(\textit{trans}) > J_{\text{Sn-C}}(\textit{gem}) > J_{\text{Sn-C}}(\textit{cis})$. In each case the relative magnitudes of the tin-hydrogen and tin-carbon coupling constants were consistent with the expected structure. However, the effects of methyl substituents on the ^{119}Sn chemical shifts were not as straightforward. Mitchell and Kummetat^[36] found good correlation between structure and ^{119}Sn chemical shifts for a series of isomeric mixtures of compounds with the general formula $\text{Me}_n\text{Sn}(\text{CH}=\text{CHMe})_{4-n}$. Using their ^{119}Sn chemical shift values of -42 , -58 and -34 ppm for (*E*-) and (*Z*-)1-(trimethylstannyl)propene, and 2-(trimethylstannyl)propene, respectively and -39 ppm for trimethylvinylstannane,^[37] we predicted the chemical shift effect of a *trans*-methyl group to be -3 ppm , a *cis*-methyl group to be -19 ppm and a *gem*-methyl group to $+5\text{ ppm}$. These values would result in ^{119}Sn chemical shifts in compounds (**1**)–(**4**) to be -37 , -53 , -61 and -56 ppm , respectively. The experimental values were -30.61 , -49.39 , -58.76 and -45.64 ppm , respectively. The correlation is close but in each

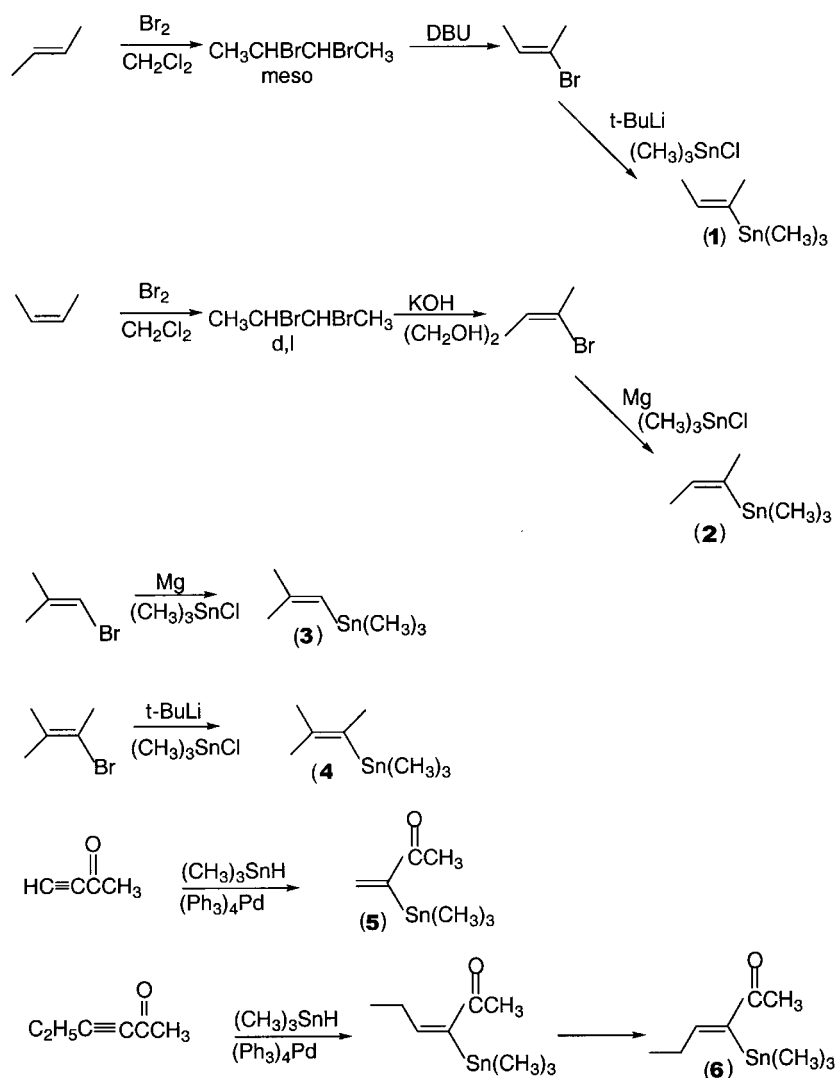


Figure 1. Synthesis of (1)–(6).

case the tin resonance appears somewhat downfield from the expected value. Since ^{119}Sn chemical shifts are well known to exhibit large solvent effects,^[38] a possible explanation for the observed deshielding effect is increased disruption of the solvent shell by multiple methyl groups.

