mere superpositions of those of isolated Cr(I) and Cr(0) sites. The ca. 10–20-cm^{-1} shift for the carbonyls at the formal Cr(0) site is the key piece of evidence here. The ESR results (two inequivalent ^{31}P splittings for $VIII^+$) and voltammetry results (moderate $\Delta E°$ values) offer support for this interpretation.

The 10–20-cm^{-1} CO IR shift may arise from through-bond coupling involving either the Cr–P–P–Cr σ framework or the biphenyl linkage. There is precedent for this magnitude of shift in redox studies of heterobimetallic metal carbonyl complexes with inherently different redox sites. Examples include tricobalt clusters with an attached ferrocene,[39] $Mo(CO)_4(PR_2)_2$ linked to bis(arene)chromium,[40] and $Re(CO)_3$ with a coordinated benzoylpyridine,[41] all of which showed $\nu_{sym}(CO)$ shifts of 12–24 cm^{-1} even though the $M(CO)_x$ moiety was not formally involved in the redox process.

Why is the dppm-bridged complex VI^+ a class III mixed-valent complex (totally delocalized) whereas the tetramethyldiphosphino-bridged complex VII^+ is a class II species? This question cannot be answered with confidence without knowledge of the structure of the monocation of VII. Our previous work[16] showed that significant structural changes may occur upon oxidation of this general class of compounds. Unfortunately, the slow regeneration of VII from VII^+ has precluded success in efforts to grow crystals of the cation suitable for X-ray analysis. We are left, then, to briefly consider some of the possibilities.

In earlier work we noted that the dihedral angle of the biphenyl group in VI^+ was only 3°, as opposed to 50° in neutral VI,[16] and implied that the delocalization of VI^+ arose from interactions across the (almost coplanar) biphenyl bridge. It is possible that the shorter P_2 bridge in VII imparts greater rigidity to the complex and does not allow a significant structural rearrangement in the monocation. This would leave the biphenyl group in a twisted configuration (25.7° in neutral VII) and cut down on the possibility of electron transfer through the π system.[42]

We should, however, also consider the possibility of through-space interactions arising from direct M–M orbital overlap. The Cr–Cr distance in neutral VII is 4.773 Å, which may be compared to 4.828 Å in VI and 4.374 Å in VI^+. It is difficult to specify the maximum M–M distance that could give rise to the type of delocalization being considered here, so it is quite possible that the delocalization of VI^+ arises from a through-space metal–metal interaction. Without a crystal structure of VII^+ it is not possible to say whether the poorer delocalization in the P_2Me_4 complexes arises from a larger metal–metal distance or a twisted biphenyl system. The question of M–M delocalization vs ligand-bridged delocalization in these systems remains open to debate and is the subject of ongoing studies with systems that are geometrically rigid.

Note Added in Proof. A recent paper on the dication of (biphenyl)bis[(benzene)chromium] is relevant to this work: Elschenbroich, C.; Heck, J.; Massa, W.; Birkhahn, M. *Chem. Ber.* **1990**, *123*, 2321.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen positional and thermal parameters (4 pages); a table of structure factors (19 pages). Ordering information is given on any current masthead page.

(39) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 952.
(40) Elschenbroich, C.; Stohler, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 174.
(41) Shu, C.-F.; Wrighton, M. S. *Inorg. Chem.* **1988**, *27*, 4326.
(42) Roberts, J. D. *Notes on Molecular Orbital Calculations*; W. A. Benjamin, Inc.: New York, 1966; Chapter 7.

Synthesis and Electrophilic Destannylation Reactions of Trimethylstannyl-Substituted Methyl Crotonates

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Four methyl(trimethylstannyl)crotonates have been prepared. Methyl (*E*)-2-(trimethylstannyl)crotonate and methyl (*E*)-3-(trimethylstannyl)crotonate were obtained from the Pd(0)-catalyzed hydrostannation of methyl-2-butynoate. Methyl (*Z*)-2-(trimethylstannyl)crotonate and methyl (*Z*)-3-(trimethylstannyl)-crotonate were obtained from the AIBN-catalyzed hydrostannation of the same alkynoic ester. Structures were confirmed by ^1H and ^{13}C NMR spectra. Reactivity in protodestannylation was determined from kinetic studies and the stereochemistry of the reaction determined by deuteriodestannylation. The 2-trimethylstannyl derivatives react by the allenol mechanism, while the 3-trimethylstannyl derivatives react by the normal S_E2 mechanism. Bromodestannylation of the four isomers is accomplished with retention of configuration. Methyl (*Z*)-3-(trimethylstannyl)crotonate is the least reactive to electrophilic destannylation, and methyl cleavage from tin is competitive with vinyl cleavage for reaction with both acid and bromine.

Introduction

In recent years the chemistry of vinylstannanes has received considerable interest from the standpoint of both synthesis and reactions. Hydrostannation of alkynes, when catalyzed by transition metals, results in good control of both the regiochemistry and stereochemistry of addition for a number of functionally substituted internal and terminal alkynes. We have recently shown that hydro-

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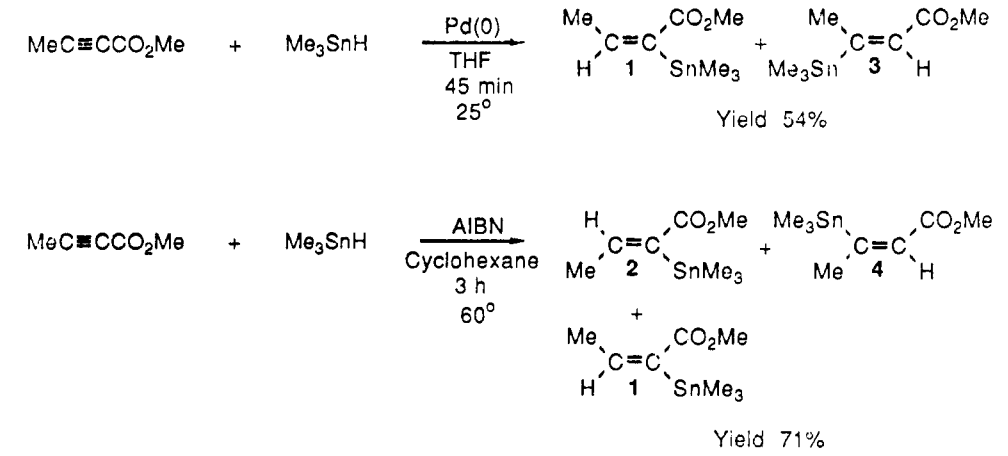
Scheme I



stannation with trimethylstannane, catalyzed by palladium(0), leads to predominantly syn addition of the stannyl group and hydrogen to the triple bond when conjugated to an ester carbonyl. On the contrary, when the carbonyl is a ketone, anti addition is preferred. In both cases the regiochemistry leads primarily to the stannyl group bonded to the vinyl carbon proximate to the carbonyl.[1] Oshima and co-workers have reported similar stereochemical results with triphenylstannane and triphenylgermane with a series of palladium catalysts.[2] Guibé and co-workers, in an extensive study, have reported hydrostannation of a number of alkynes by tributylstannane using either a palladium(II) or molybdenum(II) catalyst.[3] In some cases the catalysts were similar in their regiochemical and stereochemical control while in other cases they were complimentary and thus gave mixtures enriched with different isomers.

