Phenyl-Substituted Vinylstannanes: Synthesis and Reactivity in Electrophilic Substitution Reactions

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Seven phenyl-substituted vinylstannanes have been prepared. (*Z*)-β-(trimethylstannyl)styrene, α-(trimethylstannyl)styrene, and 1,1-diphenyl-2-(trimethylstannyl)ethene were prepared by Grignard coupling between the appropriate phenyl-substituted vinyl bromide and chlorotrimethylstannane. (*E*)-β-(Trimethylstannyl)styrene and (*Z*)-(trimethylstannyl)stilbene were prepared by AIBN catalyzed hydrostannation of the appropriate phenyl-substituted acetylene. (*E*)-(Trimethylstannyl)stilbene and methyl (*E*)-2-(trimethylstannyl)cinnamate were prepared by palladium(0) catalyzed hydrostannation of diphenylacetylene and methyl phenylpropiolate, respectively. Each compound was characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR. Reactivity of each compound to protodestannylation was determined by spectrophotometric or ^{1}H NMR measurement of second order rate constants. The relative reactivity is interpreted on the basis of the electronic and steric effects of the phenyl substituents. The stereochemistry of destannylation resulted in retention of configuration for four of the compounds, consistent with an S_E2 mechanism. However, methyl (*E*)-2-(trimethylstannyl)cinnamate gave an *E*/*Z* product ratio of essentially 1. This result is consistent with an allenol mechanism for protodestannylation of this compound.

Introduction

In recent years vinylstannanes have become increasingly important as intermediates in carbon–carbon bond forming reactions.[1-13] However, because of the inefficiency of preparations that give mixtures of stereo- and/or regioisomeric products and the difficulty in separation of these mixtures, much effort has been directed to processes that are either isomer specific or highly isomer selective. Most productive have been addition reactions in which a tin moiety and another group are added across a carbon–carbon triple bond with controlled stereo- and regiochemistry. Palladium(0) catalyzed hydrostannation of alkynes leads to products of *syn* addition of tin and hydrogen. When the triple bond is substituted with an ester or ketone carbonyl, the major regioisomer is that with the trialkylstannyl group proximate to the carbonyl.[14] The phenylthio group also serves to direct the trialkylstannyl group to the carbon proximate to sulfur.[15] Mitchell and co-workers have extensively studied the vinylic and allylic products resulting from both palladium(0) catalyzed and free radical catalyzed hydrostannation of allenes.[16] These workers have also reported palladium(0) catalyzed addition of distannanes and silylstannanes to allenes and stannylacetylenes.[17] The latter reaction introduces a new catalyst system, palladium bis(dibenzylideneacetone)/$P(OEt)_3$ and results in 1,1,2-tristannylalkenes.

Electrophilic destannylation at the double bond has been an extremely useful reaction for stereospecific elaboration of a vinyl group. Electrophilic fluorine can be generated from $XeF_2/AgPF_4$ and replaces a stannyl group on a double bond with preservation of regiospecificity and stereospecificity.[18] Dehydrochlorination of hydroxyimoyl chlorides in the presence of vinylstannanes results in protodestannylation, followed by cycloaddition of the alkene with the dipolar nitrile oxide.[19] This latter reaction of vinylstannanes, protodestannylation, has been of interest to us for some years. In this paper we describe the synthesis and characterization of three isomeric (trimethylstannyl)styrenes, two isomeric (trimethylstannyl)stilbenes, 1,1-diphenyl-2-(trimethylstannyl)ethene, and methyl (*Z*)-2-(trimethylstannyl)cinnamate. We have determined rate constants for protodestannylation and, where appropriate, the stereochemistry of the reaction. The effect of the phenyl group on reactivity is consistent with previously studied vinylstannanes.

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Results and Discussion

Compounds 1–7 were prepared by one of three general methods; free radical catalyzed hydrostannation of alkynes, palladium(0) catalyzed hydrostannation of alkynes, or coupling of a vinyl Grignard reagent with chlorotrimethylstannane. The first process, free radical catalyzed hydrostannation is well-known to give the product of *anti* addition as the kinetically controlled product.[20] However the radical process can result in extensive isomerization if the stereoisomeric product is thermodynamically more stable.[21] These consequences can be seen in the AIBN catalyzed hydrostannation of phenylacetylene and diphenylacetylene. The former resulted in almost complete isomerization of β-(trimethylstannyl)styrene to an *E*/*Z* isomeric ratio of 14/1. However, similar hydrostannation of diphenylacetylene showed little isomerization and gave an *E*/*Z* isomeric ratio of 1/10 for the mixture of (trimethylstannyl)stilbenes. It would appear that the longer carbon–tin bonds impart less steric bulk to the trimethylstannyl group than that of a phenyl group. Separation of the major products 1 and 5, from the minor products, 2 and 4, respectively, was accomplished by preparative gas chromatography.

Palladium(0) catalyzed hydrostannation of diphenylacetylene and methyl phenylpropiolate gave exclusively (*E*)-(trimethylstannyl)stilbene, 4, and methyl (*E*)-2-(trimethylstannyl)cinnamate, 7. The stereospecificity of both reactions and the regiospecificity in the latter case have been observed in previous reports.[14,22] A difference in reactivity of the alkynes was noted, with the ester substituted carbon–carbon triple bond being the more reactive. In the case of diphenylacetylene, excess trimethylstannane was necessary because palladium(0) catalyzed coupling of trimethylstannane to give hexamethyldistannane and hydrogen was observed as a competing process.[23] The product mixture did not contain bis(trimethylstannyl)stilbene, which is not surprising since Mitchell observed that hexaalkylditins rarely undergo palladium(0) catalyzed addition to internal carbon–carbon triple bonds.[24]

(*Z*)-β-(Trimethylstannyl)styrene, 2, α-(trimethylstannyl)styrene, 3, and 1,1-diphenyl-2-(trimethylstannyl)-ethene, 6, were prepared by coupling the Grignard reagent of the appropriate vinyl bromide with chlorotrimethylstannane. (*Z*)-β-Bromostyrene was prepared by addition of bromine to (*E*)-cinnamic acid and the debrominative decarboxylation of the dibromide by sodium bicarbonate in acetone.[25] Sonication was used to initiate the Grignard formation reaction. Although the vinyl bromide was isomerically pure, some isomerization occurred, either in the Grignard step or the succeeding coupling reaction. The product mixture, after Kugelrohr distillation showed, by gas chromatography, an *E*/*Z* ratio of 1/4. Separation of the isomers was effected by preparative gas chromatography. α-(Trimethylstannyl)styrene, 3, was prepared similarly from commercially available α-bromostyrene. The crude sample was subjected to Kugelrohr distillation and then final purification by preparative gas chromatography.

