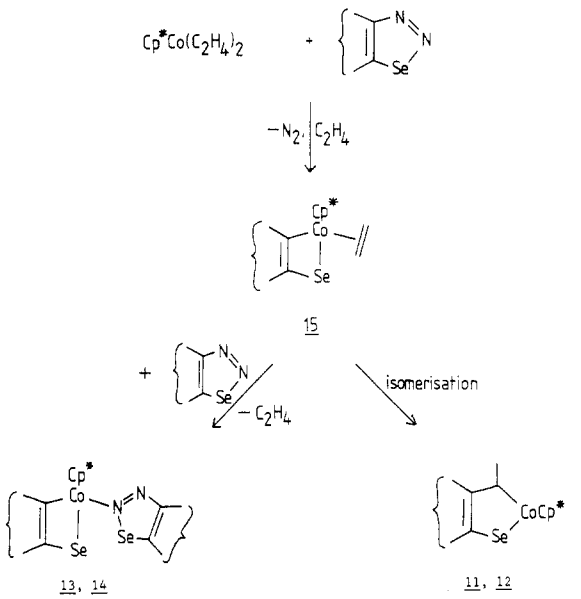
Scheme II



general too complex to be interpreted (see Table II). ^{13}C NMR spectroscopy is more useful. For example, in the ^{13}C NMR spectrum of **14** the expected eighteen resonances are observed. Particularly informative are the peaks corresponding to the quaternary carbons in the eight-membered rings. In **14** these are found at δ 122.1, 159.2, 159.5, and 160.5; in **10** they are at δ 117.8 and 150.3 and in **6** are at δ 159.2 and 161.0. Peaks characteristic of both the $C_8H_{12}Se$ ligand and the $C_8H_{12}SeN_2$ molecule are therefore present in the ^{13}C NMR spectrum of **14**. The presence of an intact 1,2,3-selenadiazole ligand in these compounds was confirmed by infrared spectroscopy (see Table III)—there is a medium-to-strong band at ca. 1540 cm^{-1} which may be assigned to a N=N stretching mode (this band occurs at ca. 1515 cm^{-1} in free 1,2,3-selenadiazoles).

The two types of product resulting from reaction of 1,2,3-selenadiazoles with **2** may both be derived from the same hypothetical intermediate **15** (see Scheme II). Displacement of ethene by an intact 1,2,3-selenadiazole molecule leads to products like **13** and **14**; isomerization via a succession of olefin insertion and β-elimination steps leads to products like **11** and **12**. Which pathway is preferred appears to depend on the degree of unsaturation in the bicyclic 1,2,3-selenadiazole. That the preference is never strong is evidenced by the moderate yields obtained of any one particular product, and other reaction pathways probably also compete. No binuclear products analogous to **7–10** are formed presumably because of the steric effect of the pentamethylcyclopentadienyl ligand.

It is clear that a range of interesting and unusual complexes may be formed from 1,2,3-selenadiazoles. Work is now in progress to examine the reactivity of these novel compounds.

Acknowledgment. We thank Herrn K. Steines for experimental assistance and the Max-Planck-Gesellschaft for the provision of a stipendium.

Protodestannylation of Carbomethoxy-Substituted Vinylstannanes: Kinetics, Stereochemistry, and Mechanisms

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Five carbomethoxy- and four carboethoxy-substituted vinylstannanes have been prepared. Methyl 2-(trimethylstannyl)acrylate and ethyl 2-(trimethylstannyl)acrylate were prepared by hydrostannation of methyl and ethyl propiolate under polar conditions. The former compound was also prepared by Pd(0) catalyzed hydrostannation of methyl propiolate. The *E* and *Z* isomers of methyl and ethyl 3-(trimethylstannyl)acrylate were prepared by free radical hydrostannation of methyl and ethyl propiolate. Methyl and ethyl 2-(trimethylstannyl)fumarate were synthesized by hydrostannation of dimethyl and diethyl acetylenedicarboxylate under polar conditions. Methyl 2-(trimethylstannyl)maleate was prepared by Pd(0)-catalyzed hydrostannation of dimethyl acetylenedicarboxylate. Structures were confirmed by ^1H and ^{13}C NMR. The stereochemistry of stannyl cleavage was determined by deuteriodestannylation and ^1H NMR of the products. The methyl 3-(trimethylstannyl)acrylate isomers gave retention of configuration while the methyl 2-(trimethylstannyl)fumarate and -maleate resulted in approximately equal ratios of isomeric deuteriodestannylation products. In this latter case an allenol intermediate is proposed. Second-order rate constants for protodestannylation, in methanol–5% water, were determined at three temperatures for the carbomethoxy compounds. Activation parameters were calculated from the rate data. The carbomethoxy group was found to be deactivating for all compounds except methyl 2-(trimethylstannyl)maleate. In this case, interaction of the syn carbomethoxy groups may serve to provide a more reactive route to the allenol intermediate.

Introduction

In recent years there has been considerable interest in the synthesis and reactions of vinylstannanes. Methods have been developed which provide both regioselectivity and stereoselectivity in the preparation of vinylstannanes through additions to an alkyne. Early work by Neumann[1] and Leusink[2] showed that hydrostannation can take place either by a free radical mechanism or, in the presence of appropriate electron-withdrawing substituents, by a polar mechanism. The mechanism of addition can determine the regiospecificity, but the initial addition of tin and

(1) Neumann, W. P.; Sommer, R. *Leibigs Ann. Chem.* **1964**, *675*, 10.

(2) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295.

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hydrogen in both mechanisms is anti. However, under free radical conditions considerable isomerization at the double bond is usually observed.[3] When a proton source, such as methanol as solvent, is available, the polar mechanism leads to addition of dihydrogen to the triple bond.[4]

Free radical hydrostannation of alkynes with an alcohol or ether function in the propargyl position results in regiospecificity which depends on whether the triple bond is terminal or internal. In the terminal case the predominant or exclusive product arises from attack of the tin radical at the terminal carbon[5a,b] while in the internal case the tin radical is directed to the carbon proximate to the propargyl alcohol or ether.[5a,c] The stereochemistry of the initial product is the result of anti addition, but excess tin hydride, high temperatures, and protracted reaction times lead to mixtures of stereoisomers.[5c] Similar regioselectivity is obtained, under free radical conditions, in the triethylborane-catalyzed hydrostannation of carbon–carbon triple bonds.[6] The tin radical again attacks the terminal carbon with or without a proparglylic oxygen function. In the case of 1,6-enynes, cyclization of the intermediate vinylstannane radical to a five-member ring results. Mixtures of stereoisomers are usually observed. Hydrostannation, catalyzed by palladium(II), favors syn addition to carbon–carbon triple bonds, and mixtures of regioisomers are frequently obtained.[7]

Vinylstannanes have been prepared by palladium(0)-catalyzed addition of hexamethyldistannane[8] and (trimethylsilyl)trimethylstannane[9] to terminal carbon–carbon triple bonds. The addition is syn in each case; however, thermal isomerization, especially in the presence of the catalyst, or photochemical isomerization is observed. Addition of the silylstannanes is regiospecific with the silyl group attached at the terminal carbon of the alkene and the stannyl group attached at the adjacent olefinic carbon.

Versatility in both the methods of preparation of vinylstannanes and of the compounds themselves is illustrated in the addition of bimetallic species, in which one metallic group is stannyl, to triple bonds. Several stannylcuprate reagents undergo conjugate addition to α,β-acetylenic esters.[10] The reaction is successful with both terminal and internal triple bonds and is regiospecific. Stereochemical control of the vinylstannane is a function of the stannyl cuprate, the substrate, and the temperature. Although electrophilic replacement of the cuprate group is only accomplished by a proton,[11] further elaboration of the molecule can take place through the ester function. A very useful variation on this process is the diaddition of two stannyl groups to α,β-acetylenic esters when an excess of stannylcuprate reagent is used.[12] The stannyl group proximate to the ester is more reactive in transmetalation with methyllithium and affords a second route to elaboration of the molecule.