Transition-metal catalysis has also been successful for the addition of germylstannanes to allenes[4] and α,β-acetylenic esters[5] and disilanylstannanes to acetylene esters.[6] In the reaction with allenes, the regiochemistry of addition is dependent on the nature of the substituents at one terminus of the allene triad, with vinylstannanes predominating when the substituents are smaller. With α,β-acetylenic esters the reactions of tin–metal bonds are both regioselective and stereoselective.

Free radical hydrostannation of alkynes has shown to be considerably enhanced when carried out in the presence of high-intensity ultrasound.[7] These reactions are carried out in homogeneous media and in the absence of a free radical catalyst.

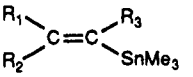
Vinylstannanes have been prepared by reaction of a number of stannylcopper species. Piers and Chong[8] have reported addition of $Me_3SnCu{\cdot}Me_2S$ to a number of terminal acetylenes to give 2-(trimethylstannyl)-1-alkenes. Higher order stannylcuprates add to allenes[9] and couple with vinyl triflates[10] to give, in both cases, vinylstannanes. Also Lipshutz and co-workers[11] have shown that vinylogous higher order stannylcuprates react with terminal epoxides to give β-hydroxy-(*E*)-vinylstannanes.

Organoboration of 1-stannylalkynes results in vinylstannanes in which the tin and boron are in a cis relationship.[12] Also alkyl groups are found to exchange between tin and boron. Finally, vinylstannanes have been prepared by coupling of tributyltin chloride with a β-sodium salt of an enol ether.[13]

Of the many reactions of vinylstannanes, the one which is most exploited is the palladium-catalyzed coupling between a vinylstannane and various substrates bearing reactive leaving groups.[14] Recent papers report coupling of vinylstannanes with aryl and vinyl triflates and halides,[15] allylic acetates and bromides,[16] acid chlorides and sulfonyl chlorides,[15f,17] perfluoroalkyl iodides,[18] and vinyl epoxides.[19] Also of current interest are reactions of vinylstannanes as precursors of vinylic–homoallylic donor–acceptor synthons,[20] higher order vinylcuprates,[21] and stannylaziridines.[22] Vinylstannanes have been shown to add P–H groups across the double bond,[23] undergo facile Claisen rearrangements,[24] undergo radical annulation to give

(1) (a) Cochran, J. C.; Williams, L. E.; Bronk, B. S.; Calhoun, J. A.; Fassberg, J.; Clark, K. G. *Organometallics* **1989**, *8*, 804. (b) Cochran, J. C.; Bronk, B. S.; Terrence, K. M.; Phillips, H. K. *Tetrahedron Lett.* **1990**, *31*, 6621.
(2) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468.
(3) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1957.
(4) Mitchell, T. N.; Schneider, U.; Frohling, B. *J. Organomet. Chem.* **1990**, *384*, C53.
(5) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1987**, 1025.
(6) Murakami, M.; Morita, Y.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 428.
(7) Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849.
(8) Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425.
(9) Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1030.
(10) Gilbertson, S. R.; Challener, C. A.; Bos, M. E.; Wulff, W. D. *Tetrahedron Lett.* **1988**, *29*, 4795.
(11) Behling, J. R.; Ng, J. S.; Babiak, K. A.; Campbell, A. L.; Elsworth, E.; Lipshutz, B. H. *Tetrahedron Lett.* **1989**, *30*, 27.
(12) Wrackmeyer, B.; Wagner, K.; Abu-Oradi, S. T. *J. Organomet. Chem.* **1988**, *346*, 333.
(13) Ley, S. V.; Wadsworth, D. J. *Tetrahedron Lett.* **1989**, *30*, 1001.
(14) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(15) (a) Krolski, M. E.; Renaldo, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170. (b) Cook, C. K.; Hornback, W. J.; Jordan, C. L.; McDonald, J. H.; Munroe, J. E. *J. Org. Chem.* **1989**, *54*, 5828. (c) Crisp, G. T.; Papadopoulos, S. *Aust. J. Chem.* **1989**, *42*, 279. (d) Stille, J. K.; Sweet, M. P. *Tetrahedron Lett.* **1989**, *30*, 3645. (e) Laborde, E.; Lesheski, L. E.; Kiely, J. S. *Tetrahedron Lett.* **1990**, *31*, 1837. (f) Parrain, J.-L.; Duchene, A.; Quintard, J.-P. *Tetrahedron Lett.* **1990**, *31*, 1857. (g) Martorell, G.; Garcia-Raso, A.; Saa, J. M. *Tetrahedron Lett.* **1990**, *31*, 2357. (h) Kwon, H. B.; McKee, B. H.; Stille, J. K. *J. Org. Chem.* **1990**, *55*, 3114.
(16) (a) Tolslikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Ya. L.; Spirikhin, L. V. *Synthesis* **1989**, 625. (b) Valle, L. D.; Stille, J. K.; Hegedus, L. S. *J. Org. Chem.* **1990**, *55*, 3019.
(17) (a) Labadie, S. S. *J. Org. Chem.* **1989**, *54*, 2496. (b) Colson, P.-J.; Franck-Neumann, M.; Sedrati, M. *Tetrahedron Lett.* **1989**, *30*, 2393.
(18) Matsubara, S.; Mitani, M.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857.
(19) Echavarren, A. M.; Tueting, D. R.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 4039.
(20) Piers, E.; Gavai, A. *J. Org. Chem.* **1990**, *55*, 2379.
(21) Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.
(22) Atkinson, R. S.; Kelly, B. *J. J. Chem. Soc., Chem. Commun.* **1989**, 836.
(23) Mitchell, T. N.; Belt, H.-J. *J. Organomet. Chem.* **1988**, *345*, C28.
(24) Ritter, K. *Tetrahedron Lett.* **1990**, *31*, 869.

Table I. Rate Constants for Protodestannylation



compd	R_1	R_2	R_3	10^3k_2[a]	k_{2rel}	10^3k_{pred}[b]
1	Me	H	CO_2Me	12.2	2.3	16.7
2	H	Me	CO_2Me	1.60	0.30	12.2
3	CO_2Me	H	Me	0.119	0.023	0.0821
4	H	CO_2Me	Me	0.015	0.0029	0.022
5[c]	H	H	H	5.26	1.0	
6[c]	H	H	Me	3.13	0.60	
7[c]	H	Me	H	108	21	
8[c]	Me	H	H	152	29	
9[d]	H	H	CO_2Me	0.570	0.11	
10[d]	H	CO_2Me	H	0.0368	0.007	
11[d]	CO_2Me	H	H	0.139	0.026	

[a] [Sn] = 1.00×10^{-3} M; [HCl] = 5.00×10^{-2} M; [H_2O] = 5% in MeOH. Agreement of rate constants from multiple runs was ±5% except for compound 4 for which the agreement was ±10%. In M^{-1} s^{-1}. [b] Calculated from the product of relative rate factors, for appropriately substituted vinylstannanes, and k_2 for 5. E.g., compound 1, $k_{pred} = 0.11 \times 29 \times 5.26 \times 10^{-3}$. [c] Reference 33. [d] Reference 1a.

functionalized cyclopentanes,[25] and produce radiopharmaceuticals from electrophilic destannylation.[26]

This last mentioned reaction of vinylstannanes, electrophilic displacement of the stannyl group, has been of considerable interest to us. In a previous paper we reported synthesis and protodestannylation of a number of carbomethoxy-substituted vinylstannanes,[1a] in which retention of configuration was observed when the stannyl group was vicinal to the carbonyl. On the other hand, when the stannyl group was geminal to the carbonyl, a mixture of isomeric products was formed. An allenol intermediate was proposed to account for the observed stereochmistry. In this paper we report the synthesis and electrophilic destannylation of the four isomeric trimethylstannyl-substituted methyl crotonates.