Addition of bromine to 1,1-diphenylethene, followed by dehydrobromination in hot water yielded 2-bromo-1,1-phenylethene.[26] The resulting Grignard reagent was treated with chlorotrimethylstannane to give 1,1-diphenyl-2-trimethylstannylethene, 6. Final purification was effected by Kugelrohr distillation followed by fractional distillation under reduced pressure. The reactions described above for the synthesis of 1–7, are shown in Scheme 1.

The structures of compounds 1–7 were confirmed by ^{1}H and ^{13}C NMR spectroscopy. As can be seen in Scheme 1, the stereochemical relationship of each vinyl hydrogen to tin can be specified from the tin–hydrogen coupling constants (^{119}Sn and ^{117}Sn). Three-bond *trans* coupling between hydrogen and tin fall in the range 124–149 Hz. Three-bond *cis* coupling and two-bond *gem* coupling occur in similar ranges, 65–77 Hz for the former and 63–75 Hz for the latter. Compound 1 is the only structure with both a *cis* coupling and a *gem* coupling and results in equivalent values for both coupling constants, an unusual coincidence noted earlier by Seyferth and co-workers.[27]

In the ^{13}C NMR spectra, the vinyl carbon proximate to tin can be identified by the large tin–carbon, one-bond coupling constant. These coupling constants ranged from 400 to 455 Hz for compounds 1–6 and about 350 Hz for compound 7. This last value is intermediate beteen values reported earlier for stannyl-substituted methyl crotonates[22] and stannyl-substituted methyl fumarate and maleate.[28] The chemical shifts of these carbons appear in a narrow range, 129.9–133.7 ppm, when the cosubstituent at the proximate carbon is hydrogen (compounds 1, 2, and 6). When the cosubstituent with tin is a carbomethoxy group, the chemical shift of the proximate vinyl carbon increases to 139.3 ppm (compound 7), and when the cosubstituent is a phenyl group, the chemical shift appears in the range 149.9–154.6 ppm (compounds 3–5).

The vinyl carbon remote to tin is characterized by a chemical shift in the range 142.5–147.3 ppm when substituents are hydrogen and phenyl (compounds 1, 2, 4, 5, and 7). This carbon is shielded to 126.3 ppm when substituted by two hydrogens (compound 3) and deshielded to 158.6 ppm when substituted by two phenyl groups (compound 6). The two-bond tin–carbon coupling constants are considerably smaller in magnitude, ranging from about 6 to 27 Hz.

Of interest also are the chemical shifts and tin–carbon coupling constants for carbons bonded to the vinyl system. In compounds 1, 2, and 4–7 the carbon remote to tin is substituted by a phenyl group. When the phenyl group is *trans* to tin, C_1 of the ring appears in the narrow range 136.7–142.8 ppm (compounds 1, 4, 6, and 7), while C_1 *cis* to tin is slightly more deshielded in the range 140.9–144.2 ppm (compounds 2, 5, and 6). In the former case the three-bond *trans* coupling to tin falls in the range 53–70 Hz compared to 26–32 Hz for the three-bond coupling between tin and C_1 of a *cis* phenyl group.

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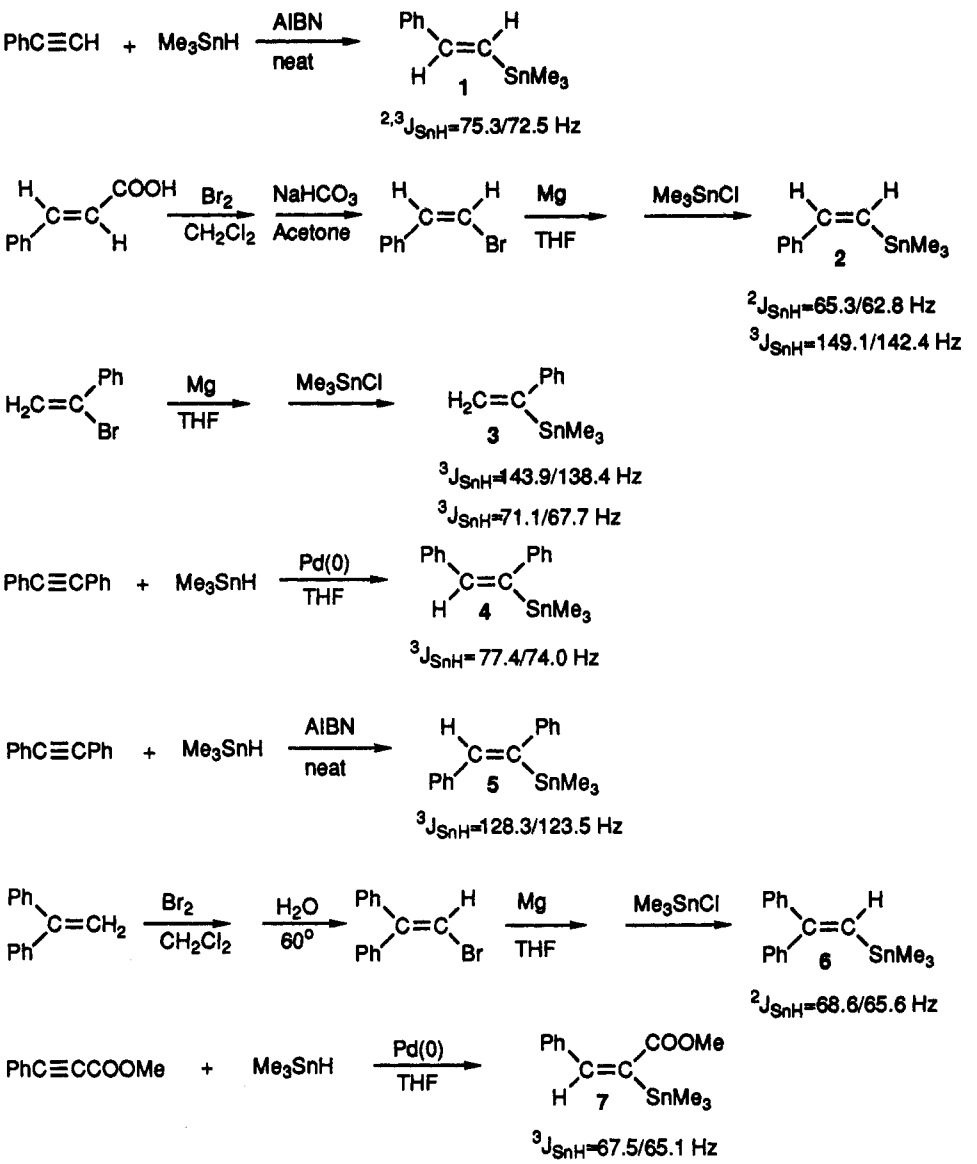
Scheme 1