Bimetallic additions to triple bonds have been successful for stannylzinc, stannylmagnesium, and stannylaluminum compounds[13] and stannyl-B-OMe-9-BBN.[14] In all cases the addition is syn and mixtures of regioisomers are obtained. In the former reaction the zinc, magnesium, or aluminum are replaced by a proton in the workup while in the latter, boron can be replaced by a number of carbon electrophiles.

Substitution methods for the preparation of vinylstannanes include the use of $PhS(Me_3Sn)CuLi$ with a number of β-iodo-α,β-unsaturated cyclic ketones[15] and Bu_3SnCu with β-halo or -tosyl acrylates.[16] Presumably these reactions involve an addition elimination process. In each case the stannyl group is placed in the position from which the leaving group departed. A similar method involves the Pd(0)-catalyzed coupling of enol triflates with the trimethylstannyl group provided by hexamethyldistannane.[17] With unsymmetrical ketones the regiospecificity of the vinylstannane is dependent upon the ability to selectively prepare kinetic and thermodynamic enolates. Finally homolytic substitution for a sulfone group has been accomplished by reaction with tributylstannane at 140 °C.[18] No mention is made of stereochemistry, but the reaction is regiospecific.

Synthetic applications of vinylstannanes have increased dramatically in recent years with the discovery that these compounds are among the several R_3SnR' derivatives which, in the presence of a palladium(0) or palladium(II) catalyst, will transfer a single group (R') from tin to carbon.[19] The vinyl group from a vinylstannane will replace a halogen bonded to acyl, allyl, vinyl, or aryl substrates. Enol and aryl triflates are also easily replaced. A further elaboration of the palladium-catalyzed coupling process involves insertion of a carbonyl, from carbon monoxide, between the carbon substrate and the vinyl group from tin.[19f] Again the group replaced on carbon is a halide or a triflate. In all cases the regiochemistry and the stereochemistry of the vinylstannane are preserved.

Other useful synthetic processes involving vinylstannanes include transmetalation with alkylithiums, yielding substituted vinyllithiums for further elaboration,[10,12,20] Diels–Alder reactions in which the vinylstannane acts as dienophile,[21] conversion to substituted cyclobutanes

(3) (a) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616. (b) Leusink, A. J., Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *11*, 541. (c) Cochran, J. C.; Leusink, A. J.; Noltes, J. G. *Organometallics* **1983**, *2*, 1099.

(4) Quintard, J.-P.; Pereyre, M. *J. Organomet. Chem.* **1972**, *42*, 75.

(5) (a) Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.* **1982**, *47*, 404. (b) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. (c) Nativi, C.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 820.

(6) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547.

(7) Zhang, H. X.; Guibe, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, *29*, 619.

(8) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45.

(9) (a) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354. (b) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

(10) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905 and references therein.

(11) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184.

(12) Piers, E.; Chong, J. M. *J. Org. Chem.* **1982**, *47*, 1602.

(13) (a) Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716. (b) Matsubara, S.; Hibino, J.-I.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163.

(14) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1988**, *29*, 261.

(15) Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1033.

(16) Seitz, D. E.; Lee, S.-H. *Tetrahedron Lett.* **1981**, *22*, 4909.

(17) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 279.

(18) Watanabe, Y.; Ueno, Y.; Araki, T.; Endo, T.; Okawara, M. *Tetrahedron Lett.* **1986**, *27*, 215.

(19) For reviews see: (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47. Recent reports: (c) Pena, M. R.; Stille, J. K. *Tetrahedron Lett.* **1987**, *28*, 6573. (d) Solberg, J.; Undheim, K. *Acta Chem. Scand.* **1987**, *41B*, 712. (e) Katsumura, S.; Fujiwara, S.; Isoe, S. *Tetrahedron Lett.* **1988**, *29*, 1173. (f) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1557. (g) Renaldo, A. F.; Ito, H. *Synth. Commun.* **1987**, *17*, 1823. (h) Haack, R. A.; Penning, T. D.; Djuric, S. W.; Dziuba, J. A. *Tetrahedron Lett.* **1988**, *29*, 2783.

(20) (a) Corey, E. J.; Wollenberg, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5581. (b) Wollenberg, R. H.; Albizati, K. F.; Peries, R. *J. Am. Chem. Soc.* **1977**, *99*, 7365. (c) Chen, S.-M. L.; Schaub, R. E.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3450. (d) Collins, P. W.; Jung, C. J.; Gasiecki, A.; Pappo, R. *Tetrahedron Lett.* **1978**, 3187.

(21) Rahm, A.; Ferkous, F.; Degueil-Castaing, M.; Jurczak, J.; Golebiowski, A. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 937.

Table I. ^{13}C NMR Data for Compounds 1a-5a[a,b]

compd	C_p	C_r	$(C=O)_p$	$(C=O)_r$	$SnMe_3$	OMe	$^1J_{SnC_p}$	$^2J_{SnC_r}$[c]	$^2J_{Sn(C=O)_p}$[c]	$^3J_{Sn(C=O)r}$[c]	$^1J_{SnMe_3}$
1a	145.8	139.5	170.1		-9.1	51.7	403.7/386.6	59	42		367.0/351.4
2a	158.1	134.5		167.8	-7.8	51.6	392.7/376.0	69		28	375.8/359.8
3a	152.4	135.6		165.2	-9.7	51.6	378.6/360.4	67		n.o.[d]	364.1/348.9
4a	161.2	134.4	167.2	171.9	-6.7	52.1 51.0	305.9/291.8	67	74	30	385.3/368.6
5a	158.2	128.8	163.5	172.2	-8.9	51.7 51.6	266.8/256.0	67	61	26	367.6/351.3

[a] $CDCl_3$, 75.45 MHz. Coupling constants in hertz. Chemical shifts in ppm are referenced to the central peak of $CDCl_3$ triplet at 77.00 ppm. [b] C_p and $(C=O)_p$ refer to the olefinic and carbonyl carbons proximate to the stannyl group. C_r and $(C=O)_r$ refer to the olefinic and carbonyl carbons remote to the stannyl group. [c] $^{119}Sn/^{117}Sn$ coupling unresolved. [d] n.o. = not observed.

in which the stereochemistry of the vinylstannane is translated to the ring substituents,[22] use of vinylstannanes as substrates for the study of free radical chain addition–elmination reactions,[23] and stereospecific preparation of radiolabeled steroids by electrophilic destannylation of a vinylstannane side chain.[24] Electrophiles include H^+, D^+, I_2, Br_2, and PhSeBr.

This last mentioned reaction of vinylstannanes, electrophilic displacement of the stannyl group, has been of considerable interest to us. In a previous paper[25] we presented kinetic and activation parameter evidence to show that protodestannylation at an olefinic carbon proceeds through an "open" type transition state[26] with substantial solvent participation to stabilize the developing positive charge on tin. We also determined that cleavage of a phenyl group takes place preferentially to a vinyl group and that for one vinylstannane the reaction proceeds with retention of configuration at the double bond.

In this paper we have extended our study of protodestannylation to vinylstannanes in which the vinyl moiety is substituted by carbomethoxy groups. The initial intent was to determine substituent effects in a system in which a carbonium ion intermediate[27] would be unlikely. In the preparation of the stannyl acrylates we have been able to separate the ionic and free radical addition of trimethylstannane to methyl propiolate and to add trimethylstannane stereospecifically to dimethyl acetylenedicarboxylate to give the corresponding fumarate and maleate isomers. We have determined rate constants for protodestannylation at 25, 35, and 45 °C, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and the stereochemistry of deuteriodestannylation in appropriate cases.

