Studies of Silyl-Accelerated 1,5-Hydrogen Migrations in Vinylcyclopropanes

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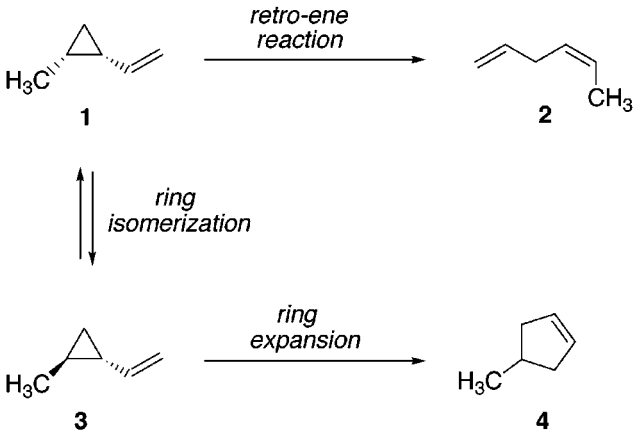
Thermal 1,5-hydrogen (retro-ene) rearrangements of 1-silylmethylated 2-vinylcyclopropanes have been studied. *cis*-1-Silylmethyl-2-vinylcyclopropanes **17** and **19** undergo facile 1,5-hydrogen transposition upon mild thermolysis in benzene or toluene solution (80−110 °C) to give nearly quantitative yields of ring-opened 1-silyl-1,4-diene products. These reactions occur at temperatures at least 100 °C lower than those of the nonsilylated substrates. The silicon center and its ligands influence both the rate and stereoselectivity of diene formation, with the triphenylsilyl substrate providing the fastest reaction and highest (exclusive) stereoselectivity in forming the diene, regardless of the *E*/*Z* geometry of the vinylcyclopropane. The trimethylsilyl and triethoxysilyl compounds (**19b** and **19c**) rearrange more slowly and with lower stereoselectivity. It is proposed that the rearrangement process takes place via a concerted suprafacial migration by one of two diastereotopic methylene hydrogens through a transition state having the silyl−carbon bond antiperiplanar to the breaking C−C bond of the cyclopropane ring. This conformational arrangement leads to weakening of the cyclopropane ring bond through orbital hyperconjugation, which facilitates the hydrogen transfer. The corresponding *trans*-1-silylmethyl-2-vinylcyclopropanes are thermally stable under these conditions. In contrast, *cis*-1-stannylmethyl-2-vinylcyclopropanes **19d**,**e** undergo loss of the stannyl group at room temperature to afford a ring-opened 1,5-diene product **25** through a process that may take place by initial 1,5-stannyl migration.

Introduction

Thermal rearrangements of vinylcyclopropanes have been well-studied and widely applied to organic synthesis.[1−8] The most common types of vinylcyclopropane rearrangements are the (1) concerted 1,5-hydrogen migration (retro-ene reaction) of *cis*-disubstituted vinylcyclopropane **1** to ring-opened 1,4-diene **2**, (2) thermal equilibration of *cis*-vinylcyclopropane **1** with its *trans* isomer **3**, and (3) 1,3-alkyl migration (ring expansion) of *trans*-vinylcyclopropane **3** to cyclopentene **4** (Scheme 1). The calculated[9] heats of formation of the four isomeric structures **1**−**4**, and the experimentally observed activation energies[4] for their interconversions, are given in Scheme 2. Substituents affect both the direction of these equilibria as well as their activation barriers. The best understood of these substituent effects are those of the thermal ring expansion, in which electron-donating

Scheme 1. Thermal Isomerizations of Alkyl-Substituted Vinylcyclopropanes



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(1) (a) Neureiter, N. P. *J. Org. Chem.* **1959**, *24*, 2044. (b) Overberger, C. G.; Borchert, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 1007. (c) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 3547. (d) Marshall, D. C.; Frey, H. M. *J. Chem. Soc.* **1962**, 3981. (e) Ellis, R. J.; Frey, H. M. *Proc. Chem. Soc.* **1964**, 221.