The C_1 carbon of phenyl groups bonded to the vinyl carbon proximate to tin (compounds **3**–**5**) display chemical shifts in the range 138.1–147.1 ppm. The two-bond tin–carbon coupling constants fall in the range 33–38 Hz. Included in this range is the two-bond coupling to the carbonyl carbon of compound **7**. These coupling constants are slightly larger than the three-bond tin to *cis* carbon coupling, a phenomenon noted previously.[22,28,29] Indeed, in compound **5**, there is no basis on which to differentiate between the C_1 carbons of the two phenyl groups. In this case C_1 of the phenyl bonded to the proximate carbon was assigned the larger coupling, 32.9 Hz, and C_1 of the phenyl bonded to the remote carbon was assigned the smaller coupling, 26.0 Hz.

Very few correlations have been observed between the structure and the chemical shift in ^{119}Sn NMR.[30] Using the chemical shift at −39 ppm (10% in CCl_4) for (trimethylvinyl)stannane[31] as a reference point, compounds **1**–**3** show the effect of one phenyl group on the tin resonance. The *trans* phenyl group of **1** deshields the ^{119}Sn resonance by 8 to −31 ppm; the *cis* phenyl group of **2** shields the ^{119}Sn resonance by 11 to −50 ppm; the *gem* phenyl group of **3** deshields the ^{119}Sn resonance by 12 to −27 ppm. The values for **1** and **2** agree favorably with those reported by Quintard and co-workers[32] (in C_6D_6). The effect of a second phenyl is approximately additive. Compound **4**, with a *trans* phenyl group and a *gem* phenyl group would be predicted to exhibit a ^{119}Sn resonance at −19 ppm whereas the actual chemical shift is −16 ppm. In compound **5**, a *cis* phenyl group and a *gem* phenyl predict a resonance at −38 ppm and the observed resonance falls at −39 ppm. Finally, in compound **6**, with both a *trans* and *cis* phenyl group, the predicted chemical shift is −42 ppm while the observed chemical shift is −48 ppm. The additivity correlation breaks down in compound **7** with a *trans* phenyl group and a *gem* carbomethoxy group. The effect of the latter group has been shown to be deshielding by 11 ppm.[32]

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The combined effect of the two substituents would be predicted to deshield the ^{119}Sn resonance to −20 ppm. The observed chemical shift, while in the predicted direction, exhibits greater deshielding to −1 ppm. Exact values for the ^{119}Sn chemical shifts can be found in the Experimental Section.

In previous papers we have reported the reactivity to protodestannylation for a number of substituted vinylstannanes.[22,28,33] Second order rate constants in methanol/5% water have been determined from the decrease in absorbance associated with the vinyl carbon–tin bond as a function of time. This method was applicable here for compounds **1**, **2**, **3**, **6**, and **7**. However, compounds **4** and **5**, the stilbene structures, could not be studied by the UV method because absorbance associated with the extended aromatic conjugated systems masked the carbon–tin absorbance. To circumvent this problem we turned to ^1H FT-NMR, using a thermostated probe, as the method for monitoring the rate of these protodestannylation reactions. Reactions were run in methanol-d_3/5% H_2O as solvent, and at timed intervals a single FID was collected and stored in memory. When the reaction had proceeded through about 3 half-lives, the signals associated with the trimethylstannyl group in the vinylstannane and with chlorotrimethylstannane were integrated. A plot of peak area for the vinylstannane vs time produced a typical exponential decay curve while the corresponding plot for chlorotrimethylstannane gave a complementary exponential growth curve. The graphs for compound **4** are seen in Figure 1. Since the reactions were run under pseudo first order conditions, the first order rate constant was determined from a nonlinear least squares fit of the peak area/time data and the second order rate constant was then obtained by dividing through by the acid concentration. The precision between individual runs was not as good by this method as by the UV spectrophotometric method, and for this reason the rate constants determined by the NMR method are reported only to two significant figures. As a check on the comparability of the spectrophotometric method and the ^1H NMR method, the second order rate constant for **6** was determined by both methods. Each method was run four times, and the ^1H NMR method provided two values (decrease in concentration of the vinylstannane and increase in concentration of chlorotrimethylstannane) in each run. The averaged values from each method agreed to three significant figures.