Results and Discussion

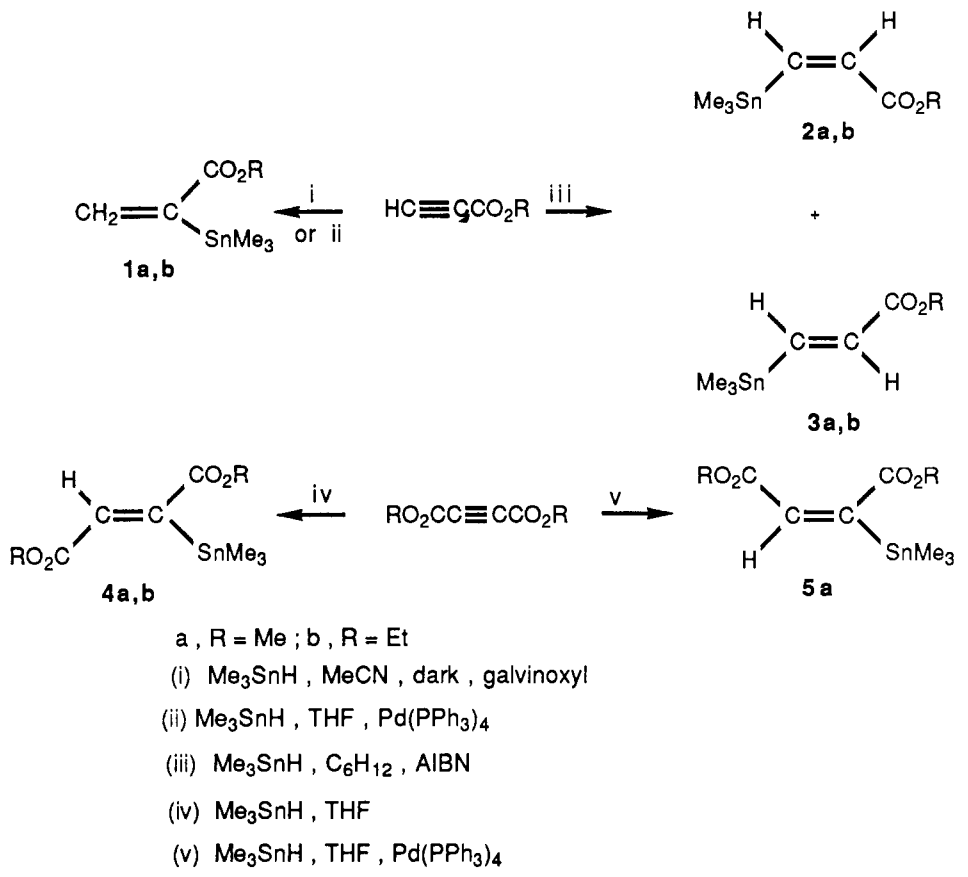
In our study of protodestannylation it was necessary to prepare pure regio- and stereoisomers of the carbomethoxy-substituted vinylstannanes. Three isomers of methyl trimethylstannylacrylate are available from neat hydrostannation of methyl propiolate. However, we were unable to separate, by gas chromatography, methyl 2-(trimethylstannyl)acrylate (**1a**) and methyl (*Z*)-3-(trimethylstannyl)acrylate (**2a**). Similar problems were encountered for the corresponding ethyl esters, **1b** and **2b**, and also were reported by Jung and Light.[5b] On the basis of the work of Leusink and co-workers,[2] we suspected that **1a** and **1b** were formed by hydride attack at the terminal carbon of triple bond, **2a** and **2b** were formed by trimethylstannyl radical attack at the same carbon, and the corresponding *E* isomers **3a** and **3b** resulted from free radical isomerization of **2**. Thus we were able to separate the ionic and free radical processes. When the addition was carried out in acetonitrile, in the dark and in the presence of galvinoxyl, compound **1** was the only product. Using cyclohexane as the solvent and AIBN as the catalyst, a separable mixture of **2** and **3** was obtained. Thus the regiospecificity is a function of the mechanism and can be controlled by polarity of the solvent and the appropriate catalyst or inhibitor. Both methyl and ethyl esters gave similar results differing only in the *Z*/*E* ratio from the free radical addition and subsequent isomerization; *Z*/*E* = 4/1 for the methyl ester and *Z*/*E* = 3/2 for the ethyl ester.

Hydrostannation without solvent of dimethyl acetylenedicarboxylate afforded a 9/1 mixture of dimethyl 2-(trimethylstannyl)fumarate (**4a**) and dimethyl 2-(trimethylstannyl)maleate (**5a**). We were unable to separate this mixture by gas chromatography and attempts to alter the ratio by AIBN or UV/trimethylstannane catalyzed isomerization of **4a** to **5a** led only to polymerization. However, we were able to effect a stereoselective addition of trimethylstannane to dimethyl acetylenedicarboxylate in THF to produce **4a** in 84% yield with less than 2% contamination by **5a**, as determined by ^1H NMR. Lower yields (40–70%) of **4a** were obtained when acetonitrile, cyclohexane, or benzene was used as solvent.

Since we were unable to obtain dimethyl 2-(trimethylstannyl)maleate (**5a**) from isomerization of **4a**, we explored palladium(0) catalysis of hydrostannation of these carbomethoxy-substituted carbon–carbon triple bonds. Four and Guibe[28] reported that various palladium species catalyze the reduction of acyl chlorides to aldehydes with tributystannane. When a conjugated double bond was present, the saturated aldehyde was a minor product. The addition of trimethylstannane to dimethyl acetylenedicarboxylate in THF, catalyzed by tetrakis(triphenylphosphine)palladium(0), gives as the only product, dimethyl 2-(trimethylstannyl)maleate (**5a**) in 68% yield. The addition is stereospecific and is syn. When this same catalyst was applied to the addition of trimethylstannane to methyl propiolate, the sole product was methyl 2-(trimethylstannyl)acrylate (**1a**). These reactions suggest that hydrostannations catalyzed by tetrakis(triphenylphosphine)palladium(0) are both stereospecific, giving syn addition, and regiospecific, with the stannyl group directed to the carbon α to the carbonyl.[29] The reactions described

(22) Piers, E.; Lu, Y.-F. *J. Org. Chem.* **1988**, *53*, 926.
(23) Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I. *Organometallics* **1988**, *7*, 696.
(24) Hanson, R. N.; El-Wakil, H. *J. Org. Chem.* **1987**, *52*, 3687.
(25) 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.
(26) (a) Baekelmans, P.; Gielen, M.; Malfroid, P.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1968**, *77*, 85. (b) Abraham, M. H.; Spalding, T. R. *J. Chem. Soc. A* **1969**, 399.
(27) A two-step addition elimination mechanism has been proposed for protodestannylation of phenyl substituted β-styryltrimethylstannanes: Alvanipour, A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *201*, 233.
(28) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.
(29) Guibe and co-workers[7] recently reported catalysis by $PdCl_2(PPh_3)_2$ for the addition of tributylstannane to several acetylenes including methyl propiolate and dimethyl acetylenedicarboxylate. They observe the opposite regiospecificity with the former acetylene and both stereoisomers with the latter.

Scheme I



a , R = Me ; b , R = Et

(i) Me_3SnH , MeCN , dark , galvinoxyl

(ii) Me_3SnH , THF , $Pd(PPh_3)_4$

(iii) Me_3SnH , C_6H_{12} , AIBN

(iv) Me_3SnH , THF

(v) Me_3SnH , THF , $Pd(PPh_3)_4$

above are shown in Scheme I.

The structures of compounds 1–5 were established by ^1H NMR and ^{13}C NMR. The ^1H NMR spectral data are given for each compound in the Experimental Section, and good agreement was obtained with the data of Leusink[30] and Quintard.[31] The structure assignments were based on the $^2J_{HH}$ and $^3J_{HH}$ coupling constants and $^{119/117}Sn$ coupling to the olefinic hydrogens. These data are consistent with the observation that in vinylstannanes, $^3J_{SnH(trans)} > {}^2J_{SnH(gem)} > {}^3J_{SnH(cis)}$,[32] an order different from that found for proton–proton coupling.