(2) (a) Mazzocchi, P. H.; Tamburin, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 7220. (b) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705. (c) Hudlicky, T.; Koszyk, F. J. *Tetrahedron Lett.* **1980**, *21*, 2487. (d) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247. (e) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229. (f) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717. (g) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432. (h) Baldwin, J. E.; Ghatlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273.

(3) (a) Dolbier, W. R., Jr.; Sellers, S. F. *J. Am. Chem. Soc.* **1982**, *104*, 2494. (b) Piers, E.; Maxwell, A. R.; Moss, N. *Can. J. Chem.* **1984**, *63*, 555. (c) Piers, E.; Maxwell, A. R. *Can. J. Chem.* **1984**, *62*, 2392. (d) Dolbier, W. R., Jr.; Alty, A. C.; Phanstiel, O., IV *J. Am. Chem. Soc.* **1987**, *109*, 3046. (e) Nakamura, E.; Kubota, K.; Isaka, M. *J. Org. Chem.* **1992**, *57*, 5809. (f) Nakamura, E.; Kubota, K.; Isaka, M. *Heterocycles* **1996**, *42*, 565.

(4) (a) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578. (b) Frey, H. M. *Adv. Phys. Org. Chem.* **1966**, *4*, 147. (c) Jorgenson, M. J.; Thacher, A. F. *Tetrahedron Lett.* **1969**, *10*, 4651.

(5) Roth, W. R.; König, J. *Justus Liebigs Ann. Chem.* **1965**, *688*, 28.

(6) Dolbier, W. R., Jr.; Al-Sader, B. H.; Sellers, S. F.; Koroniak, H. *J. Am. Chem. Soc.* **1981**, *103*, 2138.

(7) (a) Simpson, J. M.; Richey, H. G., Jr. *Tetrahedron Lett.* **1973**, *14*, 2545. (b) Richey, H. G., Jr.; Shull, D. W. *Tetrahedron Lett.* **1976**, *17*, 575.

(8) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020.

(9) The heat of formation values were calculated using the CS Chem3D Pro (Version 4.0) molecular modeling program on structures that were initially energy minimized with MM2 then with MOPAC at the AM1 level.

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Scheme 2. Comparison of the Activation Energies and Calculated Gas Phase Heats of Formation

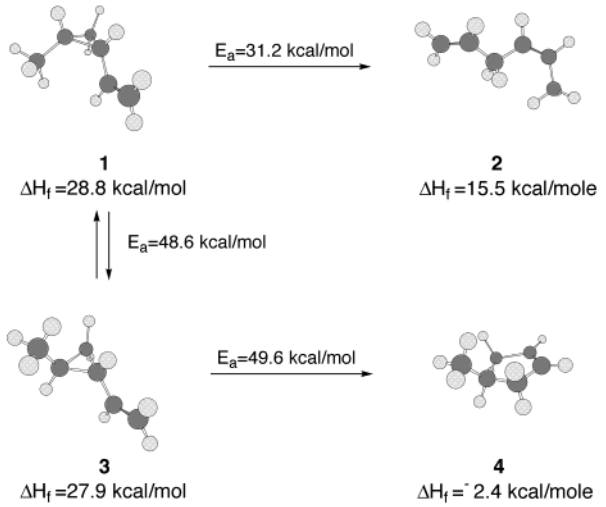
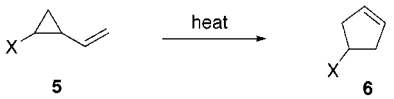


Table 1. Effect of Substituents on the Activation Energy and Reaction Temperature of the Vinylcyclopropane Ring Expansion