Compounds **(5)** and **(6)** exhibited ^{119}Sn NMR chemical shifts very similar to those of vinylstannanes substituted with an ester carbonyl rather than a ketone carbonyl. Also in the case of **(6)** the ester bore a methyl group on the remote carbon instead of an ethyl group. The tin chemical shift for compound **(5)** was recorded at -31.59 ppm compared to -27.8 ppm for the ester.^[15] Compound **(6)** gave a tin value of -47.30 ppm compared to -41.1 ppm for methyl (Z)-2-(trimethylstannyl)crotonate.^[27] In each case the ketone-substituted compound was slightly more shielded indicating less delocalization of π electron density from the carbon-carbon double bond to the carbonyl.

Reactivity and Stereochemistry

The second-order rate constants for protodestannylation of compounds **(1)**–**(6)** are listed in Table 1 along with, for comparison, those from the unsubstituted, the mono-methyl, and the carbomethoxy substituted derivatives.

Consistent with the results of our previous study,^[24] compounds **(1)** and **(2)** showed increased reactivity due to a *trans* or *cis* methyl group, with

Table 1. Rate Constants for Protodestannylation

$ \begin{array}{c} \text{R}_1 \quad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}_2 \quad \text{SnMe}_3 \end{array} $					
Cpd	R ₁	R ₂	R ₃	k ₂ (M ⁻¹ s ⁻¹) ^d	k ₂ (rel)
(1)	Me	H	Me	1.65×10^{-1}	31
(2)	H	Me	Me	3.82×10^{-2}	7.3
(3)	Me	Me	H	5.25	998
(4)	Me	Me	Me	5.50	1046
(5)	H	H	COMe	4.90×10^{-3}	0.93
(6)	H	Et	COMe	6.79×10^{-2}	13
(7) ^a	H	H	H	5.26×10^{-3}	1
(8) ^a	Me	H	H	1.52×10^{-1}	29
(9) ^a	H	Me	H	1.08×10^{-1}	21
(10) ^a	H	H	Me	3.13×10^{-3}	0.60
(11) ^b	H	H	CO ₂ Me	5.70×10^{-4}	0.11
(12) ^c	H	Me	CO ₂ Me	1.60×10^{-3}	0.30

^aReference 24. ^bReference 27. ^cReference 26. ^dk₂ = $\frac{\text{Rate}}{[\text{Sn}][\text{H}^+]}$.

the *trans* being more reactive. The *gem* methyl group contributes a minor deactivating effect seen to a greater extent in (2). Very similar results were noted by Gielen and coworkers^[23] in the iododestannylation of (1) and (2). When methyl groups are both *cis* and *trans* to tin, as in (3) and (4), a synergistic effect is observed and the reactivity is increased considerably. The rate constant for (4), $5.50 \text{ M}^{-1} \text{ s}^{-1}$, is about five times that predicted from the product of the rate constants for (1) and (2). Again, Gielen^[23] observed an increased reactivity by a factor of about three in the iododestannylation of compound (3) compared to that expected as a result of two methyl groups on the remote carbon of the double bond. Consideration of the transition state for electrophilic destannylation, (Fig. 2), shows that this system is not unlike the transition state for nucleophilic substitution in a similar allylic system, II (Fig. 2). In that transition state, positive charge exists on the remote carbon of the double bond and is stabilized by both alkyl substituents on that carbon. In two kinetic studies of reactions of methyl-substituted allylic chlorides with iodide ion in acetone,^[39] and ethoxide ion in ethanol,^[40] two methyl groups on the γ -carbon of an allylic system provide increased stabilization to the transition state positive charge at the carbon to which they are attached.