Reactivity to protodestannylation, as measured by second order rate constants, for the seven vinylstannanes is recorded in Table 1. In addition rate constants for two previously studied reference compounds are included. Eaborn and co-workers[34] studied the reactivity of protodestannylation of compounds **1** and **2** in an acetic acid/methanol system. They found that cleavage of the styryl group from tin is faster, by a factor of about 20, than cleavage of a phenyl group. In the halodestannylation reaction, the order of reactivity is phenyl > vinyl.[35] If this order of reactivity for protodestannylation is assumed to be similar, then the β-phenyl group is seen to be activating for protodestannylation. Eaborn also noted that the configurational position of the β-phenyl was essentially unimportant, with the *cis* isomer being slightly more reactive by a factor of 1.1. In our system, hydrogen chloride/methanol/5% water, the β-phenyl group is again activating for protodestannylation, with compounds **1** and **2** more reactive than the unsubstituted vinylstannane, **8**,

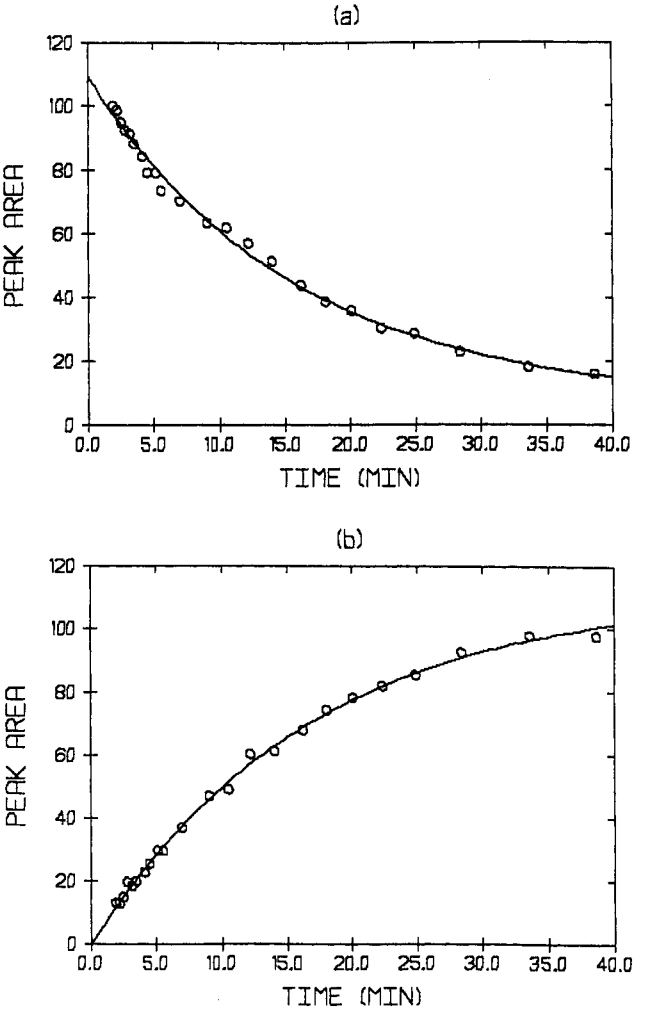
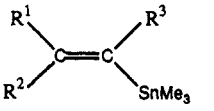


Figure 1. Reaction of **4** with HCl in CD_3OH/H_2O: (a) plot of the ^1H NMR peak area of the trimethylstannyl group of **4** vs time; (b) plot of ^1H NMR peak area of the chlorotrimethylstannane vs time.

Table 1. Rate Constants for Protodestannylation



cpd	R^1	R^2	R^3	10^3k_2[a]	k_2^{rel}	k_2^{rel}(pred)[b]
1	Ph	H	H	138	26	
2	H	Ph	H	124	24	
3	H	H	Ph	1.27	0.24	
4	Ph	H	Ph	6.8	1.3	6.2
5	H	Ph	Ph	3.4	0.64	5.8
6	Ph	Ph	H	142	27	624
7	Ph	H	COOMe	117	22	2.9
8[c]	H	H	H	5.26	1.0	
9[d]	H	H	COOMe	0.570	0.11	

[a] Experimental details are found in the Experimental Section. The agreement of rate constants from multiple runs was ±5% for spectrophotometric determinations (compounds **1**, **2**, **3**, **6**, and **7**) and ±15% for NMR determinations (compounds **4** and **5**). In M^{-1} s^{-1}. [b] Calculated from the product of relative rate constants for appropriately substituted vinylstannanes. E.g., compound **4**, K_2^{rel}(pred) = 26 × 0.24. [c] Reference 33. [d] Reference 28.

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by factors of 26 and 24, respectively. Again, as with Eaborn's system, there is little difference in reactivity between the *cis* and *trans* isomers. However, we find that the relative order of reactivity is reversed, with **1** the more reactive. It should also be noted that the vinylstannane is more reactive by a factor of about 50 in the strong acid/methanol system as compared to the weak acid/methanol system. Also, compound **3**, in which the phenyl group resides on the carbon proximate to tin, is less reactive than **8** by factor of 4. Thus the α-phenyl substituent is deactivating for electrophilic substitution.

The substituent effects noted above can be applied to vinylstannanes with two phenyl groups substituted on the double bond, compounds **4–6**. The activating and deactivating effects of single phenyl substituent are not simply additive, probably because of strict steric limitations imposed by two phenyl substituents and the trimethylstannyl group. On the basis of the reactivity determined for **1–3**, the expected reactivity of **4**, with phenyl groups α and β-*trans* to tin, would be 6× that of **8**. Likewise **5** should exhibit reactivity 6× that of **8** and **6** should be approximately 600× more reactive than **8**. However their relative reactivities are 1.3×, 0.64×, and 27×, respectively. In each case the reactivity is considerably less than that predicted by additive substituent effects. With a single phenyl group on the double bond, the ring and the double bond can become coplanar. Phenyl groups bonded at the remote vinyl carbon (**1** and **2**) can stabilize partial positive charges generated at that carbon in the transition states for **1** and **2**. Such activation is not possible in **3** when the phenyl group resides at the vinyl carbon proximate to tin and inductive electron withdrawal is deactivating to the system.