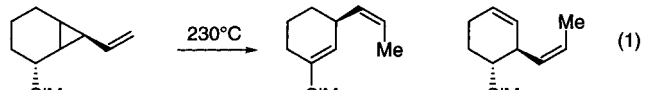


5 **6**

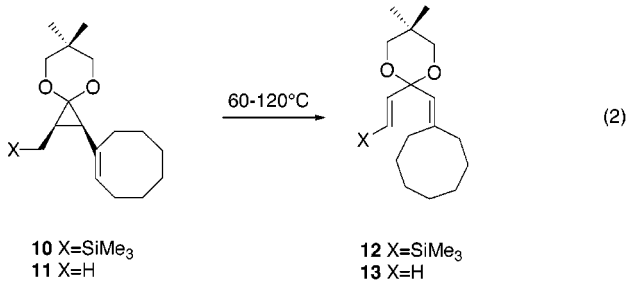
X	E_a	typical temperature range
H	49.7	500−600
Me	48.6	500−600
Ph	44.7	250−300
OMe	41.0	220−250
$F_{disubstituted}$	40.3	200−225
NMe_2	31.1	175−200

groups X on substituted vinylcyclopropane **5** accelerate the rearrangement to cyclopentene **6** (Table 1).[2] These rate enhancements cover a range of more than 600 °C and correspond closely to the electron-donating ability of the substituent X, with carbanion > oxyanion > NMe_2 > OMe > F > Ph > alkyl. The influence of substituents on the more kinetically accessible 1,5-hydrogen shift has been less well-defined. In this paper, we describe our studies[10] on the thermal 1,5-hydrogen migration of silyl-substituted *cis*-1-methyl-2-vinylcyclopropanes, where the silyl group was found to dramatically enhance the rate and stereochemical control of the ring opening process.

Prior to our studies, there had been only two isolated reports[11c,e] that describe the effect of a silyl substituent on the thermal 1,5-hydrogen migration of *cis*-1-alkyl-2-vinylcyclopropanes.[12] Piers and Maxwell found that a trimethylsilyl moiety can control the site selectivity of thermal 1,5-hydrogen migration in unsymmetrically substituted vinylcyclopropane **7** (eq 1).[11b] Upon thermolysis, diene **8** was formed exclusively over regioisomer **9**, indicating that the silicon group facilitates the transfer of its α-hydrogen relative to the *δ*-hydrogen. The authors originally attributed this to the buildup of electron density at the silyl-bearing carbon center in the transition state but later suggested that polarization of the cyclopropyl carbon−carbon bond may enable electropositive charge to preferentially develop *β* to the trimethylsilyl group.[11c] In a second report published in 1992, Nakamura and colleagues observed a similar rate enhancing effect by a silyl substituent on 1,5-hydrogen migration in vinylcyclopropane **10** (eq 2).[11e,f] In this case, the reaction



7 **8** **9** (1)



10 X=$SiMe_3$
11 X=H
12 X=$SiMe_3$
13 X=H
(2)

of **10** to *E*-diene **12** occurs at 60 °C while the rearrangement of the protio derivative **11** to **13** takes place at 120 °C. The authors point out that the rate acceleration is a consequence of the cyclooctenyl ring, which controls the formation of *E*-olefin geometry in the product. It is equally probable given the unusually low reaction temperatures for both substrates **10** and **11** that the acetal further enhances the rate of isomerization within these spirocyclic structures. We set out to study the thermal 1,5-hydrogen migration in *cis*-disubstituted 1-silylmethyl-2-vinylcyclopropanes to try to better understand the role of the silyl group in these rearrangements. In addition to the rate acceleration and enhanced stereoselectivity of the isomerization by the silyl substituent, some unexpected differences between the silyl- and the corresponding stannyl-substituted systems were also observed.