Results and Discussion

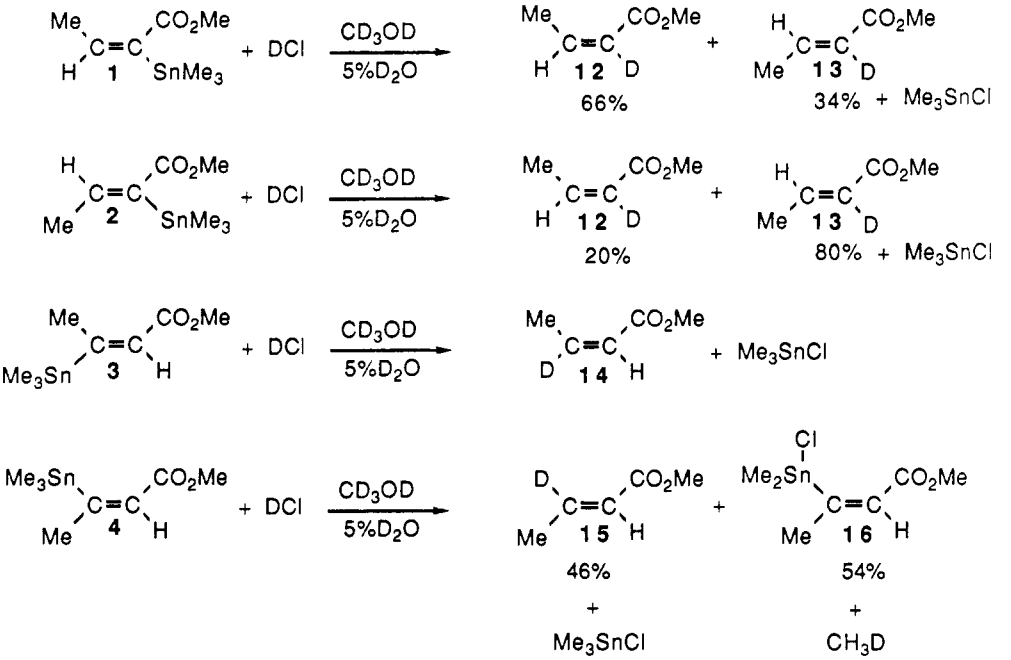
The four trimethylstannyl-substituted methyl crotonates were obtained from two hydrostannation routes (Scheme I). Two isomers, methyl (*E*)-2-(trimethylstannyl)crotonate (1) and methyl (*E*)-3-(trimethylstannyl)crotonate (3), were prepared in a 5:1 ratio by the palladium(0)-catalyzed hydrostannation of methyl 2-butynoate in THF. The combined yield was 45%, and the final product mixture was separated by preparative gas chromatography. Methyl (*Z*)-2-(trimethylstannyl)crotonate (2) and methyl (*Z*)-3-(trimethylstannyl)crotonate (4) were prepared in a 2:1 ratio by the AIBN-catalyzed hydrostannation of methyl 2-butynoate in cyclohexane. The combined yield was 71%, and the mixture was separated by preparative gas chromatography. In the latter reaction compound 1 was also present to a small extent (6%) in the product mixture. This product may have resulted from free radical catalyzed isomerization of 2. Leusink[27] observed a very similar overall yield and product ratio for the hydrostannation of the corresponding ethyl and butyl esters. His reaction temperature was slightly lower (50 °C) than ours, and his reaction times (~19–47 h) were considerably longer than ours (3 h). In the absence of a catalyst, in the dark and with galvinoxyl/THF, no addition product was obtained over a period of 120 h. Also a neat mixture of trimethylstannane and methyl 2-butynoate, when heated to 60 °C, gave a product mixture very similar to the free radical catalyzed process but at lower yield (44%) and over an extended reaction time (144 h).

Structures were assigned to the four isomers on the basis of ^1H and ^{13}C NMR spectra. The salient features of the ^1H spectra are the chemical shift of the vinyl proton, always greater when the proton is trans rather than cis to tin,[28] coupling constants of 6–7 and 1–2 Hz for the three-bond (compounds 1 and 2) and four-bond (compounds 3 and 4) methyl–vinyl hydrogen coupling, respectively, and the ^{13}C chemical shift of the vinyl carbon bearing tin, approximately 137 ppm for 1 and 2 and approximately 170 ppm for 3 and 4. This carbon was identified by the very large tin–carbon coupling of approximately 400 Hz. Tin–carbon coupling to the carbonyl carbon was largest when the groups were trans (93.2 Hz) in compound 3, intermediate when *gem* (44.2 and 42.6 Hz) in 1 and 2, and smallest when cis (22.8 Hz) in 4. A similar order was observed for tin–carbon carbon coupling to the methyl group. The largest coupling resulted when the groups were trans (47.7 Hz), while *gem* couplings (33.5 and 39.8 Hz) for 3 and 4 were similar to the value for cis coupling (33.6 Hz) in 2. This order, $^3J_{SnC(trans)} > {}^2J_{SnC(gem)} > {}^3J_{SnC(cis)}$, follows that reported for tin–hydrogen coupling.[29]

The chemical shift of the tin nucleus in a vinylstannane is quite susceptible to changes in the polarizability of the vinyl group caused by the electronic effects of the other substituents on the double bond. Also superimposed are the shielding effects of intermolecular or intramolecular coordination to a Lewis base site in the molecule. The δ values range over about 70 ppm for trimethylvinylstannanes.[30] The ^{119}Sn NMR spectra of 1–4 showed two sets of vaues: −17.0 ppm for 1 and 3 and about −42 ppm for 2 and 4. The peak at −41.1 ppm for 2 showed no shift to higher frequency when the sample was diluted 4-fold, indicating that intermolecular coordination to the carbonyl oxygen was not a contributing factor. Quintard and coworkers[31] reported chemical shifts for ethyl (tributylstannyl)crotonate derivatives of 1, 2, and 4 to be −32.9, −48.6, and −52.7 ppm, respectively. Likewise, Jousseaume and co-workers[32] found −47.9 and −57.6 ppm for the solution and solid-state ^{119}Sn NMR spectra of [2-(carbo-

(25) Curran, D. P.; van Elburg, P. A. *Tetrahedron Lett.* **1989**, *30*, 2501.
(26) (a) Musachio, J. L.; Lever, J. R. *Tetrahedron Lett.* **1989**, *30*, 3613. (b) Hanson, R. N.; El-Wakil, H. *J. Org. Chem.* **1987**, *52*, 3687.
(27) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285.
(28) (a) Leusink, A. J.; Marsman, J. W.; Budding, H. A. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 689. (b) Kuivila, H. G.; Rahman, W.; Fish, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 2835.
(29) Dehmas, M.; Maire, J. C.; Santamaria, J. *J. Organomet. Chem.* **1969**, *16*, 405.
(30) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73.
(31) Quintard, J.-P.; Dequeil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 27.
(32) Jousseaume, B.; Villeneuve, P.; Drager, M.; Roller, S.; Chezeau, J. M. *J. Organomet. Chem.* **1988**, *349*, C1.