Protodestannylation of compounds (5) and (6) shows three effects due to the substituents on the double bond. First, the ketones were more reactive than their comparison esters described above in the discussion of ^{119}Sn NMR. Since the first step of protodestannylation is attack of the electrophilic proton on the π electrons of the double bond, the greater reactivity can again be due to less delocalization of π electron density to the carbonyl.

The second effect is the activation due to an alkyl group on the vinyl carbon remote to tin. The ethyl group in compound (6) effects an increase in rate by a factor of fourteen over the rate of compound (5). In the corresponding ester compounds, a methyl group at this position results in a rate increase of only a factor of three compared to the unsubstituted ester.^[26]

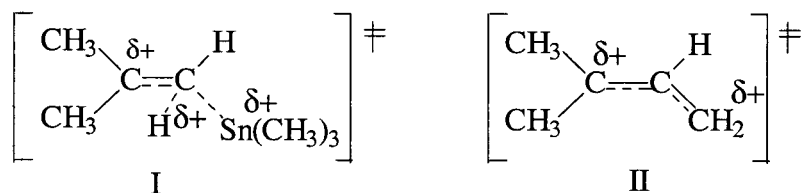


Figure 2. Transition states for electrophilic substitution and allylic nucleophilic substitution.

This difference in reactivity suggests there is greater stabilization of positive charge that develops at the remote carbon in the transition state for protodestannylation.

The third effect relates to the stereochemistry of the reaction. In the case of vinylstannanes substituted with either a conjugated ester carbonyl or ketone carbonyl, the electrophilic proton can also attack the carbonyl oxygen. Loss of the trimethylstannyl cation results in an allenol intermediate which then can transfer a proton from either face of the allene to give both isomeric substitution products. Electrophilic substitution of compound **(6)** gave a single product, (E)-3-hexen-2-one, the product of retention of configuration at the double bond. When the reaction was run in CD₃OH/H₂O with HCl as the source of electrophile, it was monitored by ¹H NMR and the vinyl region of the spectrum showed only two sets of doubled triplets indicating a single isomeric product. Each set showed a major coupling constant of 16.0 Hz, indicative of *trans* coupling between two vinyl protons. The set at 6.06 ppm also showed a minor coupling of 1.6 Hz and the set at 6.99 ppm a minor coupling of 6.4 Hz. These values are consistent with those reported for (E)-3-hexen-2-one by Hegedus and Stiverson.^[41]

The single product of retention of configuration suggests that the allenol pathway is not competitive in this protodestannylation. As discussed above, the ¹¹⁹Sn chemical shifts for **(5)** and **(6)**, the increased reactivity of ketones over comparison esters, and the greater alkyl substituent activation all point to less delocalization of electron density from the carbon-carbon double bond to the carbonyl oxygen. Thus, the oxygen is less basic and the allenol intermediate less likely to be formed, resulting in the single product of S_E2 protodestannylation.

The stereochemistry of protodestannylation was probed for compounds **(1)** and **(2)**. Electrophilic substitution in vinylstannane systems of the type of **(1)** and **(2)** has been shown to take place only with retention of configuration at the vinyl carbon.^[24-27] We carried out the electrophilic substitution with HCl in CD₃OH/H₂O. The reaction product of **(1)**, (Z)-2-butene, was identified in the ¹H NMR spectrum by a broad doublet at 1.57 ppm. Compound **(2)** gave the retention reaction product (E)-2-butene with a more complex doublet at 1.59 ppm. A synthetic mixture of (E) and (Z)-2-butene showed both doublets with overlapped peaks at 1.58 ppm.

In summary, we report the synthesis, characterization and reactivity to protodestannylation of six vinylstannanes, four substituted with two or more methyl groups and two substituted with acyl substituents. The rate data was consistent with reactivity of previous studies of vinylstannanes in this laboratory.