In compound **4**, the two phenyl groups constitute a *cis*-stilbene unit, and thus van der Waals interaction between *ortho* hydrogens prevent planarity of both rings with the double bond.[36] The consequence is greater deactivation by the proximate phenyl group than activation by the remote phenyl, resulting in reactivity 1.3× that of **8**. Additive effects of the two phenyl groups predict reactivity of approximately 6× that of compound **8**. In a similar fashion the *gem* diphenyl groups of compound **6** cannot both be coplanar with the double bond and again their combined activating effects result in lower reactivity, 27× that of **8** instead of the predicted >600× that would accrue from activation by each phenyl substituent.

The case for compound **5**, in which the remote phenyl substituent is *cis* to tin and which also has a *gem* phenyl substituent, is not so apparent. The phenyl groups and the double bond constitute a *trans*-stilbene system in which both phenyls should be essentially planar with the double bond.[37] However space filling models show that presence of the trimethylstannyl groups allows only one phenyl group to occupy a planar conformation. By necessity the second phenyl group must rotate out of planarity to avoid van der Waals interactions between methyl hydrogens of the trimethylstannyl group and ring hydrogens. The resultant reactivity, 0.6× that of **8**, is diminished by a factor of 10 from that expected due to the cumulative effects of the two phenyl groups.

Compound **7** exhibits considerable enhanced reactivity when compared with **1** and **9**. The cumulative effect of activation by a *trans* remote phenyl group (26×) and a proximate carbomethoxy group (0.11×) predicts a rate constant that is diminished by a factor of 40 compared to the measured value. Since **7** reacts via an allenol mechanism (*vide infra*), this enhanced reactivity is expected. The carbonyl oxygen and aromatic ring are conjugated through the double bond and the effect leads to increased basicity of the carbonyl oxygen.[38] There are no steric effects that disrupt the planarity of the conjugated system.

In the course of our kinetic studies, we have had occasion to measure the rate constant for deuteriodestannylation of compound **4** by the NMR method described above. The second order rate constant, at 25 °C was determined to be 6.2×10^{-3} M^{-1} s^{-1}. This value is only slightly smaller than that for protodestannylation (see compound **4**, Table 1) such that $k_H/k_D = 1.1$. The absence of an isotope effect is not surprising since the Hammett acidity function, D_o, for DCl in D_2O is essentially the same as H_o for HCl in H_2O.[39]

The stereochemistry of the destannylation reaction was also determined by ^1H NMR of samples that had been subjected to deuteriodestannylation by DCl in CD_3OD/D_2O. Compounds **1**, **2**, **4**, and **5** gave only a single phenyl-substituted alkene product. In each case the structure of the product, as determined by the magnitude of J_{HH} for compounds **1** and **2** and J_{HD} for compounds **4** and **5**, was consistent with retention of configuration and an S_E2 reaction.

In the case of compound **7**, two products of cleavage with DCl were observed, the product of retention of configuration and the product of inversion of configuration. The ratio of isomers was 55/45 with the product of retention of configuration in slight excess. Since these values were taken from integration of vinyl hydrogen peaks, the isomeric mixture can be considered to be 50/50. This phenomenon of isomeric product mixtures has been observed previously in this laboratory in protodestannylation of vinylstannanes with a carbomethoxy group proximate to the stannyl leaving group.[22,28] Initial attack of the proton on the carbonyl oxygen with subsequent loss of tin leads to an allenol intermediate. Tautomeric shift of the proton along either face of the allene leads to isomeric products. This process is depicted in Scheme 2.

In summary, we report the synthesis and characterization of seven phenyl-substituted vinylstannanes. Synthesis was achieved through AIBN and palladium(0) catalyzed hydrostannation and by Grignard coupling reactions. Determination of regio- and stereochemistry was accomplished by ^1H and ^{13}C NMR. ^{119}Sn NMR was also obtained. We have determined the reactivity of these compounds to protodestannylation and interpreted the rate constants in the context of previously studied vinylstannanes. Rate constants were obtained spectrophotometrically and from ^1H NMR peak areas. The rate constant for compound **4** showed essentially no deuterium isotope effect. Deuteriodestannylation allowed determination of the structure of the reaction products and showed that compounds **1–6** react by an S_E2 mechanism while compound **7** reacts via an allenol mechanism.

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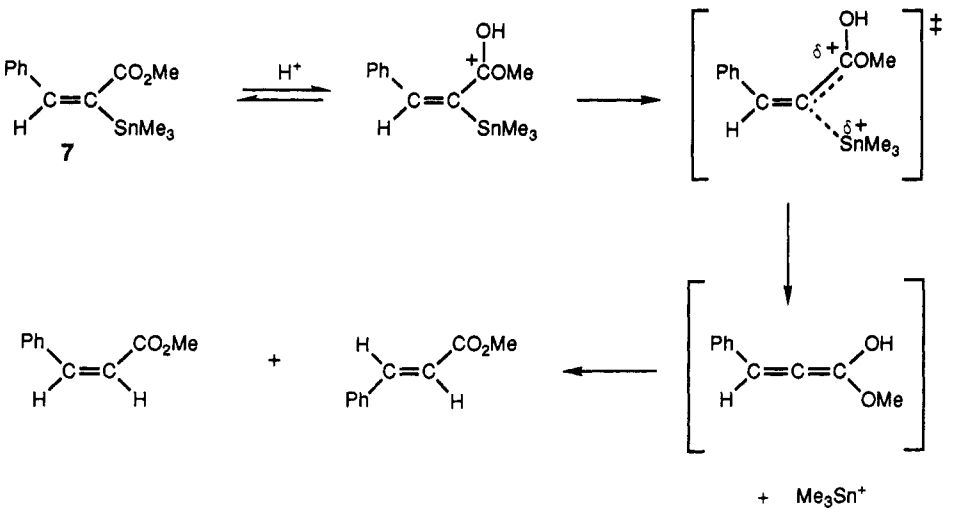
Scheme 2