Scheme II



methoxy)-1,4-cyclohexadien-1-yl]trimethyltin. ^{1}H, ^{13}C, and ^{119}Sn NMR data are found in the Experimental Section.

Continuing our study of reactivity of vinylstannanes with electrophiles,[1a,33] we have measured rate constants for the reactions of compounds 1–4 with HCl in CH_3OH/5% H_2O at 25 °C. These values, along with comparative rate constants from relevant previously studied vinylstannanes and relative rate factors based on compound 5, are found in Table I.

As we have seen, relative to hydrogen, a methyl group remote to tin is strongly activating for electrophilic substitution (×29 when trans, 8, and ×21 when cis, 7) and a methyl group proximate to tin is slightly deactivating (× 0.6, 6). The carbomethoxy group is deactivating regardless of its position, with the greater effect resulting when this group is remote (×0.026 when trans, 11, ×0.007 when cis, 10, and ×0.11 when *gem*, 9). The rate constants for the four isomeric stannyl-substituted methyl crotonates indicate the electronic (and possibly steric) effects of the substituent groups are essentially additive. For example, in compound 1, a trans methyl group and a *gem* carbomethoxy group would predict a rate constant value of 1.68 × 10^{-2} M^{-1} s^{-1} compared with the experimental value of 1.22 × 10^{-2} M^{-1} s^{-1}.[34] Likewise, rate constants for compounds 3 and 4 agree with the predicted values within a factor of 2. Compound 2 gives a predicted rate constant that is higher than the experimental value by a factor of about 8. While no reason for this difference seems evident, it should be noted that only in 2 is a hydrocarbon group cis to tin, and this group may disrupt the solvent cage around the stannyl group as it leaves and develops a positive charge. An alternate explanation involves separate effects on the relative rates of two competing protodestannylation processes (vide infra).

The stereochemistry of the electrophilic substitution was determined by substituting DCl for HCl (Scheme II). Reactions were run in methanol-d_4 containing excess DCl and approximately 4% water-d_2. The reactions were carried out in an NMR tube, and the structures of the products were assigned on the basis of proton–proton and proton–deuteron coupling. Since proton–deuteron couplings are small in magnitude (~15% of corresponding proton–proton coupling), these values were refined by simulation[35] of the vinyl proton signal until a reasonable match of line shape was realized.

Reaction of 1 with DCl resulted in two products: methyl (*Z*)-crotonate-2-d_1 (12), the product of retention of configuration, and methyl (*E*)-crotonate-2-d_1 (13), the product of inversion of configuration. The isomeric ratio, *Z*/*E*, was determined by integration of both the vinyl proton multiplets and the methyl proton doublets to be 66/34 ± 3. Likewise, reaction of 2 with DCl resulted in the same two products, 12 and 13, but in an isomeric ratio, *Z*/*E*, of 20/80 ± 5. In this case also the major product was that of retention of configuration, 13. The structure of compound 12 was assigned as the *Z* isomer from coupling of the vinyl proton with the methyl group and vinyl deuteron; $^{3}J_{HH}$ = 7.3 Hz and $^{3}J_{HD}$ = 1.8 Hz. Compound 13 was assigned the *E* configuration on the basis of coupling to the same proton; $^{3}J_{HH}$ = 6.8 Hz and $^{3}J_{HD}$ = 2.3 Hz.

Compound 3, with DCl, gives a single product, methyl (*Z*)-crotonate-3-d_1 (14). The structure was again assigned from the coupling constants of the vinyl proton, the values for which were $^{4}J_{HH}$ = 3.3 Hz and $^{3}J_{HD}$ = 1.6 Hz.

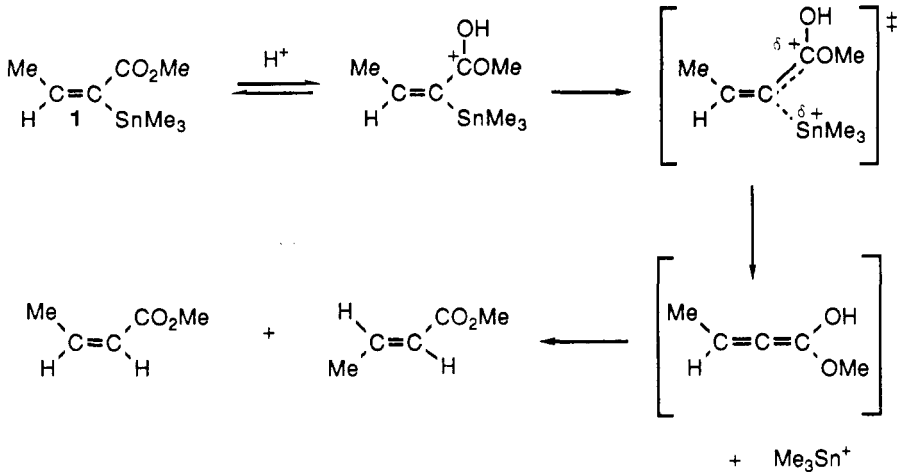
Compound 4 was considerably less reactive with DCl than the previously described isomers. The reaction took about 48 h to completion compared to minutes for 1 to about 24 h for 3. This is consistent with the relative values for the rate constants. When the reaction was complete, the ^{1}H NMR spectrum showed that the product mixture contained methyl (*E*)-crotonate-3-d_1 (15) and methyl (*E*)-3-(chlorodimethylstannyl)crotonate (16) in about equal amounts. Chlorotrimethylstannane and methane-d_1 were also present. The structure of 15 was assigned from coupling to the vinyl proton; $^{4}J_{HH}$ = 1.7 Hz and $^{3}J_{HD}$ = 2.3 Hz. Compound 16 gave peaks in the ^{1}H NMR spectrum at δ 0.62 ppm, $^{2}J_{SnH}$ = 73.1/70.3 Hz for the Me_2ClSn group,

(33) Cochran, J. C.; Bayer, S. C.; Bilbo, J. T.; Brown, M. S.; Colen, L. B.; Gaspirini, F. J.; Goldsmith, D. W.; Jamin, M. D.; Nealy, K. A.; Resnick, C. T.; Schwartz, G. J.; Short, W. M.; Skarda, K. R.; Spring, J. P.; Strauss, W. L. *Organometallics* **1982**, *1*, 586.

(34) See Footnote b, Table I.