The ^{13}C NMR spectral data for compounds **1a–5a** are summarized in Table I. The olefinic carbon α to the trimethylstannyl group and a geminal carbonyl carbon are designated as proximate while the β-olefinic carbon and a vicinal carbonyl are designated as remote. Peak assignements are based on chemical shifts and tin–carbon coupling constants. The deshielding effect of the trimethylstannyl group is most pronounced at the proximate olefinic carbon. Downfield shifts range from 17 ppm for **1a** to approximately 28 ppm for **2a**, **4a**, and **5a**, compared to the unsubstituted esters **1d**, **4d**, and **5d**.[33] The remote olefinic carbon and the carbonyl carbons are generally deshielded, but by less than 7 ppm in all cases except the remote olefinic carbon of **1a** which is deshielded by about 9 ppm. The deshielding effect at the proximate carbon is about double that reported by Kuivila[34] and Mitchell[35] for *cis*- and *trans*-propenyltrimethylstannanes.

Tin–carbon coupling constants were obtained over one, two, and three bonds. One-bond coupling was resolved into tin-119 and tin-117 coupling constants. In each case the $^1J_{^{119}SnC}/{}^1J_{^{117}SnC}$ ratio fell within 0.5% of 1.046, the ratio of magnetogyric ratios for the two isotopes.[36] The range of values for coupling of tin to the proximate vinyl carbon was quite large while the range for coupling of tin to the methyl carbons was rather narrow.

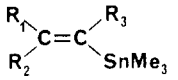
Two-bond coupling to the remote vinyl carbon or to the proximate carbonyl carbon was considerably smaller, ranging from about 10 to 25% of the one bond coupling. However, these values are larger than those reported by Kuivila[34] and Holecek[37] but similar to that reported by Mitchell and Walter[38] for styryltriethylstannane.

The three-bond coupling to the remote carbonyl carbon was again smaller, falling in the range of 23–30 Hz. In the case of **5a** the coupling to a trans carbonyl was less than that to a cis carbonyl in **4a**. Mitchell and Reimann[39] have reported that the trans/cis three-bond coupling ratios vary widely, but this is the first example of a ratio less than 1.

Kinetic studies of protodestannylation of compounds **1a–5a** have been carried out essentially as described in an earlier paper.[25] The solvent system was methanol–5% water and the concentration of vinylstannane substrate was

(30) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285 and references therein.
(31) Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 27.
(32) Delmas, M.; Maire, J. C.; Santamaria, J. *J. Organomet. Chem.* **1969**, *16*, 405.
(33) *Carbon-13 NMR Spectra*, Sadtler Research Laboratories; spectra number 2813C, 229C, and 164C, respectively.
(34) Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179.
(35) Mitchell, T. N.; Kummetat, C. *J. Organomet. Chem.* **1978**, *157*, 275.
(36) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 18.
(37) Holecek, J.; Handlir, K.; Nadvornik, M.; Teleb, S. M. *J. Organomet. Chem.* **1988**, *339*, 61.
(38) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177.
(39) Mitchell, T. N.; Reimann, W. *Organometallics* **1986**, *5*, 1991.

Table II. Rate Constants and Activation Parameters for Protodestannylation



compd	R_1	R_2	R_3	10^3k_2[a] 25 °C	35 °C	45 °C	$k_{rel}^{25°C}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1a	H	H	CO_2Me	0.570	1.70	5.01	11	20.5	−4.9
2a	H	CO_2Me	H	0.0368	0.134	0.381	0.7	20.2	−10.8
3a	CO_2Me	H	H	0.139	0.436	1.02	2.6	17.4	−17.6
4a	H	CO_2Me	CO_2Me	0.298	0.975	2.71	5.7	19.6	−8.8
5a	CO_2Me	H	CO_2Me	39.7	99.4	169	755	11.5	−25.9
6[b]	H	H	H	5.26	11.8	23.4	100	12.9	−26.0
7[b]	H	H	Me	3.13			60		
8[b]	H	Me	H	108	222	368	2100	10.5	−27.8
9[b]	Me	H	H	152	302		2900	11.8	−22.9

[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 ±4%. In M^{-1} s^{-1}. [b] Reference 25.

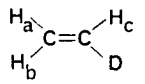
monitored at 250 nm as a function of time. Rate constants were determined for reactions at 25, 35, and 45 °C by using a nonlinear least-squares fit, and activation parameters likewise were calculated from the rate constants. The products were determined from reactions in which deuterium chloride provided the electrophile (vide infra). Compounds **1b–4b** were not suitable for kinetic studies in methanol because transesterification was a competitive process leading to mixed ester substrates. Table II lists the second-order rate constants and activation parameters for compounds **1a–5a** along with those, for comparison, of previously reported vinylstannanes.[25]

As expected, carbomethoxy substituents are generally deactivating, at least by a factor of 10, to the vinylstannane system. For the monosubstituted compounds **1a–3a** the effect is greater at the β-carbon where a significant aggregate of positive charge resides in the S_E2 transition state. Also the *Z* isomer **2a** is less reactive than the *E* isomer **3a** by a factor of about 4. Similar results are noted for the activating effect of a methyl group (**8** versus **9**) and in the report of Baekelmans and co-workers.[26a] The effect of a cis substituent is possibly a result of the disruption of the solvent cage surrounding the developing stannyl cation. It would be expected that the *E*/*Z* reactivity ratio would be greater for a carbomethoxy group since it is larger and more polar.

A second carbomethoxy group does not provide cumulative deactivation for protodestannylation. On the basis of the acrylate reactivities the relative reactivity of **4a** should be 0.4 and that of **5a** 1.5. In fact **4a** is about 15 times more reactive and **5a** is surprisingly about 500 times more reactive. This difference cannot be due only to solvent disruption. In effect the introduction of a second carbomethoxy group increases the reactivity of the vinylstannane. This fact coupled with the stereochemical effects, described below, suggest a change in mechanism.

Comparison of the activation parameters for compounds **1a–5a** with those of the unsubstituted vinylstannane **6** and the methyl-substituted vinylstannanes **8** and **9** indicates that the major contribution to diminished reactivity is in the enthalpy of activation term. Also an increase in $\Delta H^{\ddagger}$ is accompanied by a correspondingly less negative value for the entropy of activation. However, compound **5a** exhibits activation parameters of similar magnitude to **6**, **8**, and **9**, with the decrease in $\Delta H^{\ddagger}$ associated with a more negative $\Delta S^{\ddagger}$. This isokinetic relationship[40] was noted in our earlier work.[25,41]

Table III. ^{1}H NMR Data for Deuteron Cleavage of Compounds 1a–5a[a]



compd	$\delta(H_a)$	$\delta(H_b)$	$\delta(H_c)$	$^3J_{HD}$	$^2J_{HD}$	$^3J_{HH}$	$^2J_{HH}$
1c	6.38	5.93		2.7/1.6			2.5
2c	6.05		5.80	2.5	0.5	10.5	
3c		6.07	6.27	1.7	0.4	17.3	
4c	6.82			2.2			
5c		6.37		1.7			

[a] 300 or 360 MHz. CD_3OD. Chemical shifts in ppm are referenced to CH_3OH at 3.31 ppm.