EXPERIMENTAL

General Information

(E)- and (Z)-2-butene were obtained from Matheson Gas Products. DBU, *tert*-butyllithium (1.7 M in pentane), 1-bromo-2-methylpropene, 2-bromo-3-methyl-2-butene, and tetrakis(triphenylphosphine)palladium(0) were obtained from Aldrich and used without further purification. 3-Butyne-2-one and 3-hexyne-2-one were obtained from Farchan Laboratories and also used without further purification. Chlorotrimethylstannane was prepared by the disproportionation reaction of dichlorodimethylstannane and tetramethylstannane and reduced to trimethylstannane by lithium aluminum hydride in tetraglyme. THF was distilled from sodium/benzophenone ketyl. ^1H , ^{13}C , and ^{119}Sn NMR spectra were recorded on a Bruker AC-250 spectrometer at 250, 62.9, and 93.3 MHz, respectively, and referenced to TMS, CDCl_3 and Me_4Sn , respectively. Grignard reactions were initiated by ultrasound in a Bronson, Model 22-4 cleaner bath (55 kHz, 100 W). Preparative gas chromatography was carried out on a 10 foot, 20% SE-30 on Chromosorb W, 60–80 mesh, column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(E)-2-Trimethylstannyl-2-butene (1)

Meso-2,3-Dibromobutane was prepared by the addition of bromine to *trans*-2-butene in CH_2Cl_2 (99% yield). ^1H NMR (CDCl_3): δ 1.85 (d, 6 H), 4.20 (m, 2 H). This product was converted to (E)-2-bromo-2-butene by reaction with DBU in dry DMSO.^[42] To a solution of 9.75 g (45.2 mmol) of *meso*-2,3-dibromobutane in 30 mL of dry DMSO, was added 6.88 g (45.2 mmol) of DBU. The reaction mixture was allowed to stir, in the dark, for 45 min and then subjected to a 0.1 torr vacuum. The volatile product, (E)-2-bromo-2-butene was collected in a liquid N_2 trap yielding 4.32 g (71%) of (E)-2-bromo-2-butene. ^1H NMR (CDCl_3): δ 1.62 (d, 3 H, $^3J = 7.1$ Hz), 2.21 (s, 3 H), 5.88 (q, 1 H, $^3J = 7.1$ Hz). Following the procedure of Davis,^[43] to a solution of 2.00 g (14.8 mmol) of (E)-2-bromo-2-butene in 10 mL of dry THF, was added, by syringe, 17.4 mL of 1.7 M *tert*-butyllithium (29.6 mmol) in pentane at -50°C . Then a solution of 2.95 g (14.8 mmol) of chlorotrimethylstannane in 5 mL of dry THF was added. The mixture was stirred for 10 min, allowed to warm to room temperature, stirred overnight, and then washed with two 10 mL portions of water. The organic layer was dried over magnesium sulfate and the THF/pentane solvent removed on a rotary evaporator. The crude product, (E)-2-trimethylstannyl-2-butene, was purified

by preparative gas chromatography. ^1H NMR (CDCl_3): δ 0.09 (s, 9 H, $^2J_{\text{SnH}} = 52.6/50.1$ Hz), 1.66 (dq, 3 H, $^3J_{\text{HH}} = 6.4$ Hz, $^5J_{\text{HH}} = 0.9$ Hz), 1.81 (m, 3 H, $^4J_{\text{HH}} = 1.8$ Hz, $^5J_{\text{HH}} = 0.9$ Hz), 5.65 (qq, 1 H, $^3J_{\text{SnH}} = 77.5$ Hz). ^{13}C NMR: δ -11.38 (SnMe_3 , $^1J_{\text{SnC}} = 335.6/320.2$ Hz), 13.95 (C_4 , $^3J_{\text{SnC}} = 65.4$ Hz), 18.10 (C_1 , $^2J_{\text{SnC}} = 52.1$ Hz), 135.10 (C_3 , $^2J_{\text{SnC}} = 28.4$ Hz), 138.45 (C_2 , $^1J_{\text{SnC}} = 494.6/473.3$ Hz). ^{119}Sn NMR: δ -30.61.