(35) PANIC: An NMR simulation program that provides coupling constant parameter adjustment by iteration calculation. Supplied with Aspect 3000 NMR Software, Bruker Instruments, Inc.

Scheme III



δ 2.31 ppm, $^3J_{SnH}$ = 62.3 Hz for the methyl group, and δ 6.71 ppm, $^3J_{SnH}$ = 172.8 Hz. Comparison of this spectrum with that of compound **4** shows that substitution of a chlorine for methyl on tin is consistent with increased chemical shifts for the three proton signals and increased tin–proton coupling constants. In the case of **4**, the vinyl carbon–tin bond is sufficiently unreactive such that cleavage of a methyl carbon–tin bond is a competitive process. However, further cleavage of methyl groups was not observed, since all of the vinylstannane precursor was accounted for in the NMR spectrum of **15** and **16**. It should be noted that the rate constant listed for compound **4** in Table I is not factored to reflect competitive cleavage of the carbon–tin bonds. The assumption is made that substitution of a chlorine for methyl on tin will not lead to a significant perturbation of the ultraviolet absorption spectrum.[36] Since we follow the reaction at 250 nm, the shoulder of the peak, the decrease in absorbance, as a function of time, essentially reflects cleavage of vinyl carbon–tin bonds.

In a previous paper[1a] we demonstrated that protodestannylation of a vinylstannane, substituted in the remote position on the double bond with a carbomethoxy group, proceeds by a normal S_E2 mechanism. However, if the carbomethoxy group resides in the proximate position on the double bond, isomeric substitution products are formed. Since both the vinylstannane reactant and the products were configurationally stable under the reaction conditions, we proposed that the isomeric products were formed by attack of the proton (or deuteron) electrophile at the carbonyl oxygen, leading, with loss of the stannyl group, to an allenol intermediate. Transfer of the proton from oxygen to carbon from either face of allene leads to the *Z* and *E* isomeric substitution products (Scheme III).

We have extended this hypothesis in the study of the four trimethylstannyl-substituted methyl crotonates. Compounds **3** and **4**, in which the stannyl group is remote to the carbomethoxy group, exhibit the expected reactivity for a normal S_E2 reaction. Both substituents, proximate methyl and remote carbomethoxy are deactivating for electrophilic substitution and a single configurational isomer of methyl crotonate-d_1 is formed. In each case it is the product of retention of configuration. Substitution for a methyl group in **4** will be considered below.

When the stannyl and carbomethoxy groups are proximate, **1** and **2**, the remote methyl group is activating for a normal S_E2 mechanism while the carbomethoxy group is deactivating but provides the carbonyl for substitution by way of the allenol intermediate. It is difficult to predict the effects of the substituents on the reactivity of the vinylstannane in an S_E2 reaction compared to a reaction proceeding through an allenol intermediate. However, it would be unusual for the rates to be identical. The S_E2 reaction would predict 100% retention, while the allenol reaction predicts a 50/50 mixture of configurational isomers. Reaction of compound **1** gave a 66/34 mixture of isomers in which the product of retention was the major isomer. Compound **2** gave a 20/80 mixture of the same isomers, again the major product was that of retention of configuration. Therefore we propose that compounds **1** and **2** react by a combination of the S_E2 and allenol mechanisms. An alternative explanation for the unequal distribution of isomers is suggested by the observation of unequal rates of proton transfer from quenched copper allenolates, which were generated from the addition of dimethyllithiocuprates to α,β-acetylenic esters.[37]

Compound **4** is the only structure in which the carbomethoxy group is cis to the stannyl group. In this case, both substituents are deactivating for electrophilic substitution and thus the reactivity of the vinyl carbon–tin is very low. This isomer is also capable of forming a pentacoordinate tin by coordination with the carbonyl oxygen, a structure which has been demonstrated in the solid state.[32] Intramolecular coordination of this type has been proposed in a number of systems in which halodestannylation (vide infra) results in preferential alkyl cleavage from tin rather than cleavage of the usually more reactive vinyl,[28a,38] aryl,[39] or benzyl[40] groups. However, cleavage of the vinyl carbon–tin bond is noted exclusively when the electrophile is the proton or deuteron.[41] Whether the effect is deactivation by substituents on the

(36) Data relating substituents on tin to ultraviolet absorption spectra of vinylstannanes are scarce. However, Petukhov and co-workers have reported that the absorption spectra of trimethylvinylgermane and trichlorovinylgermane are practically identical in wavelength and molar absorptivity of the peak: Petukhov, V. A.; Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim (Eng. Transl.)* **1966**, 134.

(37) (a) Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851. (b) Siddall, J. B.; Biskup, M.; Fried, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1853. (c) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, *24*, 3951.

(38) Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 513.

(39) Al-Allaf, T. A. K.; Kobs, U.; Neumann, W. P. *J. Organomet. Chem.* **1989**, *373*, 29.

(40) Chopa, A. B.; Koll, L. C.; Podesta, J. C.; Mitchell, T. N. *J. Organomet. Chem.* **1989**, *376*, 283.

(41) Jousseaume, B.; Villeneuve, P. *J. Labelled Compd. Radiopharm.* **1988**, *25*, 717.

double bond or coordination by the vicinal carbonyl oxygen, cleavage of a methyl group occurs at a rate similar to cleavage of the vinyl group.

We have also studied electrophilic destannylation of the methyl crotonates by bromine in methylene-d_2 chloride as solvent. The reactions were run in an NMR tube and the products characterized by their ^1H NMR spectra.

Halodestannylation in vinyl systems has been shown to always take place with retention of configuration.[26b,42] However, in norbornyl systems, the stereochemistry of destannylation depends on the position of the stannyl: retention when exo and inversion when endo.[43] Benzylic systems are stereoselective for retention with increased inversion with more polar solvents.[40]

Bromodestannylation of the trimethylstannyl-substituted methyl crotonates proceeded with retention of configuration in each case although extensive isomerization of the product was noted in two cases. Compound **2** when treated with bromine at room temperature and at −20 °C, gave only methyl (*Z*)-2-bromocrotonate (**17**). The reaction was essentially instantaneous, as indicated by the disappearance of the bromine color. After standing at room temperature for 5 h, no change was noted in the ^1H NMR spectrum. The structure of **17** was assigned from the ^1H NMR spectrum, and the parameters agreed with previous assignments for this isomer.[44]

Compound **1** also gave a single product, methyl (*E*)-2-bromocrotonate (**18**) when treated with bromine at −20 °C. However, on warming to room temperature, **18** underwent complete isomerization to **17** over a period of 18 h. The structure of **18** was assigned from the ^1H NMR spectrum and agreed with a previously published spectrum.[44b] In both reactions, the stannyl group appeared at δ 0.75 ppm, $^2J_{SnH}$ = 58.3/55.9 Hz, which is characteristic for bromotrimethylstannane.