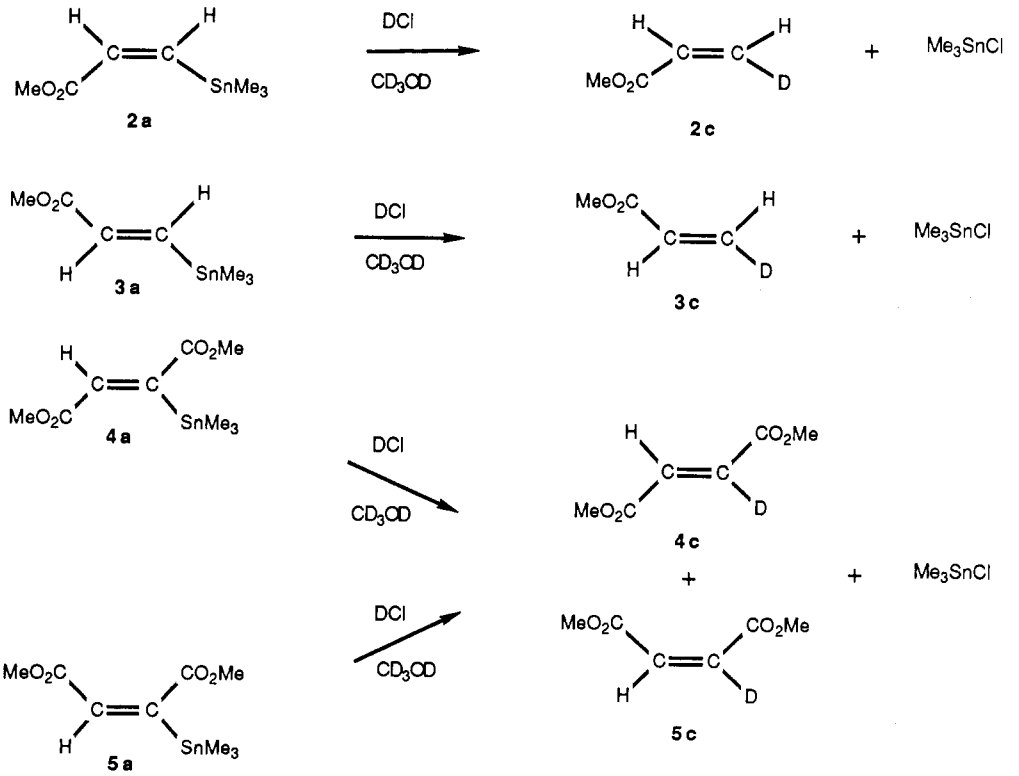
In order to study the stereochemical results of the protodestannylation, we replaced the proton as electrophile with the deuteron. Reactions were run in methanol-d_4 solution containing excess deuterium chloride and approximately 4% water-d_2. The reactions were carried out in an NMR tube and the structure of the products assigned on the basis of proton–proton coupling and proton–deuteron coupling. Table III lists the pertinent chemical shift and coupling constant data. Compound **1c**, the deuterium substitution product of compound **1a**, is included for comparison of the $^2J_{HD}$ coupling constant.

Scheme II shows the stereochemical outcome of the reactions of **2a–5a** with deuterium chloride. Both isomers of methyl 3-(trimethylstannyl)acrylate, **2a** and **3a**, gave single products with the deuterium residing in the same position from which the stannyl groups departed. Conversion of **2a** stereospecifically to **2c** is confirmed by cis proton–proton coupling of 10.5 Hz and trans and gem proton–deuteron coupling of 2.5 and 0.5 Hz, respectively. Likewise **3c**, as the exclusive product from **3a**, is confirmed by trans proton–proton coupling of 17.3 Hz and cis and gem proton–deuteron coupling of 1.7 and 0.4 Hz, respectively. Retention of configuration at the double bond is the usual result for electrophilic substitution in vinylstannanes when the proton,[25,27] iodine,[26a] or sulfur dioxide[42] is the electrophile.

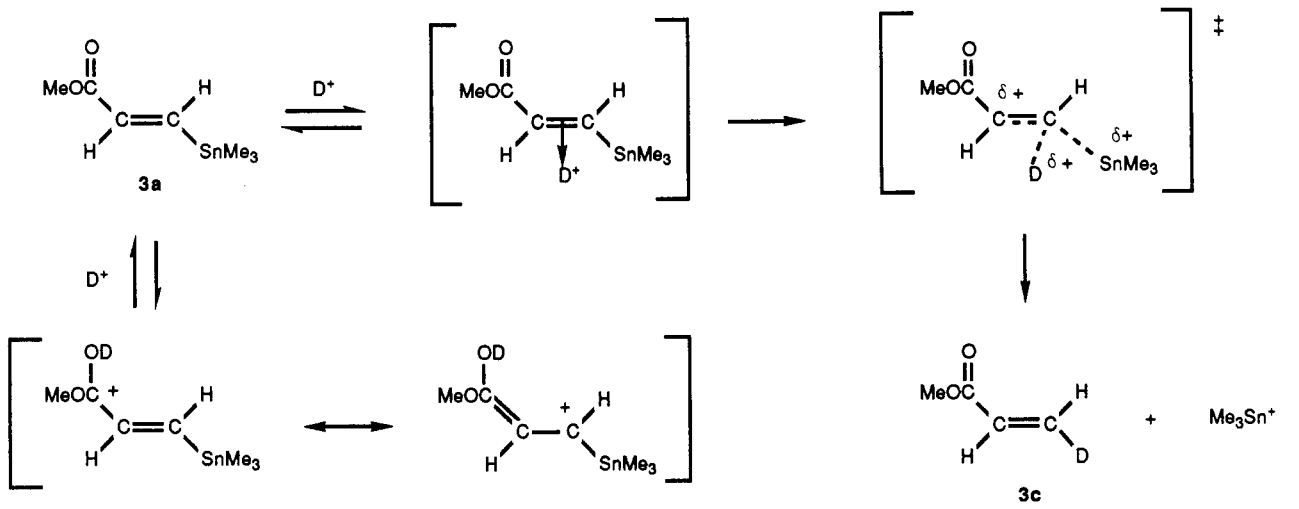
Very different results were obtained in the deuteron cleavage of compounds **4a** and **5a**. Practically identical mixtures of dimethyl fumarate-2-d_1 (**4c**) and dimethyl maleate-2-d_1 (**5c**) were obtained from deuteron cleavage of **4a** and **5a**. From **4a** the **4c**/**5c** ratio was 43/57 while that from **5a** was 46/54. The structure of **4c** was determined from trans proton–deuteron coupling of 2.2 Hz and **5c** from cis proton–deuteron coupling of 1.7 Hz. The

(40) Leffler, J. *J. Org. Chem.* **1955**, *20*, 1202.
(41) Cochran, J. C.; Kuivila, H. G. *Organometallics* **1982**, *1*, 97.
(42) Fong, C. W.; Kitching, W. *J. Organomet. Chem.* **1973**, *59*, 213.

Scheme II



Scheme III



product ratios were determined by integration of the peaks at δ 6.82 (**4c**) and 6.37 (**5c**). NMR spectra run prior to the completion of each reaction did not indicate the presence of the isomeric starting material, and the protonated products **4d** and **5d** were configurationally stable in methanol-d_4 in the presence of deuterium chloride and trimethyltin chloride. Also it should be noted that the less stable isomer predominates in each reaction mixture.

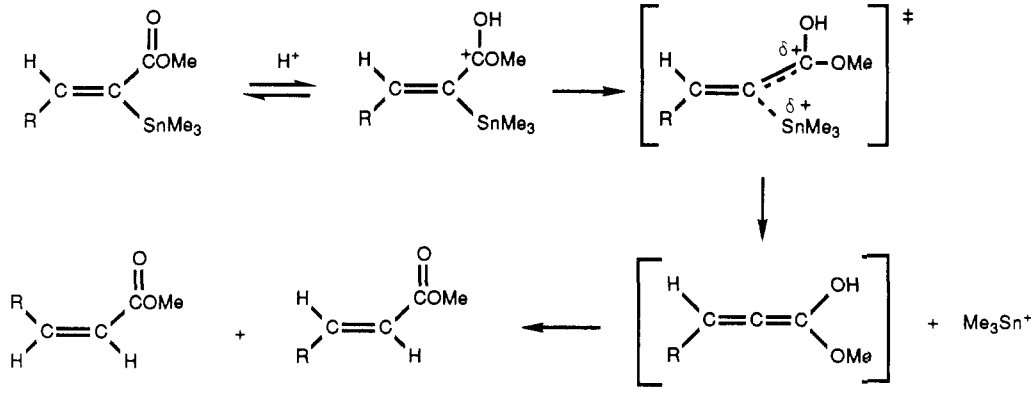
On the basis of the rate data, activation parameters, and stereochemical course of the protodestannylation reactions, it would appear that at least two possibly three mechanisms are operating for the five carbomethoxy-substituted vinylstannanes.