(Z)-2-Trimethylstannyl-2-butene (2)

d,l-2,3-Dibromobutane was prepared by the addition of bromine to *cis*-2-butene in CH_2Cl_2 (97% yield). ^1H NMR (CDCl_3): δ 1.76 (d, 6 H), 4.43 (m, 2 H). This product was converted to (Z)-2-bromo-2-butene by reaction with KOH in ethylene glycol. A solution of 9.70 g (44.9 mmol) of *d,l*-2,3-dibromobutane in 10 mL of ethylene glycol was placed in a 50 mL, 3 necked flask fitted with a dropping funnel, thermometer and a still head. The flask was covered with foil, stirred, and heated to 115 °C in an oil bath. Over a period of 45 m, a solution of 2.77 g (49.4 mmol) of KOH in 10 mL of ethylene glycol was added dropwise. The product, (Z)-2-bromo-2-butene distilled from the flask along with a small amount of water. The sample was dried with molecular sieves and redistilled under atmospheric pressure to give 3.93 g (65%) of product, bp 77 °C (lit.^[44] 83.5 – 84 °C). ^1H NMR (CDCl_3): δ 1.71 (d, 3 H, $^3J = 8.4$ Hz), 2.29 (s, 3 H), 5.70 (q, 1 H, $^3J = 7.4$ Hz). A solution of 7.41 g (54.8 mmol) of (Z)-2-bromo-2-butene in 10 mL of dry THF was added dropwise to 1.34 g (55.1 mmol) of magnesium in 50 mL of dry THF. After initiation with ultrasound, the mixture was heated to reflux for 3 h followed by the addition of 9.13 g (54.7 mmol) of chlorotrimethylstannane in 20 mL of dry THF. The reaction mixture was stirred at room temperature over night, hydrolyzed with 20 mL of aqueous saturated ammonium chloride solution, the organic layer separated, and dried over magnesium sulfate. The remaining THF was removed on a rotary evaporator. Final purification was affected by preparative gas chromatography. ^1H NMR (CDCl_3): δ 0.08 (s, 9 H, $^2J_{\text{SnH}} = 53.7/51.5$ Hz), 1.60 (dq, 3 H, $^3J_{\text{HH}} = 6.5$ Hz, $^5J_{\text{HH}} = 1.6$ Hz), 1.79 (m, 3 H, $^4J_{\text{HH}} = 1.6$ Hz, $^5J_{\text{HH}} = 1.6$ Hz), 6.00 (qq, 1 H, $^3J_{\text{SnH}} = 142.5$ Hz). ^{13}C NMR: δ -9.12 (SnMe_3 , $^1J_{\text{SnC}} = 334.1/318.9$ Hz), 19.53 (C_4 , $^3J_{\text{SnC}} = 45.2$ Hz), 26.15 (C_1 , $^2J_{\text{SnC}} = 54.4$ Hz), 134.62 (C_3 , $^2J_{\text{SnC}} = 33.0$ Hz), 139.14 (C_2 , $^1J_{\text{SnC}} = 470.0/447.1$ Hz). ^{119}Sn NMR: δ -49.39.

2-Methyl-1-(trimethylstannyl)propene (3)

This compound was prepared from 2-bromo-2-methylpropene by a Grignard reaction similar to that for (2). In the process 7.23 g (53.5 mmol) of

2-bromo-2-methylpropene were converted to 4.19 g (41%) of **(3)** bp 60–63 °C/40 torr (lit.^[45] bp 135–140 °C). ¹H NMR (CDCl₃): δ 0.13 (s, 9 H, ²J_{SnH} = 54.6/52.2 Hz), 1.78 (s, 3 H, ⁴J_{SnH} = 10.1 Hz), 1.89 (d, 3 H, ⁴J_{HH} = 1.3 Hz), 5.45 (m, 1 H, ²J_{SnH} = 82.2 Hz). ¹³C NMR: δ –8.95 (SnMe₃, ¹J_{SnC} = 346.6/331.1 Hz), 25.54 (C_{cis}, ³J_{SnC} = 42.3 Hz), 28.55 (C_{trans}, ³J_{SnC} = 69.2 Hz), 123.70 (=CSn, ¹J_{SnC} = 486.9/465.6 Hz), 121.67 (=CMe₂, ²J_{SnC} = 6.1 Hz). ¹¹⁹Sn NMR: δ –58.76 (lit.⁴⁶ –58.8).