Compound **3**, on reaction with bromine at 0 °C, gave a single product. The reaction was complete within 30 s. The product was determined to be methyl (*E*)-3-bromocrotonate (**19**) on the basis of the ^1H NMR spectrum, the values of which agreed with a previously published spectrum.[45]

Compound **4**, with bromine, gave a much more complex reaction profile. Addition of the initial stoichiometric portion of bromine resulted in four products. More than 90% of the reaction mixture reflected cleavage of a methyl group, methyl (*Z*)-3-(bromodimethylstannyl)crotonate (**20**) and methyl bromide, while the remaining less than 10% represented cleavage of the vinyl carbon–tin bond, methyl (*Z*)-3-bromocrotonate (**21**) and bromotrimethylstannane. Addition of a second stoichiometric portion of bromine, at 0 °C, led primarily to cleavage of a second methyl group, yielding methyl (*Z*)-3-(dibromomethylstannyl)crotonate (**22**) and increased methyl bromide. Minor vinyl cleavage of **20** was evident from an increase in the amount of **21** and by the appearance of dibromodimethylstannane. Finally, a third stoichiometric portion of bromine resulted in complete vinyl cleavage, as shown by the presence of tribromomethylstannane and a 20/80 mixture of **21** and **19**. The bromodestannylation reactions of **1**–**4** are summarized in Scheme IV.

The reactions of compounds **1**–**4** with bromine in CD_2Cl_2 can be characterized by three features. First, all reactions involving cleavage of the vinyl carbon–tin bond take place with retention of configuration. Thus, the bromine attacks the π system of the carbon–carbon double bond and proceeds through a normal S_E2 mechanism. In contrast to bromodestannylation, protodestannylation of **1** and **2** involves attack of the proton at the carbon oxygen and the reaction proceeds, at least partially, through an allenol intermediate. The difference in the preferential site for attack by the electrophile can be explained by the hardness of the proton and carbonyl oxygen and softness of bromine and the carbon–carbon double bond.[46]

Second, two bromocrotonate products, **18** and **21**, were unstable under the reaction conditions and underwent isomerization to their geometric isomers. Acid-catalyzed isomerization of α,β-unsaturated acids has been reported;[47] however, the process in this case may be more complex because the Lewis acid catalyst is a stannyl halide or mixture of stannyl halides. No predictable pattern of the direction of isomerization was ascertained.

Finally, both bromine and DCl effected methyl cleavage in compound **4**. This reaction was the favored process with bromine and proceeded to remove two methyl groups before all of the vinyl carbon–tin bonds reacted. This is another example of deactivation of the vinyl carbon–tin bond by coordination with the remote carbonyl oxygen.[38]

In summary, we report the synthesis of the four trimethylstannyl-substituted methyl crotonates. We have determined their reactivity to protodestannylation and related the rate constants to those previously measured for similar compounds. Deuteriodestannylation allowed determination of the structure of the products and suggests that compounds **1** and **2** react simultaneously by S_E2 and allenol mechanisms while **3** and **4** react by an S_E2 mechanism. Bromodestannylation takes place also by an S_E2 mechanism. Compound **4** is unique in that the reactivity of the methyl groups on tin rivals the reactivity of the vinyl carbon–tin bond.

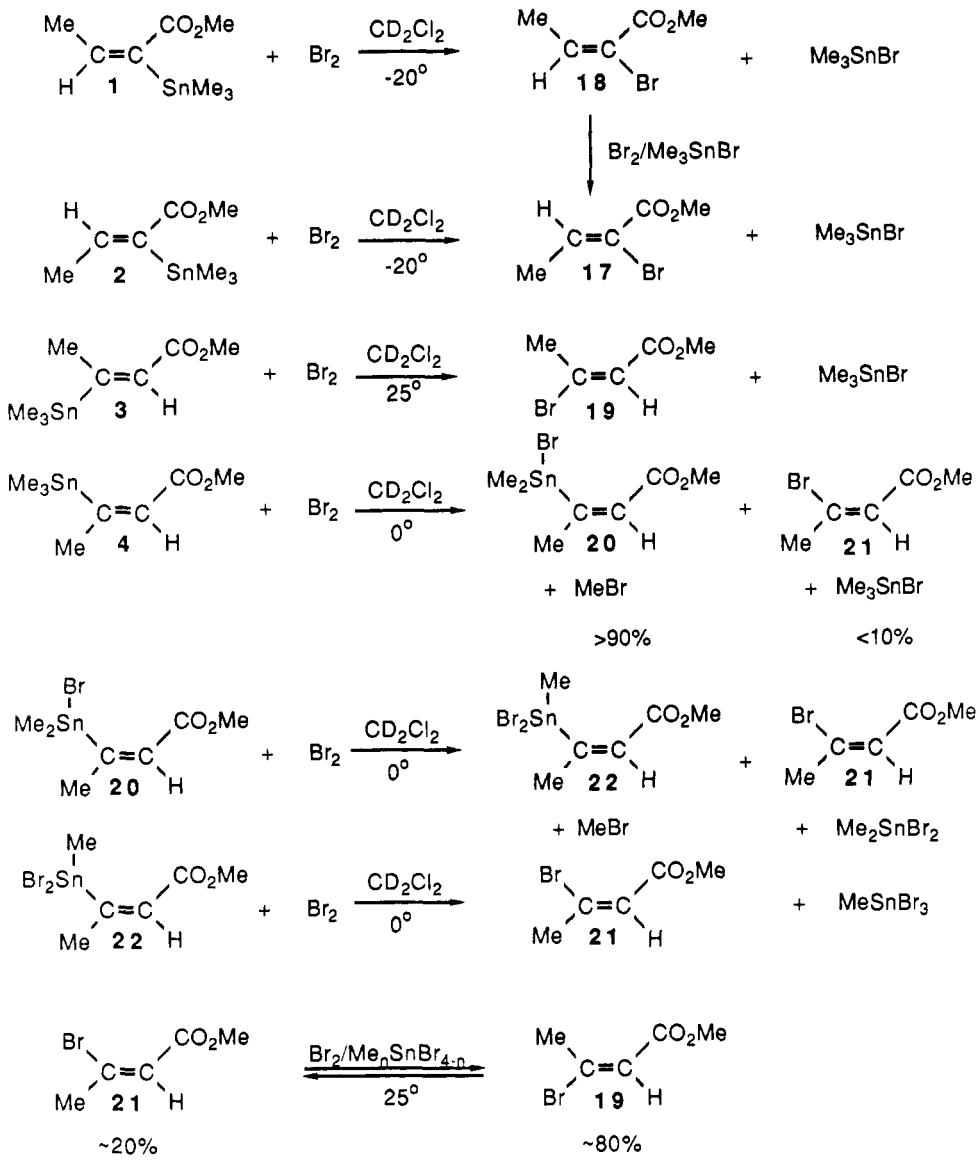
Experimental Section

General Information. Methyl 2-butynoate, methyl crotonate, tetrakis(triphenylphosphine)palladium(0), methanol-d_4, and deuterium chloride were obtained from Aldrich. Methyl 2-bromocrotonate was obtained from Fluka, and AIBN, from MCB. All compounds were used without further purification. Trimethylstannane was prepared by reaction of chlorotrimethylstannane with $LiAlH_4$ in dry tetraglyme,[48] followed by distillation to a liquid nitrogen cooled trap. THF was distilled from sodium/benzophenone ketyl, and cyclohexane was dried and stored over molecular sieves. ^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. Simulation of NMR spectra was performed by using PANIC, an iteration program supplied with the ASPECT 3000 system. IR spectra were recorded on a Perkin-Elmer Model 1310 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Pd(0)-Catalyzed Hydrostannation of Methyl 2-Butynoate. A three-necked flask was fitted with a magnetic stirrer, gas inlet, and a rubber septum. Methyl 2-butynoate (0.594 g, 6.06 mmol), dry THF (5 mL) and tetrakis(triphenylphosphine)palladium(0) (0.141 g, 0.122 mmol) were added, and the flask was swept with argon. Trimethylstannane (1.02 g, 6.19 mmol) in dry THF (10 mL) was added via syringe over a period of 0.5 h. After an additional 0.25 h of stirring, the IR spectrum of an aliquot showed the absence of the SnH stretching frequency at 1800 cm^{-1}, indicating the reaction was complete. The THF was removed on