The reactivity of compounds **2a** and **3a** suggest that protodestannylation proceeds by a normal S_E2 mechanism. The β-carbomethoxy group reduces the reactivity by a factor of 140 when the substituent is cis (**2a**) and 40 when it is trans (**3a**) compared to the unsubstituted case. The deactivating effect of the carbomethoxy group is not as great as the activating effect of a methyl group (**8** and **9**), but it is of a similar order of magnitude. In each case the substituent operates directly on the olefinic carbon remote to tin. This carbon bears some positive charge in the transition state. Also both **2a** and **3a** proceed with retention of configuration as expected for an S_E2 reaction of a vinylstannane.

Scheme III shows the reaction path for **3a** with deuterium chloride, in which the electrophile first coordinates with the π-electrons of the carbon–carbon double bond. Subsequent bond formation to the α-carbon, with concurrent loss of the stannyl group, yields the product with retention of configuration. Scheme III also indicates that attack of the electrophile at the other site of π-electron density, the carbonyl, results in a cul-de-sac. Loss of the stannyl group from this protonated intermediate would be highly unlikely.

Compound **1a** does not provide a stereochemical probe for the reaction. The reactivity of **1a** is decreased only by

Scheme IV



a factor of 9 compared to **6**; a significant amount of this effect is seen in the entropy term. An α-methyl group is also slightly deactivating so the decreased rate may be due to both electron withdrawal from the π-system and disruption of the solvent cage surrounding the incipient stannyl cation.

Compounds **4a** and **5a** show a dramatic departure from the S_E2 mechanism. The presence of a second carbomethoxy group should result in further deactivation of the vinylstannane system. The effects may not be additive since the carbomethoxy groups are each conjugated with the double bond. However, compound **4a** would be expected to be less reactive than **2a**, but it is more reactive by a factor of 8. Also compound **5a** would be expected to be less reactive than **3a**, but it is more reactive by a factor of 290. In fact compound **5a** is more reactive than the unsubstituted case **6** and nearly as reactive as the β-methyl-substituted vinylstannanes (**8** and **9**). Clearly the second carbomethoxy group must alter the mechanism from initial attack at the carbon–carbon double bond.

A second unique characteristic of the protodestannylation of **4a** and **5a** is the stereochemistry. Instead of the expected retention of configuration, **4a** and **5a** give E/Z product ratios of 43/57 and 46/54, respectively. These ratios are probably identical within experimental error. Identical product ratios suggest a common intermediate formed after the rate-determining step.

Compounds **1a**, **4a**, and **5a** share a common structural component, a carbonyl α to the olefinic carbon bearing the stannyl group. Attack of the proton at this carbonyl oxygen results in an intermediate with a partially empty p orbital on the carbonyl carbon. Rotation of this carbon, and its substituents, by 90° allows maximum σ–π hyperconjugation with the electron density of the carbon–tin bond. Loss of the stannyl group and formation of a new π-bond leads to an allenol intermediate. Transfer of the proton to carbon from either face of the allenol results in E/Z isomers. Scheme IV illustrates this reaction path.

A similar hyperconjugative overlap between a carbon–tin σ-bond and a developing carbocation has been proposed by Lambert[43] to account for the very large rate enhancement in the solvolysis of β-stannylcyclohexyl acetates. This effect is observed when the stannyl group and the leaving group are antiperiplanar.

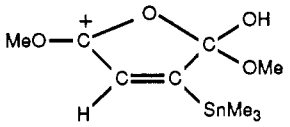
Allenol or allenolate intermediates have been proposed in a number of reactions. Michael-type additions of triethylgermyllithiuum to α,β-acetylenic acid chlorides,[44] DIBAL to α,β-acetylenic ketones,[45] and lithium dimethylcopper to α,β-acetylenic esters[46] proceed through allenolate intermediates. Calculation predicts the allenolate ion to be more stable than the corresponding carbonyl conjugated vinyl anion.[47] Protonation or reaction with another electrophile completes the Michael-type addition and reestablishes the carbonyl and conjugated double bond. In the case of the copper reagent the stereochemistry at the carbon–carbon double bond is determined by the reaction time and temperature.[46b] Allenolate ions have been trapped as silyl allenol ethers by alkylation of siloxypropargyllithium reagents or β-elimination of 2-(halosiloxyallyl)lithium reagents[48] and by reaction of trimethylchlorosilane with α,β-acetylenic ketones in the presence of magnesium and hexamethylphosphoric triamide.[49] Again reaction with various electrophilic agents leads to α,β-unsaturated ketones. A variation on this theme is the silyl-Wittig rearrangement of 1-lithio-2-propynyl silyl ethers to an α-silyallenolate, hydrolysis of which produces an isomeric mixture of α'-silyl-α,β-unsaturated ketones, in which the Z isomer predominates.[50] Finally the Lewis acid catalyzed addition of allylic sulfides to methyl propiolate or dimethylacetylene dicarboxylate is proposed to proceed by way of a pair of zwitterions which interconvert through an allenolate ion. The isomeric product ratio is a function of the Lewis acid which controls the barrier to inversion.[51]

The mechanism proposed in Scheme IV provides a new access to an allenol intermediate as the common intermediate for the protodestannylation of compounds **4a**, **5a**, and possibly **1a**. Transfer of the proton from oxygen to carbon has been shown to be rapid, at least 100 times faster than the protodestannylation reaction, run under pseudo-first-order conditions with a 50-fold excess of acid.[52] This suggests that the rate-limiting step involves loss of the stannyl group, or this event may occur simultaneously with protonation of the carbonyl oxygen.

The allenol intermediate, proposed in Scheme IV, does not necessarily account for the large difference in reactivity (×130) between **4a** and **5a**. However, the carbonyl oxygen

(43) Lambert, J. B.; Wang, G.-T. *Tetrahedron Lett.* **1988**, *29*, 2551.
(44) Medvedeva, A. S.; Safronova, L. P.; Vyazankin, N. S. *Zh. Obshch. Khim.* **1980**, *50*, 2044; *Chem. Abstr.* **1981**, *94*, 47430.
(45) Tsuda, T.; Yoshida, T.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 1037.
(46) (a) Siddall, J. B.; Biskup, M.; Fried, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1853. (b) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696.
(47) (a) Caramella, P.; Houk, K. N. *Tetrahedron Lett.* **1981**, *22*, 819. (b) Lavallee, J.-F.; Berthiaume, G.; Deslongchamps, P. *Tetrahedron Lett.* **1986**, *27*, 5455.
(48) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791.
(49) Merault, G.; Bourgeois, P.; Dunogues, J.; Duffaut, N. *J. Organomet. Chem.* **1974**, *76*, 17.
(50) Kruithof, K. J. H.; Klumpp, G. W. *Tetrahedron Lett.* **1982**, *23*, 3101.
(51) Hayakawa, K.; Kamikawaji, Y.; Wakita, A.; Kanematsu, K. *J. Org. Chem.* **1984**, *49*, 1985.
(52) Degrand, C.; Compagnon, P. L.; Lacour, M. *Electrochim. Acta* **1978**, *23*, 705.

remote to the stannyl group may serve to enhance the basicity of the proximate carbonyl. If so, this suggests that protonation and destannylation occur either simultaneously or the reaction passes through a stablizied intermediate, such as **5e**, which then undergoes β-elimination.



5e

Another factor that cannot be discounted involves stabilization of the stannyl group by coordination with a Lewis base bonded cis at the remote vinyl carbon. Jousseaume and co-workers have observed when the coordinating group is a carbonyl oxygen or a tertiary amine and iodine the electrophile, alkyl groups on tin are cleaved preferentially to the vinyl carbon–tin bond.[53a] Coordination by a carbonyl oxygen was also observed in the crystalline state.[53b] Compounds **2a** and **4a** present the possibility for coordination to the remote carbonyl oxygen, and both exhibit diminished reactivity compared to the corresponding trans isomers **3a** and **5a**. However, if this stabilization of tin is a significant factor, the relative reactivities, **3a** to **2a** and **5a** to **4a**, should be similar instead of approximately 4 and 130, respectively. Also it should be noted that alkyl cleavage takes place in noncoordinating solvents, chloroform-d_1 and benzene-d_6, while methanol may preclude intramolecular coordination. Finally iodine would be less likely to attack at oxygen, a requisite for the allenol intermediate.