Experimental Section

General Information. Phenylacetylene, α-bromostyrene, diphenylacetylene, *trans*-cinnamic acid, 1,1-diphenylethylene, and tetrakis(triphenylphosphine)palladium(0) were obtained from Aldrich. Methyl phenylpropiolate was obtained from Farchan, and AIBN, from MCB. All chemicals were used without further purification. Trimethylstannane was prepared by reduction of chlorotrimethylstannane with $LiAlH_4$ in dry tetraglyme, followed by distillation to a liquid nitrogen cooled trap.[40] 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. IR spectra were recorded on a Perkin-Elmer, Model 1310, spectrometer or a Nicolet, Model 740, FT-IR spectrometer. Grignard reactions were initiated by ultrasound in a Bronson, Model 22-4, cleaner bath (55 kHz, 100 W). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(*E*)-β-(Trimethylstannyl)styrene, 1. Compound 1 was prepared by the neat, AIBN catalyzed reaction trimethylstannane and phenylacetylene.[32] Kugelrohr distillation (125 °C, 2 Torr) was utilized to isolate the volatile products, consisting primarily of *E* and *Z* isomers of β-(trimethylstannyl)styrene (yield 42%), *E*/*Z* = 14/1. Final purification was obtained by preparative gas chromatography (10 ft., 20% SE-30 on Chromosorb W, 60–80 mesh). ^1H NMR ($CDCl_3$): δ 0.26 (s, 9H, $^2J_{SnH}$ = 55.2/53.4 Hz), 6.93 (s, 2H, $^{2,3}J_{SnH}$ = 75.3/72.5 Hz), 7.2–7.5 (m, 5H). ^{13}C NMR: δ −9.6 (CH_3Sn, $^1J_{SnC}$ = 355.5/340.1 Hz), 126.0, 127.7, 128.5 (C_{2-4}), 129.9 (=CSn, $^1J_{SnC}$ = 451.7/430.3 Hz), 138.5 (C_1, $^3J_{SnC}$ = 69.9 Hz), 145.7 (=CPh, $^2J_{SnC}$ = 13.8 Hz). ^{119}Sn: δ −31.0.

(*Z*)-β-(Trimethylstannyl)styrene, 2. (*Z*)-β-Bromostyrene was prepared from (*E*)-cinnamic acid by the method of Cristol and Norris,[25] overall yield 82%. ^1H NMR ($CDCl_3$): δ 6.44 (d, 1H, $^3J_{HH}$ = 8.1 Hz), 7.07 (d, 1H, $^3J_{HH}$ = 8.1 Hz), 7.28–7.43 (m, 3H), 7.64–7.73 (m, 2H). The bromide was converted to the Grignard reagent and coupled with chlorotrimethylstannane.[27] After standard workup, the crude product was subjected to Kugelrohr distillation (105 °C, 0.3 Torr) to isolate the volatile products, consisting of primarily *E* and *Z* isomers of β-(trimethylstannyl)-styrene (yield 64%), *E*/*Z* = 1/4. Final purification was obtained by preparative gas chromatography (10 ft., 20% SE-30 on Chromosorb W, 60–80 mesh). ^1H NMR ($CDCl_3$): δ 0.26 (s, 9H, $^2J_{SnH}$ = 55.3/53.3 Hz), 6.39 (d, 1H, $^3J_{HH}$ = 13.6 Hz, $^2J_{SnH}$ = 65.3/62.8 Hz), 7.23–7.42 (m, 5H), 7.76 (d, 1H, $^3J_{HH}$ = 13.6 Hz, $^3J_{SnH}$ = 149.1/142.4 Hz). ^{13}C NMR: δ −8.1 (CH_3Sn, $^1J_{SnC}$ = 355.3/339.9 Hz), 127.3, 127.3, 128.2 (C_{2-4}), 133.7 (=CSn, $^1J_{SnC}$ = 431.8/412.1 Hz), 141.1 (C_1, $^3J_{SnC}$ = 32.0 Hz), 147.3 (=CPh, $^2J_{SnC}$ = 6.3 Hz). ^{119}Sn NMR: δ −49.7. Anal. Calcd for $C_{11}H_{16}Sn$: C, 49.49; H, 6.04. Found: C, 48.86; H, 6.06.

α-(Trimethylstannyl)styrene, 3. Compound 3 was prepared from the Grignard of α-bromostyrene and chlorotrimethylstannane.[34] The crude product subjected to Kugelrohr distillation (100 °C, 1.5 Torr) followed by preparative gas chromatography resulted in a pure sample of α-(trimethylstannyl)styrene. ^1H NMR ($CDCl_3$): δ 0.23 (s, 9H, $^2J_{SnH}$ = 54.9/52.9 Hz), 5.46 (d, 1H, $^2J_{HH}$ = 2.3 Hz, $^3J_{SnH}$ = 71.1/66.7 Hz), 6.05 (d, 1H, $^2J_{HH}$ = 2.3 Hz, $^3J_{SnH}$ = 143.9/138.4 Hz), 7.17–7.38 (m, 5H). ^{13}C NMR: δ −8.7 (CH_3Sn, $^1J_{SnC}$ = 346.4/331.3 Hz), 126.3, 126.5, 128.4 (C_{2-4}), 126.3 (=CH_2, $^2J_{SnC}$ = 26.4 Hz), 145.1 (C_1, $^2J_{SnC}$ = 38.1 Hz), 154.6 (=CSn, $^1J_{SnC}$ = 431.9/413.5 Hz). ^{119}Sn NMR: δ −26.5. Anal. Calcd for $C_{11}H_{16}Sn$: C, 49.49; H, 6.04. Found: C, 49.69; H, 6.13.