3-Methyl-2-trimethylstannyl-2-butene (**4**)

This compound was also prepared by a method similar to that of Davis^[43] and compound **(1)**. In the process, 6.42 g (43.1 mmol) of 2-bromo-3-methyl-2-butene were converted to 5.1 g (51%) of **(4)**. ¹H NMR (CDCl₃): δ 0.14 (s, 9 H, ²J_{SnH} = 52.9/50.6 Hz), 1.73 (s, 3 H), 1.79 (s, 6 H). ¹³C NMR: δ –8.44 (SnMe₃, ¹J_{SnC} = 329.7/315.8 Hz), 19.19 (=CSnMe, ²J_{SnC} = 55.3 Hz), 20.35 (Me_{trans}, ³J_{SnC} = 55.8 Hz), 27.84 (Me_{cis}, ³J_{SnC} = 51.1 Hz), 130.57 (=CSn, ¹J_{SnC} = 519.3/494.3 Hz), 140.78 (=CMe₂, ²J_{SnC} = 31.8 Hz). ¹¹⁹Sn NMR: δ –45.64. Anal. Calcd. for C₈H₁₈Sn (F.W. 232.91): C, 41.25; H, 7.79. Found: C, 41.53; H, 7.66.

3-Trimethylstannyl-3-butene-2-one (**5**)

To a solution of 0.410 g (6.02 mmol) of 3-butyne-2-one and 0.141 g (0.121 mmol) of tetrakis(triphenylphosphine)palladium(0) in 5 mL of dry THF and an argon atmosphere, was added 1.02 g (6.19 mmol) of trimethylstannane in 5 mL of dry THF. The addition was accomplished in 5 min. After 1 h the IR spectrum of the reaction mixture showed the absence of an IR peak at 1800 cm^{–1} attributed to the Sn–H bond. THF was removed on a rotary evaporator and 10 mL of dry pentane added to the resulting oil. The mixture was cooled to –10 °C for 1 h to reduce the solubility of tetrakis(triphenylphosphine)-palladium(0) and the precipitate filtered on a sintered glass funnel (porosity M) under an atmosphere of argon. Pentane was removed on a rotary evaporator yielding 0.812 g (58%) of crude **(5)**. Further purification by preparative gas chromatography gave a pure product. ¹H NMR (CDCl₃): δ 0.13 (s, 9 H, ²J_{SnH} = 56.4/54.0 Hz), 2.25 (s, 3 H), 6.14 (d, 1 H, ²J_{HH} = 1.4 Hz, ³J_{SnH} = 67.8/65.1 Hz), 6.62 (d, 1 H, ²J_{HH} = 1.4 Hz, ³J_{SnH} = 134.2/128.2 Hz). ¹³C NMR: δ –9.07 (SnMe₃, ¹J_{SnC} = 357.6/341.9 Hz), 24.70 (COMe), 137.52 (=CH₂, ²J_{SnC} = 20.5 Hz), 158.16 (=CSn, ¹J_{SnC} = 403.2/386.8 Hz), 203.57 (C=O, ²J_{SnC} = 22.2 Hz). ¹¹⁹Sn NMR: δ –31.59. Anal. Calcd. for C₇H₁₄OSn (F.W. 232.87): C, 36.10; H, 6.06. Found: C, 35.70; H, 6.27.