Results and Discussion

Synthesis of 1-Silylmethyl-2-Vinylcyclopropanes. Our initial experiments were conducted with 1-(triphenylsilylmethyl)-2-vinylcyclopropanes **17**, which were prepared as outlined in Scheme 3. Metal-catalyzed cyclopropanation[13] of allyltriphenylsilane (**14**) with ethyl diazoacetate in the presence of 5 mol % of rhodium acetate dimer afforded a 1.4:1 mixture of *trans*- and *cis*-adducts **15**, which were separated by flash chromatography. The individual esters were reduced using lithium

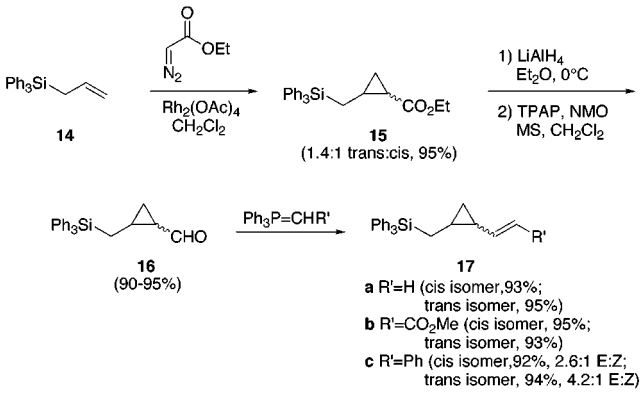
(10) This work is based on the M. S. thesis of Yi-Lun Lin, SUNY Buffalo 1999, and on the preliminary results published in Lin, Y.-L.; Turos, E. *J. Am. Chem. Soc.* **1999**, *121*, 856.

(11) (a) Dolbier, W. R., Jr.; Sellers, S. F. *J. Am. Chem. Soc.* **1982**, *104*, 2494. (b) Piers, E.; Maxwell, A. R.; Moss, N. *Can. J. Chem.* **1984**, *63*, 555. (c) Piers, E.; Maxwell, A. R. *Can. J. Chem.* **1984**, *62*, 2392. (d) Dolbier, W. R., Jr.; Alty, A. C.; Phansteil, O., IV *J. Am. Chem. Soc.* **1987**, *109*, 3046. (e) Nakamura, E.; Kubota, K.; Isaka, M. *J. Org. Chem.* **1992**, *57*, 5809. (f) Nakamura, E.; Kubota, K.; Isaka, M. *Heterocycles* **1996**, *42*, 565.

(12) In addition to the examples shown in eqs 1 and 2, thermal ring expansions of silyl-bearing vinylcyclopropanes have been reported in which the silyl center is bound directly to the ring. However, the effects of the silyl group in these reactions were not noted. (a) Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron Lett.* **1982**, *23*, 263. (b) Yan, T.-H.; Paquette, L. A. *Tetrahedron Lett.* **1982**, *23*, 3227.

(13) (a) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssié, P. *Synth. Commun.* **1976**, 600. (b) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695. (c) Doyle, M. P.; van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787.