(*E*)-(Trimethylstannyl)stilbene, 4. A three neck, round bottom flask was fitted with a magnetic stirrer, rubber stopper septum, and gas addition adapter. The flask was flushed with argon, and diphenylacetylene (1.81 g, 10 mmol), dry THF (5 mL), and tetrakis(triphenylphosphine)palladium(0) (0.20 g, 0.17 mmol) were added. After a second flush with argon, trimethylstannane (4.5 g, 27.5 mmol) in dry THF (10 mL) was added dropwise from a syringe over a period of 1 h. The THF was removed under reduced pressure, taking care to maintain an argon atmosphere. Pentane (25 mL) was added and the mixture cooled to −10 °C for 0.5 h to decrease the solubility of the palladium(0) catalyst. The precipitated catalyst was filtered on a sintered glass funnel in an argon atmosphere. The pentane was removed on a rotary evaporator and the crude product (yield 68%) purified by Kugelrohr distillation (185 °C, 1 Torr). Further purification by preparative gas chromatography gave a pure product. ^1H NMR ($CDCl_3$): δ 0.18 (s, 9H, $^2J_{SnH}$ = 54.0/51.7 Hz), 6.67 (s, 1H, $^3J_{SnH}$ = 77.4/74.0 Hz), 6.95–7.32 (m, 10H). ^{13}C NMR (C′ refers to the phenyl bonded to the vinyl carbon remote to tin): δ −9.2 (CH_3Sn, $^1J_{SnC}$ = 343.6/328.6 Hz), 125.3, 126.4, 126.8, 127.9, 128.7, 129.3 (C_2–C_4, $C_{2'}$–$C_{4'}$), 137.6 ($C_{1'}$, $^3J_{SnC}$ = 69.9 Hz), 138.1 (C_1, $^2J_{SnC}$ = 33.5 Hz), 145.2 (=CH, $^2J_{SnC}$ = 26.9 Hz), 149.9 (=CSn, $^1J_{SnC}$ = 435.3/415.9). ^{119}Sn NMR: δ −16.0. Anal. Calcd for $C_{17}H_{20}Sn$: C, 59.52; H, 5.88. Found: C, 59.47; H, 5.84.

(*Z*)-(Trimethylstannyl)stilbene, 5. Diphenylacetylene (1.08 g, 6.07 mmol), trimethylstannane (1.01 g, 6.07 mmol) and AIBN (0.042 g, 0.24 mmol) were placed in a reaction vial, and the vial was flushed with argon and sealed. The mixture was heated to 70 °C and held at that temperature overnight. The IR spectrum of the product mixture showed no peak at 1800 cm^{-1}, indicating the absence of trimethylstannane. The crude product was purified by Kugelrohr distillation (190 °C, 1.5 Torr), yielding a mixture of isomers (*E*/*Z* = 1/10) and some starting alkyne. Final purification by preparative gas chromatography provided, in 55% yield, a white crystalline solid product, mp 57 °C. ^1H NMR ($CDCl_3$): δ −0.03 (s 9H, $^2J_{SnH}$ = 54.1/52.2 Hz), 7.30–7.54 (m, 10H),

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7.60 (s, 1H, $^3J_{SnH}$ = 128.3/123.5 Hz). ^{13}C NMR (C′ refers to the phenyl group bonded to the vinyl carbon remote to tin): δ −6.9 (CH_3Sn, $^1J_{SnC}$ = 350.5/334.8 Hz), 125.9, 126.8, 127.2, 128.0, 128.2, 128.2 (C_2–C_4, C_2–C_4′), 140.9 (C_1′, $^3J_{SnC}$ = 26.0 Hz), 143.2 (=CH, $^2J_{SnC}$ = 22.8 Hz), 147.1 (C_1, $^2J_{SnC}$ = 32.9 Hz), 150.2 (=CSn, $^1J_{SnC}$ = 420.9/402.8 Hz). ^{119}Sn NMR: δ −38.6. Anal. Calcd for $C_{17}H_{20}Sn$: C, 59.52; H, 5.88. Found: C, 59.92; H, 5.77.

1,1-Diphenyl-2-(trimethylstannyl)ethene, 6. 2-Bromo-1,1-diphenylethene was prepared by a modification of the method of Wittig and Kethur.[26] 1,2-Dibromo-1,1-diphenylethane was prepared by the addition of bromine to 1,1-diphenylethene in CH_2Cl_2. The product was suspended in water at 60 °C for 3 h. The resulting oil was separated, dried over molecular sieves, and recrystallized from absolute ethanol, mp (after a second recrystallization) 42.5–43.5 °C. ^1H NMR ($CDCl_3$): δ 6.78 (s, 1H), 7.18–7.46 (m, 10H). The bromide was converted to its Grignard reagent and coupled with chlorotrimethylstannane.[34] After the standard workup the crude product was subjected to Kugelrohr distillation (200 °C, 0.5 Torr). Final purification was effected by fractional distillation under reduced pressure, bp 98–100 °C (0.05 Torr) (lit.[34] bp 114–118 °C, 0.4 Torr). ^1H NMR ($CDCl_3$): δ −0.08 (s, 9H, $^2J_{SnH}$ = 55.6/53.1 Hz), 6.67 (s, 1H, $^2J_{SnH}$ = 68.6/65.6 Hz), 7.19–7.37 (m, 10H). ^{13}C NMR (C′ refers to the *cis* phenyl group bonded to the vinyl carbon remote to tin): δ −8.4 (CH_3Sn, $^1J_{SnC}$ = 356.9/341.3 Hz), 127.3, 127.4, 128.0, 128.1, 128.1, 129.4 (C_2–C_4, C_2–C_4′), 131.9 (=CSn, $^1J_{SnC}$ = 454.8/433.4 Hz), 142.8 (C_1, $^3J_{SnC}$ = 60.0 Hz), 144.2 (C_1′, $^3J_{SnC}$ = 30.4 Hz), 158.6 (=CPh_2, $^2J_{SnC}$ = 7.3 Hz). ^{119}Sn NMR: δ −48.0. Anal. Calcd. for $C_{17}H_{20}Sn$: C, 59.52; H, 5.88. Found: C, 60.38; H, 6.12.