Alternative pathways leading to isomeric products are also possible. Conjugate addition of hydrogen chloride to the α,β-unsaturated ester, rotation about the carbon–carbon σ-bond, and then elimination of chlorotrimethylstannane and a tautomeric proton shift would lead to isomeric products. We know of no precedent for this sequence of events, especially elimination of the elements of chlorotrimethylstannane from adjacent carbons. Also possible is an S_E1 process which would lead to a vinyl anion and a trimethylstannyl cation. This anion should have a low barrier for inversion. Protonation and tautomeric shift would give the observed products. This process differs from Scheme IV only in the order of events.

In summary, we report successful separation of the ionic and free radical pathways for the addition of trimethylstannane to an α,β-acetylenic ester, a Pd(0)-catalyzed addition of trimethylstannane to α,β-acetylenic esters which is both stereospecific and regiospecific, and a new pathway for electrophilic substitution in vinyl systems when the stannyl leaving group is proximate to a carbonyl. We are currently investigating the scope of transition-metal catalysis of trialkylstannanes to ynones and the allenol mechanism for protodestannylation.

Experimental Section

General Information. Methyl propiolate, galvinoxyl, dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, dimethyl fumarate, dimethyl maleate, and tetrakis (triphenylphosphine)palladium(0) were obtained from Aldrich and used without further purification; AIBN was obtained from Matheson Coleman and Bell and likewise used without further purification. Trimethyltin hydride was prepared by reaction of trimethyltin chloride with $LiAlH_4$ in tetraglyme.[54] The trimethyltin hydride was distilled from the reaction mixture, under reduced pressure, and trapped in liquid nitrogen traps. Trimethyltin hydride addition reactions were run in an atmosphere of argon. THF was dried by distillation from Na/benzophenone. Acetonitrile was dried over P_2O_5, distilled from dry K_2CO_3, and stored over molecular sieves. Cyclohexane was dried and stored over molecular sieves. ^1H NMR spectra were recorded on a Varian EM360-L at 60 MHz, a Varian XL-300 at 300 MHz, and a Bruker WM-360 at 360 MHz. ^{13}C NMR spectra were recorded on a Varian XL-300 at 75.4 MHz. IR spectra were recorded on Perkin-Elmer Model 1310 and 599B spectrometers. UV spectra were recorded on a Cary 219 spectrometer. The GC column for separation of compounds **2** and **3** was 20% SE-30 on Chromosorb W, 60–80 mesh UV, 60–80 mesh. Rate data was obtained on a Beckman DU-Gilford with a thermostated cell compartment. The glassware preparation and solution manipulation have been described previously.[25]

The compounds described below have been previously prepared but characterized as isomeric mixtures.[30] The ^1H NMR spectral data which we report for individual isomers agree satisfactorily with that reported by Leusink.[30]

Methyl 2-(Trimethylstannyl)acrylate (1a). Method I. In a 50-mL flask fitted with a septum cap were placed acetonitrile (20 mL), methyl proprolate (3.0 g, 36 mmol), galvinoxyl (300 mg, 0.71 mmol), and trimethyltin hydride (5.9 g, 36 mmol). The flask was swept with argon and wrapped in aluminum foil. After 2 days at 50 °C the reaction was deemed complete by the disapperance of the SnH peak at 1800 cm^{-1} in the IR spectrum of an aliquot. The acetonitrile was removed by distillation under reduced pressure, and methyl 2-(trimethylstannyl)acrylate was purified by preparative gas chromatography (10 ft × 0.25 in. i.d., SE-30 on Chromosorb W, 60–80 mesh). ^1H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 9, $^2J_{SnH}$ = 56.8/54.2 Hz), 3.74 (s, 3), 5.95 (d, 1, $^2J_{HH}$ = 2.6 Hz, $^3J_{SnH}$ = 62.3/59.4 Hz), 6.88 (d, 1, $^2J_{HH}$ = 2.6 Hz, $^3J_{SnH}$ = 125.8/123.5 Hz).

Method II. In a 25-mL flask, fitted with a magnetic stir bar and a septum, were placed THF (5 mL), methyl propiolate (510 mg, 6.07 mmol), and tetrakis(triphenylphosphine)palladium(0) (141 mg, 0.122 mmol). The flask was flushed with argon and trimethyltin hydride (650 mg, 3.95 mmol) in the THF (3 mL) added slowly by syringe. The mixture was allowed to stir, at room temperature, for 0.5 h. After this time the reaction was deemed complete because of the absence of the SnH peak at 1800 cm^{-1} in the IR spectrum of an aliquot. The THF was removed on a rotary evaporator and 5 mL of pentane added. After the solution was cooled at −10 °C for 0.5 h, the precipitated Pd(0) catalyst was filtered in an argon atmosphere on a sintered glass funnel (porosity M). The pentane was removed on a rotary evaporator leaving 697 mg (71%) of pure **1a**.

Ethyl 2-(Trimethylstannyl)acrylate (1b). Compound **1b** was prepared by method I described above. The reaction time, at 50 °C, was 4 days. ^1H NMR (60 MHz, CCl_4): δ 0.18 (s, 9, $^2J_{SnH}$ = 58 Hz), 1.28 (t, 3, $^3J_{HH}$ = 7 Hz), 4.14 (q, 2, $^3J_{HH}$ = 7 Hz), 5.97 (d, 1, $^2J_{HH}$ = 3 Hz), 6.86 (d, 1, $^2J_{HH}$ = 3 Hz).

Methyl 3-(Trimethylstannyl)acrylate, *Z* (2a) and *E* (3a). In a 25-mL flask, fitted with a magnetic stirrer bar and rubber septum, were placed cyclohexane (5 mL), methyl propiolate (1.03 g, 12.3 mmol), trimethyltin hydride ((2.01 g 12.2 mmol), and AIBN (40 mg, 0.24 mmol). The flask was swept with argon and heated to 60 °C with stirring. After 5 h the reaction was deemed complete due to the disappearance of the SnH peak at 1800 cm^{-1} in the IR spectrum. The cyclohexane was removed on a rotary evaporator and the resulting oil subjected to separation by gas chromatography (10 ft × 0.25 in i.d., 20% SE-30 on Chromosorb W, 60–80 mesh). The ratio of *Z* isomer (**2a**) to *E* isomer (**3a**) was determined to be 4:1 by integration of the GC peak areas and by integration of the OMe peaks in the ^1H NMR spectrum of the crude mixture. ^1H NMR (300 MHz, $CDCl_3$): *Z* isomer (**2a**), δ 0.20 (s, 9, $^2J_{SnH}$ = 57.1/54.7 Hz), 3.76 (s, 3), 6.70 (d, 1, $^3J_{HH}$ = 12.8 Hz, $^3J_{SnH}$ = 125.8/120.2 Hz), 7.16 (d, 1, $^3J_{HH}$ = 12.8 Hz, $^2J_{SnH}$ = 66.2/63.6 Hz); *E* isomer (**3a**), δ 0.21 (s, 9, $^2J_{SnH}$ = 57.3/54.3 Hz), 3.75 (s, 3), 6.31 (d, 1, $^3J_{HH}$ = 19.3 Hz, $^3J_{SnH}$ = 63.4/61.0 Hz), 7.76

(53) (a) Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 513. (b) Jousseaume, B.; Villeneuve, P.; Drager, M.; Roller, S.; Chezeau, J. M. *J. Orgranomet. Chem.* **1988**, *349*, C1.

(54) 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.

(d, 1, $^3J_{HH}$ = 19.3 Hz, $^2J_{SnH}$ = 69.4/67.8 Hz).