(42) Baekelmans, P.; Gielen, M.; Malfroid, P.; Nasielski, J. *Bull. Chem. Soc. Belg.* **1968**, *77*, 85.
(43) Rahm, A.; Grimeau, J.; Pereyre, M. *J. Organomet. Chem.* **1985**, *286*, 305.
(44) (a) Klein, J.; Zitrin, S. *J. Org. Chem.* **1970**, *35*, 666. (b) Allan, R. D. *J. Chem. Res. Synop.* **1980**, 392.
(45) Brouwer, H.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 601.
(46) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A*; Plenum Press: New York, 1990; pp 230, 288.
(47) Nozaki, K.; Ogg, R. *J. Am. Chem. Soc.* **1941**, *63*, 2583.
(48) Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89.

Scheme IV



a rotary evaporator with care taken to maintain an argon atmosphere. Pentane (15 mL) was added and the mixture cooled to −10 °C to decrease the solubility of tetrakis(triphenylphosphine)palladium(0). The precipitate was filtered on a sintered glass funnel (porosity M), under an argon atmosphere, and the pentane was removed on a rotary evaporator. The resulting oil was distilled under reduced pressure in a Kugelrohr apparatus (57 °C, 0.1 Torr), yielding 0.860 g (54%) of a 5:1 mixture of **1** and **3**, which were separated by preparative GC (10 ft, 15% Carbowax 20M on Anakrom Q, 70/80 mesh).

Methyl (*E*)-2-(Trimethylstannyl)crotonate (1). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9 H, $^2J_{SnH}$ = 56.0/53.4 Hz), 2.05 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, $^4J_{SnH}$ = 4.8 Hz), 3.72 (s, 3 H), 6.27 (q, 1 H, $^3J_{HH}$ = 6.6 Hz, $^3J_{SnH}$ = 70.5/67.5 Hz). ^{13}C NMR: δ −8.9 ($SnMe_3$, $^1J_{SnC}$ = 362.6/346.9 Hz), 18.3 (=CMe, $^3J_{SnC}$ = 47.7 Hz), 51.2 (OMe), 136.7 (=CSn, $^1J_{SnC}$ = 409.6/393.7 Hz), 148.0 (=CH, $^2J_{SnC}$ = 17.7 Hz), 170.9 (C=O, $^2J_{SnC}$ = 44.2 Hz). ^{119}Sn NMR: δ −17.0. Anal. Calcd for $C_8H_{16}O_2Sn$: C, 36.54; H, 6.15. Found: C, 36.51; H, 6.26.

Methyl (*E*)-3-(Trimethylstannyl)crotonate (3). ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 9 H, $^2J_{SnH}$ = 55.0/52.5 Hz), 2.40 (d, 3 H, $^4J_{HH}$ = 1.9 Hz, $^3J_{SnH}$ = 50.8/48.5 Hz), 3.70 (s, 3 H), 6.00 (q, 1 H, $^4J_{HH}$ = 1.9 Hz, $^3J_{SnH}$ = 78.9/75.2 Hz). ^{13}C NMR: δ −10.0 ($SnMe_3$, $^1J_{SnC}$ = 347.7/332.7 Hz), 21.5 (=CMe, $^2J_{SnC}$ = 33.5 Hz), 50.8 (OMe), 127.4 (=CH, $^2J_{SnC}$ = 40.9 Hz), 164.8 (C=O, $^3J_{SnC}$ = 93.2 Hz), 168.6 (=CSn, $^1J_{SnC}$ = 407 Hz). ^{119}Sn NMR: δ −17.0. Anal. Calcd for $C_8H_{16}O_2Sn$: C, 36.54; H, 6.15. Found: C, 36.70; H, 5.86.

AIBN-Catalyzed Hydrostannation of Methyl 2-Butynoate. A three-necked flask was fitted with a magnetic stirrer, gas inlet, and rubber septum. Methyl 2-butynoate (1.18 g, 12.1 mmol), dry cyclohexane (10 mL), and AIBN (40 mg, 0.240 mmol) were added, and the flask was swept with argon. The mixture was heated to 60 °C and trimethylstannane (2.01 g, 12.2 mmol) in dry cyclohexane (5 mL) added dropwise via syringe. The reaction was monitored by IR spectrometry, and after 3 h the SnH stretching frequency at 1800 cm^{-1} was absent, indicating the reaction was complete. The cyclohexane was removed on a rotary evaporator and the resulting oil distilled in a Kugelrohr apparatus (62 °C, 0.1 Torr), yielding 2.10 g (71%) of mixture of **2**, **4**, and **1** in the ratio 10:6:1. The isomers were separated by preparative GC (10 feet, 15% Carbowax 20M on Anakrom Q, 70/80 mesh).

Methyl (*Z*)-2-(Trimethylstannyl)crotonate (2). ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9 H, $^2J_{SnH}$ = 56.4/54.0 Hz), 1.91 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, $^4J_{SnH}$ = 9.9 Hz), 3.70 (s, 3 H), 7.45 (q, 1 H, $^3J_{HH}$ = 6.9 Hz, $^3J_{SnH}$ = 117.3/112.5 Hz). ^{13}C NMR: δ −8.9 ($SnMe_3$, $^1J_{SnC}$ = 363.4/347.9 Hz), 19.3 (=CMe, $^3J_{SnC}$ = 33.6 Hz), 51.5 (OMe), 137.1 (=CSn, $^1J_{SnC}$ = 425.5/407.3 Hz), 152.6 (=CH, $^2J_{SnC}$ = 17.8 Hz), 171.9 (C=O, $^2J_{SnC}$ = 42.6 Hz). ^{119}Sn NMR: δ −41.1. Anal. Calcd for $C_8H_{16}O_2Sn$: C, 36.54; H, 6.15. Found: C, 36.50; H, 6.09.