Scheme 3. Synthesis of 1-Triphenylsilylmethyl-2-Vinylcyclopropanes 17

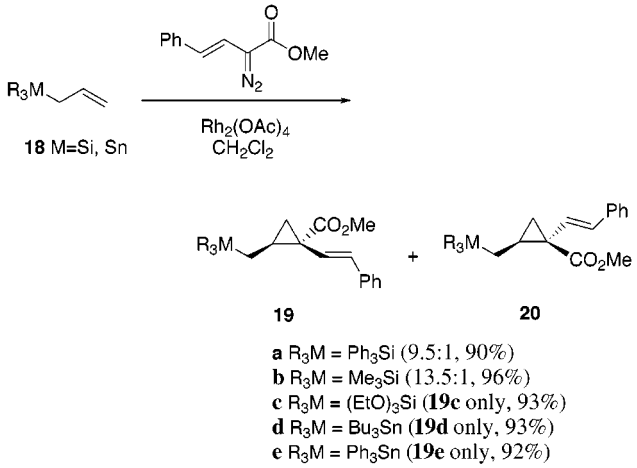


aluminum hydride to give an 80% yield of the *trans*-alcohol and a 75% yield of the *cis*-alcohol, respectively. Oxidation of the alcohols with *tetra*-propylammonium perruthenate[14] (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) produced *trans*- and *cis*-aldehydes **16**. The aldehydes were subsequently converted to vinylcyclopropanes **17** by Wittig olefination using ((methoxycarbonyl)methylene)triphenylphosphorane, or the ylides generated from methyltriphenylphosphonium bromide or benzyltriphenylphosphonium chloride by deprotonation with *n*-butyllithium. *trans*- and *cis*-Vinylcyclopropyl esters **17b** were obtained in diastereomerically pure *E*-form,[15] as confirmed from their ^{1}H and ^{13}C NMR spectra, while *trans*- and *cis*-vinylcyclopropanes **17c** were each isolated as inseparable mixtures of *E*- and *Z*-olefins.

When the cyclopropanation procedure was repeated using allyltrimethylsilane and allyltriethoxysilane as the starting alkenes, the cyclopropyl esters were obtained in a 2.1:1 and 1.2:1 *trans:cis* ratio, respectively. Unfortunately, the *trans* and *cis* stereoisomers could not be easily separated by column chromatography, due primarily to the fact that the trimethylsilyl compounds were volatile and non-UV active and the triethoxysilyl esters decomposed upon exposure to silica gel. Therefore, we abandoned our efforts to carry these compounds on to the vinylcyclopropane derivatives, and instead opted to prepare the vinylcyclopropane esters **19** and **20**.

Vinylcyclopropanes **19** and **20** were synthesized from the commercially available allylsilanes and allystannanes **18** by rhodium(II) acetate-catalyzed vinylcyclopropanation[16] with methyl 4-phenyl-2-diazobutenoate[17] (Scheme 4). The trimethylsilyl (R_3M = Me_3Si) and triphenylsilyl (R_3M = Ph_3Si) substituted products **19** and **20** were stable to column chromatography, allowing the isolation of each isomer. Diastereoisomer **19** predominated in both cases. On the other hand, triethoxysilyl compound **19c** was obtained from the reaction mixture as a single diastereomer in 93% yield, but this adduct was unstable to silica gel chromatography. Similarly, the stannyl vinylcyclopropanes **19d** and **19e** were formed as the only

Scheme 4. Synthesis of Silylmethyl- and Stannylmethyl Vinylcyclopropane Esters



products of the reaction but also decomposed upon attempted flash chromatography. For these three labile compounds, **19c**−**e**, we were able to remove most of the reaction impurities by trituration with hexane to give products that were judged by ^{1}H NMR to be sufficiently pure for further use. The relative stereochemistry of all vinylcyclopropanes was ascertained through a combination of one-dimensional (^{1}H and ^{13}C NMR, ^{1}H decoupling, NOE) and two-dimensional (COSY, NOESY, TOCSY, ROESY) NMR experiments (see Supporting Information).

Thermolyses of 1-Silylmethyl-2-Vinylcyclopropanes. Table 2 summarizes our results of the thermolyses reactions of *cis*-vinylcyclopropanes **17** and **19**. These rearrangements were carried out in a dilute solution (0.1 M) of refluxing benzene or toluene under an argon atmosphere. The progress of the reactions was monitored by periodic aliquot analysis using ^{1}H NMR spectroscopy with 1,4-dinitrodurene serving as an internal reference. In each case, the reactions followed first-order kinetics both in the disappearance of the starting material and in the formation of the diene products. The stereomeric ratios of products **21**:**22** remain constant throughout the course of the reaction and do not change even after prolonged reaction times. The yields and ratios shown in Table 2 are those obtained after purification by flash column chromatography.