Methyl (*E*)-2-(Trimethylstannyl)cinnamate, 7. Into a 25-mL flask, fitted with a magnetic stirrer, were placed dry THF (5 mL), methyl phenylpropiolate (0.971 g, 6.07 mmol), and tetrakis(triphenylphosphine)palladium(0) (141 mg, 0.121 mmol). The flask was flushed with argon and sealed with a septum. Trimethylstannane (1.00 g, 6.07 mmol) in dry THF (5 mL) was added dropwise from a syringe over a period of 5 min. After 0.5 h the reaction was deemed complete by the absence of a Sn–H peak at 1800 cm^{-1} in the IR spectrum. The THF was removed on a rotary evaporator, taking care to maintain an argon atmosphere. Pentane (10 mL) was added to the flask and the mixture stored at −10 °C for 0.5 h. The resulting precipitate was removed by filtration on a sintered glass funnel (porosity M) in an argon atmosphere. The pentane was removed on a rotary evaporator, and the crude product was purified by Kugelrohr distillation (97 °C, 0.1 Torr) yielding 1.24 g (63%) of methyl (*E*)-2-(trimethylstannyl)cinnamate. ^1H NMR ($CDCl_3$): δ 0.28 (s, 9H, $^2J_{SnH}$ = 56.4/53.9 Hz), 3.62 (s, 3H), 6.74 (s, 1H, $^3J_{SnH}$ = 67.5/65.1 Hz), 7.25 (m, 5H). ^{13}C NMR: δ −8.8 (CH_3Sn, $^1J_{SnC}$ = 362.0/346.4 Hz), 51.4 (OMe), 127.9, 128.2, 128.3 (C_{2-4}), 136.7 (C_1, J_{SnC} = 53.1 Hz), 139.3 (=CSn, $^1J_{SnC}$ = 348.1/333.1 Hz), 142.5 (=CH, $^2J_{SnC}$ = 16.2 Hz) 173.2 (C=O, $^2J_{SnC}$ = 35.1 Hz). ^{119}Sn NMR: δ −1.4. Anal. Calcd for $C_{13}H_{18}O_2Sn$: C, 48.05; H, 5.58. Found: C, 48.61; H, 5.44.

Kinetic Studies. Reaction rate constants for the protodestannylation reaction were measured spectrophotometrically on a Beckman DU-Gilford spectrophotometer equipped with a cell compartment thermostated at 25 °C or by integration of the ^1H NMR signal of the trimethylstannyl peak from both the reactant vinylstannane and the product chlorotrimethylstannane. NMR reactions were run in a thermostated probe at 25 °C.

The glassware preparation and solution manipulation for the spectroscopic method have been described previously.[33] The absorbances 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 in the range of 250 nm as a function of time. The wavelength is on the shoulder of the intense absorption associated with the vinyl carbon–tin bond. All reactions were continued through at least 1.5 half-lives. Rate constants were derived from a nonlinear least squares fit of the absorbance/time data.

Reactions, from which rate data were obtained by integration of ^1H NMR spectra, were run in NMR tubes. Samples of approximately 5 mg (0.0146 mmols) of stannylstilbene were weighted into NMR tubes. In order were added, by syringe, 0.50 mL of CD_3OH, 0.020 mL of H_2O, and 0.006 mL (0.072 mmols) of 12 M aqueous HCl. Final concentrations were as follows: stannylstilbene, 2.8×10^{-2} M; HCl 1.4×10^{-1} M; water 5%. Each liquid was prethermostated at 25 °C. On addition of the HCl, the tube was inverted several times and time zero marked. The tube was immediately placed in the thermostated NMR probe at 25 °C. A single pulse was taken at timed intervals and the FID's stored. After the run the individual FID's were transformed and the trimethylstannane peaks of the stannylstilbene and chlorotrimethylstannane integrated. At least 20 points were obtained in each run, and the reaction was followed to about 80% completion. Rate constants were obtained from a nonlinear least squares fit of the area/time data.

Reactions of 1, 2, 4, 5, and 7 with DCl in CD_3OD/D_2O. Approximately 1.0 M solutions of each compound were prepared in CD_3OD. To 0.5 mL of each solution in an NMR tube was added 0.1 mL of 12 M DC1 in D_2O. ^1H NMR spectra were obtained after about 1 h. The stereochemistry of the deuterated cleavage product was determined from the magnitude of the H–H or H–D coupling constant.

Configurational Stability of 7 and Methyl (*E*)-Cinnamate. In the preceding experiment for compound 7, the reaction with DCl was monitored several times by ^1H NMR during the period of reaction. At no time did a new peak appear in the 0–0.5 ppm region of the spectrum, indicating no isomerization of compound 7 to its *Z* isomer prior to reaction with DCl. Likewise, a solution of methyl (*E*)-cinnamate (prepared by esterification of *E*-cinnamic acid) in CD_3OD/D_2O, containing DCl and chlorotrimethylstannane, was found, by ^1H NMR, to be configurationally stable. Vinylic proton peaks were observed at 6.45 and 7.46 ppm, while peaks in the range of 5.9 and 6.9 ppm, attributed to the *Z* isomer, were absent.[41]

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