(Z)-3-Trimethyistannyl-3-hexene-2-one (6)

This compound was prepared by the same procedure as (5). The crude yield was 1.02 g (65%). Further purification by preparative gas chromatography gave a pure product. ^1H NMR (CDCl_3): δ 0.22 (s, 9 H, $^2J_{\text{SnH}} = 55.8/53.7$ Hz), 1.09 (t, 3 H, $^3J_{\text{HH}} = 7.6$ Hz), 2.28 (s, 3 H), 2.28 (m, 2 H, $^3J_{\text{HH}} = 7.6$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{SnH}} = 27$ Hz), 7.17 (t, 1 H, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{SnH}} = 127.2/121.5$ Hz). ^{13}C NMR: δ -6.83 (SnMe_3 , $^1J_{\text{SnC}} = 357.6/341.9$ Hz), 13.78 (CH_3CH_2), 25.52 (COMe), 27.14 (CH_3CH_2 , $^3J_{\text{SnC}} = 34$ Hz), 148.31 ($=\text{CSn}$, $^1J_{\text{SnC}} = 424.1/405.1$ Hz), 157.78 ($=\text{CH}$, $^2J_{\text{SnC}}$ n.o.) 203.83 ($\text{C}=\text{O}$, $^2J_{\text{SnC}} = 21.1$ Hz). ^{119}Sn NMR: δ -47.30. Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{OSn}$ (F.W. 260.92): C, 41.43; H, 6.95. Found: C, 41.55; H, 7.23.

Kinetic Studies

Kinetic measurements were obtained on a Beckman DU/Gilford spectrophotometer equipped with a cell compartment thermostated at 25.0 ± 0.1 °C [compounds (1), (2), (5) and (6)] or a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Hi-Tech SFA-12 Rapid Kinetics Accessory [compounds (3) and (4)]. The glassware preparation and solution manipulation have been previously described.^[24] The absorbance of solutions containing the stannane (initial concentration 1.00×10^{-3} M) and HCl (initial concentration 5.00×10^{-2} M in methanol/5% water) were monitored as a function of time, at 225 nm for compounds (1)–(4), 235 nm for compound (5) and 245 nm for compound (6). This wavelength is on the shoulder of the intense absorption associated with the vinyl carbon-tin bond. All reactions were continued through at least two half-lives and the agreement of rate constants from multiple runs was within $\pm 5\%$. Rate constants were derived from a non-linear least-squares fit of the absorbance/time data.

Reactions of (1) and (2) with HCl in $\text{CD}_3\text{OH}/\text{H}_2\text{O}$

Approximately 20 mg of (1) or (2) were placed in an NMR tube and 0.5 mL of methanol- d_3 and 0.05 mL of 12 M aqueous HCl added. After 2 h the ^1H NMR spectrum from (1) showed only chlorotrimethylstannane [δ 0.59 (s)] and (Z)-2 butene [δ 1.57 (d), 5.45 (m)]. After 2 h the ^1H NMR spectrum from (2) showed only chlorotrimethylstannane [δ 0.59 (s)] and (E)-2-butene [δ 1.59 (d), 5.40 (m)]. Saturated solutions of (E)-2 butene and (Z)-2-butene in methanol- d_4 , with added HCl and chlorotrimethylstannane,

showed no change due to isomerization over a period of 2 h. The ^1H NMR spectrum of a mixture of (E)-2-butene and (Z)-2-butene gave a composite triplet at δ 1.58.

Reaction of 6 with HCl in $\text{CD}_3\text{OH}/\text{H}_2\text{O}$

A solution of (6), approximately 0.17 M in methanol- d_3 , was prepared. To this solution was added 16 μL of 12 M aqueous HCl. The reaction was monitored by ^1H NMR for 2 h. The products of the reaction were determined to be chlorotrimethylstannane [δ 0.59 (s, $^2J_{\text{Sn}} = 71.3/68.3$ Hz)] and (E)-3-hexen-2-one [δ 1.08 (t, 3 H, $^3J_{\text{HH}} = 7.2$ Hz), 2.24 (s, 3 H), 2.25 (q, 2 H, $^3J_{\text{HH}} = 7.2$ Hz), 6.06 (dt, 1 H, $^3J_{\text{HH}} = 16.0$ Hz, $^3J_{\text{HH}} = 1.6$ Hz), 7.00 (dt, 1 H, $^3J_{\text{HH}} = 16.0$ Hz, $^4J_{\text{HH}} = 6.4$ Hz)].

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