The first compound examined, vinylcyclopropane **17a**, rearranged in refluxing toluene solution over a 10-h period to provide vinylsilane **21a** in 96% yield as the only product. The thermolysis reached 50% completion after only 3.3 h. The ester-substituted analogue **17b** required a significantly longer time to rearrange, proceeding at 110 °C with a half-life time of nearly 8 h. Once again, the 1*E*,4*Z*-diene was formed as the exclusive product in 97% yield. For substrates **17c**, the *E*- and *Z*-vinylcyclopropane isomers both afforded **21c** as a single stereoisomer, but to our surprise, the *Z*-compound isomerized *slower* ($t_{1/2}$ = 16.9 h) than the more stable *E*-isomer ($t_{1/2}$ = 12.9 h). This experiment demonstrates that the olefin geometry of the starting vinylcyclopropane affects the *rate* of 1,5-hydrogen migration but not the *stereochemistry* of the double bonds formed in the diene product.[18]

We next examined the thermolyses of ester-bearing substrates **19a**−**c** to evaluate the effects of the silyl

(14) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.

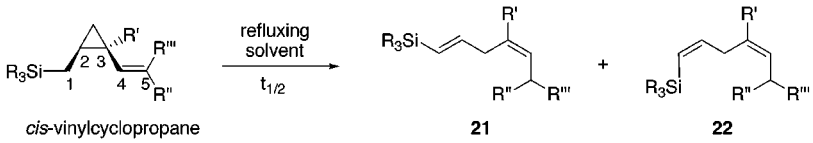
(15) (a) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (c) Ward, W. J., Jr.; McEwen, W. E. *J. Org. Chem.* **1990**, *55*, 493.

(16) Davies, H. M. L.; Hutcheson, D. K. *Tetrahedron Lett.* **1993**, *34*, 7243.

(17) For preparation procedures, see Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817.

(18) The structures of the diene products were determined by one- and two-dimensional NMR experiments (see Supporting Information).

Table 2. Thermal Rearrangement of *cis*-Vinylcyclopropanes 17 and 19

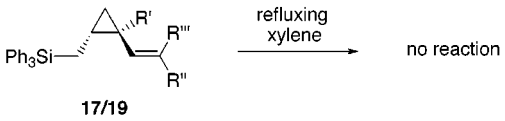


compd	R	R′	R″	R‴	solvent	$t_{1/2}$ (h)	isolated yield (%)	product ratio
17a	Ph	H	H	H	toluene	3.3	96	**21a** only
17b	Ph	H	CO_2Me	H	toluene	7.8	97	**21b** only
17c (*E*)	Ph	H	Ph	H	toluene	12.9	96	**21c** only
17c (*Z*)	Ph	H	H	Ph	toluene	16.9	96	**21c** only
19a	Ph	CO_2Me	Ph	H	benzene	48	98	**21d** only
	Ph	CO_2Me	Ph	H	toluene	0.7	98	**21d** only
19b	Me	CO_2Me	Ph	H	benzene	160	96	**e** (5.4:1)
	Me	CO_2Me	Ph	H	toluene	3.3	96	**e** (4.0:1)
19c	EtO	CO_2Me	Ph	H	benzene	120	96	**f** (1.8:1)
	EtO	CO_2Me	Ph	H	toluene	2.1	94	**f** (1.3:1)

ligand on the isomerization process. These isomerizations proceed under even milder temperatures than those of **17a**−**c**, occurring at 80 °C in refluxing benzene or toluene. Of the three silyl compounds, triphenylsilyl ester **19a** reacted the most rapidly and with the highest selectivity in forming the *E*,*E*-vinylsilane **21d**. The half-life time for the rearrangement of **19a** was 48 h at 80 °C, and 43.6 min at 110 °C. In each case, the *E*,*E*-diene was isolated as a single stereoisomer. In contrast, the trimethysilyl substrate **19b** required several weeks to finally reach completion in refluxing benzene solution ($t_{1/2}$ = 7 days) to give products **21e** and **22e** in a 5.4:1 ratio. The rate of isomerization and the product ratio were unchanged when the more polar solvent acetonitrile was used instead of benzene. In refluxing toluene solution, the half-life time for the reaction was reduced to a little more than 3 h, but the product ratio of **21e**:**22e** also dropped to 4:1. Thus, temperature seems to play a dual role in its effect on reaction rate and stereoselectivity. This was again seen for the isomerization of triethoxysilane **19c**, which had a half-life time of 5 days in refluxing benzene solution. The stereoselectivity of this reaction was also low, providing dienes **21f** and **22f** in a 1.8:1 ratio. When the rearrangement was carried out in refluxing toluene, the dienes were obtained in a 1.3:1 ratio with a reaction half-life of 2.1 h.