Methyl (*Z*)-3-(Trimethylstannyl)crotonate (4). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9 H, $^2J_{SnH}$ = 56.2/53.5 Hz), 2.15 (d, 3 H, $^4J_{HH}$ = 1.5 Hz, $^3J_{SnH}$ = 45.1 Hz), 3.72 (s, 3 H), 6.40 (q, 1 H, $^4J_{HH}$ = 1.5 Hz, $^3J_{SnH}$ = 118.7/113.9 Hz). ^{13}C NMR: δ −7.8 ($SnMe_3$, $^1J_{SnC}$ = 369.4/352.9 Hz), 27.0 (=CMe, $^2J_{SnC}$ = 39.8 Hz), 51.4 (OMe), 128.5 (=CH, $^2J_{SnC}$ = 14.0 Hz), 168.2 (C=O, $^3J_{SnC}$ = 22.8 Hz), 171.7 (=CSn, $^1J_{SnC}$ = 401.8/385.4 Hz). ^{119}Sn NMR: δ −42.3. Anal. Calcd for $C_8H_{16}O_2Sn$: C, 36.54; H, 6.15. Found: C, 36.71; H, 6.14.

Kinetic Studies. Measurements were performed on a Beckman DU-Gilford spectrophotometer equipped with a cell compartment thermostated at 25.0 °C. The glassware preparation and solution manipulation have been previously described.[33] 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 at 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, except for **4**, which was followed through about 1 half-life. Rate constants were derived from a nonlinear least-squares fit of the absorbance/time data.

Reactions of 1–4 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 was added 0.2 mL of 12 M DCl in D_2O. ^1H NMR spectra were obtained at appropriate intervals until the reactions were complete. Total reaction times varied from 2 min for **1** to 40 h for **4** at room temperature. A mixture of *trans*-methyl crotonate, chlorotrimethylstannane, and DCl in CD_3OD was shown to be configurationally stable, as indicated by the ^1H NMR spectrum.

Bromodestannylation of 1. Methyl (*E*)-2-(trimethylstannyl)crotonate (100 mg, 0.381 mmol) was placed in an NMR tube and cooled to −20 °C. To the tube was added 0.5 mL of 0.761 M (0.381 mmol) Br_2 in CD_2Cl_2, which had been precooled to −20 °C. The bromine color disappeared immediately. The ^1H NMR spectrum, run at −20 °C, showed two products, methyl (*E*)-2-bromocrotonate (**18**) [^1H NMR (CD_2Cl_2): δ 2.05 (d, 3 H, $^3J_{HH}$ = 7.6 Hz), 3.80 (s, 3 H), 6.84 (q, 1 H, $^3J_{HH}$ = 7.6 Hz)] and bromotrimethylstannane [^1H NMR (CD_2Cl_2): δ 0.77 (s, 9 H, $^2J_{SnH}$ = 58.3/56.0 Hz)]. After standing at room temperature for 18 h, the former product isomerized to >99% methyl (*Z*)-2-bromocrotonate (**17**) (^1H NMR spectrum below).

Bromodestannylation of 2. This reaction was carried out by the method described above for **1**. The products were methyl (*Z*)-2-bromocrotonate (**17**) [^1H NMR (CD_2Cl_2): δ 1.94 (d, 3 H, $^3J_{HH}$ = 6.8 Hz), 3.79 (s, 3 H), 7.37 (q, 1 H, $^3J_{HH}$ = 6.8 Hz)] and bromotrimethylstannane [^1H NMR (CD_2Cl_2): δ 0.75 (s, 9 H, $^2J_{SnH}$ = 58.3/56.0 Hz)]. On standing for 12 h at room temperature, no change was noted in the NMR spectrum.

Bromodestannylation of 3. This reaction was carried out by the method used for compounds **1** and **2** except that the temperature was maintained at 0 °C. The loss of bromine color was immediate, and the ^1H NMR spectrum (at ambient temperature) determined the products to be methyl (*E*)-3-bromocrotonate (**19**) [^1H NMR (CD_2Cl_2): δ 2.76 (d, 3 H, $^4J_{HH}$ = 1.2 Hz), 3.68 (s, 3 H), 6.33 (q, 1 H, $^4J_{HH}$ = 1.2 Hz)] and bromotrimethylstannane [^1H NMR (CD_2Cl_2): δ 0.75 (s, 9 H, $^2J_{SnH}$ = 58.0/55.8 Hz). After standing for 18 h at room temperature, the spectrum was unchanged.

Bromodestannylation of 4. This reaction was carried out by the procedure used for compound **3** except that a second portion of bromine was added after 1 h and a third portion after 60 h. The initial addition of bromine in CD_2Cl_2 resulted in a distinctly slower loss of color. After 20 min, the ^1H NMR spectrum showed that no starting material remained and four products were present. The major products (>90%) were methyl (*Z*)-3-(bromodimethylstannyl)crotonate (**20**) [^1H NMR (CD_2Cl_2): δ 0.80 (s, 6 H, $^2J_{SnH}$ = 71.7/68.7 Hz), 2.39 (d, 3 H, $^4J_{HH}$ = 1.8 Hz, $^3J_{SnH}$ = 62.7 Hz), 3.85 (s, 3 H), 6.63 (q, 1 H, $^4J_{HH}$ = 1.8 Hz, $^3J_{SnH}$ = 173.2/165.5 Hz)] and methyl bromide [^1H NMR (CD_2Cl_2): δ 2.7]. The minor products (<10%) were methyl (*Z*)-3-bromocrotonate (**21**) [^1H NMR (CD_2Cl_2): δ 2.46 (d, 3 H, $^4J_{HH}$ = 1.2 Hz), 3.71 (s, 3 H), 6.30 (q, 1 H, $^4J_{HH}$ = 1.2 Hz)] and bromotrimethylstannane [^1H NMR (CD_2Cl_2): δ 0.75 (s, 9 H, $^2J_{SnH}$ not observed)]. A second portion of bromine was added and the reaction mixture allowed to stand at room temperature, in the dark, for 60 h. The ^1H NMR spectrum showed the previously observed products of methyl cleavage and vinyl cleavage. Also present were methyl (*Z*)-3-(dibromoethylstannyl)crotonate (**22**) [^1H NMR (CD_2Cl_2): δ 1.45 (s, 3 H, $^2J_{SnH}$ = 85.9/82.5 Hz), 2.41 (d, 3 H, $^4J_{HH}$ = 1.8 Hz), 3.95 (s, 3 H), 6.68 (q, 1 H, $^4J_{HH}$ = 1.8 Hz, $^3J_{SnH}$ = 260 Hz)], methyl (*E*)-3-bromocrotonate (**19**) [^1H NMR (CD_2Cl_2): δ 2.76 (d, 3 H, $^4J_{SnH}$ = 1.3 Hz), 3.69 (s, 3 H), 6.34 (q, 1 H, $^4J_{HH}$ = 1.3 Hz)], and dibromodimethylstannane [^1H NMR (CD_2Cl_2): δ 1.40 (s, 6 H, $^2J_{SnH}$ = 67.3/64.3 Hz)]. A third portion of bromine was added and the reaction allowed to stand overnight at room temperature, in the dark. The ^1H NMR after 84 h showed the presence methyl (*E*)-3-bromocrotonate (**19**) (major), methyl (*Z*)-3-bromocrotonate (**21**) (minor), dibromodimethylstannane, methyltribromostannane [^1H NMR (CD_2Cl_2): δ 1.94 (s, 3 H, $^2J_{SnH}$ = 90.2/86.2 Hz)], and methyl bromide.

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