Ethyl 3-(Trimethylstannyl)acrylate, *Z* (2b) and *E* (3b). Compounds **2b** and **3b** were prepared by the method described for **2a** and **3a**. The isomers were separated and purified by gas chromatography (10 ft × 0.25 in. i.d., 20% SE-30 on Chromosorb W, 60-80 mesh). Integration of peak areas showed the isomer ratio to be *Z*/*E* = 3/2. ^{1}H NMR (60 MHz, CCl_4): *Z* isomer (**2b**), δ 0.16 (s, 9, $^2J_{SnH}$ = 59 Hz), 1.29 (t, 3, $^3J_{HH}$ = 7 Hz), 4.19 (q, 2, $^3J_{HH}$ = 7 Hz), 6.70 (d, 1, $^3J_{HH}$ = 13 Hz), 7.19 (d, 1, $^3J_{HH}$ = 13 Hz); *E* isomer (**3b**), 0.16 (s, 9, $^2J_{SnH}$ = 59 Hz), 1.28 (t, 3, $^3J_{HH}$ = 7 Hz), 4.17 (q, 2, $^3J_{HH}$ = 7 Hz), 6.26 (d, 1, $^3J_{HH}$ = 20 Hz), 7.73 (d, 1, $^3J_{HH}$ = 20 Hz).

Dimethyl 2-(Trimethylstannyl)fumarate (4a). In a 50-mL three-neck flask, fitted with an addition funnel, septum, stirrer bar, and condenser with a connection to an argon manifold, were placed THF (5 mL) and dimethyl acetylenedicarboxylate (1.38 g, 9.72 mmol). The reaction flask was flushed with argon. Trimethyltin hydride (1.67 g, 10.1 mmol) in THF (5 mL) was added dropwise with stirring over a period of 1 h. The reaction was monitored by IR spectra of aliquots. After 1 h the reaction was deemed complete due to the absence of the SnH peak at 1800 cm^{-1} in IR spectrum. The THF was removed on a rotary evaporator yielding 2.53 g of **4a** (84% yield). The NMR spectrum indicated that the product contained <5% of dimethyl 2-(trimethylstannyl)maleate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.27 (s, 9, $^2J_{SnH}$ = 58.0/55.4 Hz), 3.77 (s, 3), 3.79 (s, 3), 6.86 (s, 1, $^3J_{SnH}$ = 92.7/88.6 Hz).

Diethyl 2-(Trimethylstannyl)fumarate (4b). Diethyl acetylenedicarboxylate (2.82 g, 16.6 mmol) was placed in a 4-mL Reacti-vial. The vial was placed in an ice bath and trimethyltin hydride (2.73 g, 16.6 mmol) added slowly by syringe. The reaction was very exothermic, and the reaction mixture turned dark. Distillation under reduced pressure yielded 2.00 g (36%) of diethyl 2-(trimethylstannyl)fumarate (**4b**), bp 95–103 °C (0.7 Torr) [lit.[55] 71–72 °C (0.07 Torr)]. The NMR spectrum indicated the sample contained about 10% diethyl 2-(trimethylstannyl)maleate (**5b**). The distillation was avoided in subsequent reactions through purification by gas chromatography (10 ft × 0.25 in. i.d., 20% SE-30 on Chromosorb W, 60–80 mesh). ^{1}H NMR (60 MHz, CCl_4: δ 0.20 (s, 9, $^2J_{SnH}$ = 59 Hz), 1.30 (t, 6, J_{HH} = 7 Hz), 4.13 (q, 2, $^3J_{HH}$ = 7 Hz), 4.18 (q, 2, $^3J_{HH}$ = 7 Hz), 6.70 (s, 1, $^3J_{SnH}$ = 98 Hz).

Dimethyl 2-(Trimethylstannyl)maleate (5a). In a 25-mL one-necked flask, fitted with a septum and containing a stirrer bar, were placed dimethyl acetylenedicarboxylate (1.38 g, 9.72 mmol) tetrakis(triphenylphosphine)palladium(0) (0.233 g, 0.202 mmol) and THF (5 mL). The flask was flushed with argon and sealed. Trimethyltin hydride (1.67 g, 10.1 mmol) in THF (3 mL) was added slowly via syringe. After 0.5 h in the reaction was complete as determined by the absence of the SnH peak at 1800 cm^{-1} in the IR spectrum. The THF was removed on a rotary evaporator, with care taken to maintain an argon atmosphere. Pentane (5 mL) was added and the mixture cooled to −10 °C for 0.5 h. The resulting Pd(0) precipitate was filtered in an argon atmosphere on a sintered glass funnel (porosity M) and the pentane removed on a rotary evaporator, resulting in 2.06 g (68%) of dimethyl 2-(trimethylstannyl)maleate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.32 (s, 9, $^2J_{SnH}$ = 57.4/55.0 Hz), 3.73 (s, 3), 3.81 (s, 3), 6.05 (s, 1, $^3J_{SnH}$ = 52.8/50.5 Hz).

Isomerization of 4a to 5a. A 3 M solution of **4a** in cyclohexane was placed in an NMR tube and the tube positioned in a Rayonet photochemical reactor (λ = 253.7 nm). The sample was irradiated over a period of 4 days and the mixture monitored by using the NMR peaks at δ 6.88 and 6.08 for **4a** and **5a**, respectively. The ratio of **4a**/**5a** changed during this period from 9/1 to 3/2. However, the absolute amounts decreased significantly as the solution darkened and became more viscus, presumably due to polymerization. Addition of 20 mol % trimethyltin hydride to the mixture increased the rate of both isomerization and polymerization, while addition of 10 mol % 2,5-di-*tert*-butylhydroquinone inhibited both the isomerization and polymerization reactions.

Reaction of 1a–5a with DCl in CD_3OD/D_2O. Approximately 1.0 M solutions of each compound were prepared in CD_3OD. To 0.4 mL of each solution in an NMR tube was added 0.1 mL of 12 M DCl in D_2O, and the tube was allowed to stand for 5 h during which time the deuterodestannylation reaction was completed. ^{1}H NMR spectra were then run at 300 or 360 MHz. Table III lists the chemical shift and coupling constant data for the products **1c–5c**.

Configurational Stability of 4a and 5a under Protodestannylation Reaction Conditions. Separate solutions containing 100 mg (0.33 mmol) of **4a** and **5a** in 0.5 mL of CD_3OD were placed in NMR tubes and their spectra recorded (60 MHz). To each solution was added 0.2 mL of 1 M DCl in CD_3OD. The NMR spectra were repeated after 10 min and again after 60 min. No evidence was noted of isomerization of **4a** to **5a**, as indicated by the appearance of a peak at δ 6.05 or **5a** to **4a** as indicated by the appearance of a peak at δ 6.86.

Configurational Stability of Dimethyl Fumarate (4d) and Dimethyl Maleate (5d). The ^{1}H NMR (60 MHz) spectrum of a saturated solution of dimethyl fumarate in CD_3OD was recorded. To this was added 50 mg (0.25 mmol) of trimethyltin chloride, and the NMR spectrum was repeated. Finally 100 μL of 12 M DCl in D_2O was added and the NMR spectrum repeated at 10 min and 60 min. There was no evidence of isomerization to dimethyl maleate (**5d**), as indicated by the appearance of a peak at δ 6.3 in the ^{1}H NMR spectrum.

A similar experiment was carried out for dimethyl maleate except that the solution concentration was 1.4 M. No evidence of isomerization to dimethyl fumarate **4d** was noted as indicated by the appearance of a peak at δ 6.8 in the ^{1}H NMR spectrum.

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Registry No. **1a**, 3422-57-9; **1b**, 17490-10-7; **1c**, 15020-05-0; **2a**, 6150-34-1; **2b**, 17421-24-8; **2c**, 18910-51-5; **3a**, 4209-10-3; **3b**, 17421-26-0; **3c**, 103490-34-2; **4a**, 118631-31-5; **4b**, 17421-46-4; **4c**, 35300-10-8; **5a**, 118631-32-6; **5c**, 118631-33-7; $HC{\equiv}CCO_2Me$, 922-67-8; Me_3SnH, 1631-73-8; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0; $HC{\equiv}CCO_2Et$, 623-47-2.

(55) Leusink, A. J.; Marsman, J. W.; Budding, H. A. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 689.