Following the progress of these reactions by proton NMR, we observed that the product ratios for **21e**:**22e** and **21f**:**22f** were uniformly maintained throughout the course of the thermolyses and even upon continued refluxing in toluene over a two-week period. The mixture of **21e**:**22e** and **21f**:**22f** gradually was able to equilibrate[19] completely to the 1*E*,4*Z*-vinylsilanes **21**, but only upon much more vigorous heating in refluxing xylene solution over a 10 day period. The fact that the products do not equilibrate under the original thermolysis conditions (80−110 °C) indicates that the reactions we studied are *not* subject to thermodynamic interconversion. Moreover, the stereoselectivity of the rearrangement depends on the silyl substituents (Ph > Me > EtO) as well as on the temperature at which the reaction is conducted (lower temperature gives higher selectivity). These experiments show that the silyl group exerts an effect that is completely reversed to that described for a fluorine substituent, which slows down the 1,5-hydrogen rearrangement and leads to stereochemical scrambling of the resulting vinyl fluoride double bond.[11d]

Scheme 5.
***trans*-1-Silylmethyl-2-Vinylcyclopropanes 17 and 19 Are Stable up to 140 °C**



As anticipated, the *trans* stereoisomers of vinylcyclopropanes **17** and **19** are much more resistant toward thermal rearrangement than the *cis* isomers and could be recovered unchanged after more than 1 week in refluxing xylene solution (Scheme 5). Thus, under these mild thermolysis conditions (below 140 °C), the *trans* compounds show no tendency to undergo *trans*−*cis* ring interconversion, ring expansion, or 1,5-hydrogen migration.

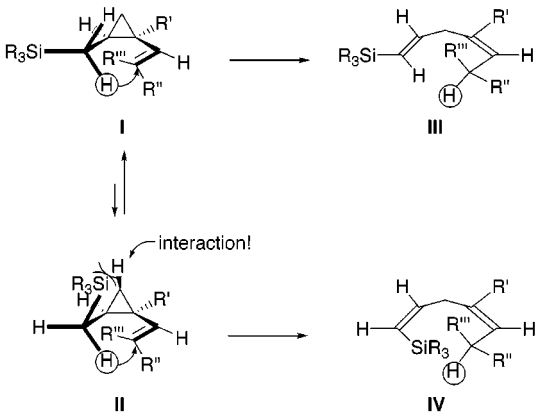
The single most prominent feature associated with these vinylcyclopropane rearrangements is the marked effect that the silyl group has on both the rate and stereochemistry of the 1,5-hydrogen shift. These reactions proceed at temperatures from 80 to 110 °C, which is at least 100 °C lower than that reported[5] for *cis*-1-methyl-2-vinylcyclopropane. Thus, the role of the silyl substituent in accelerating the reaction while also controlling the stereochemical outcome appears to be interrelated. Substituents are known to alter the hyperconjugation ability of silicon, with the relative order being trialkoxysilyl < triarylsilyl < trialkylsilyl.[20] In analyzing the differences in reactivity between our three silylated substrates, **19a**−**c**, we observe an increasing rate in the order of trialkylsilyl < trialkoxysilyl < triarylsilyl, which suggests that the acceleration is not strictly due to the difference in the electron donating ability of the silyl substituents.

The Woodward−Hoffmann rules dictate that the concerted 1,5-hydrogen migration of *cis*-1-alkyl-2-vinylcy-

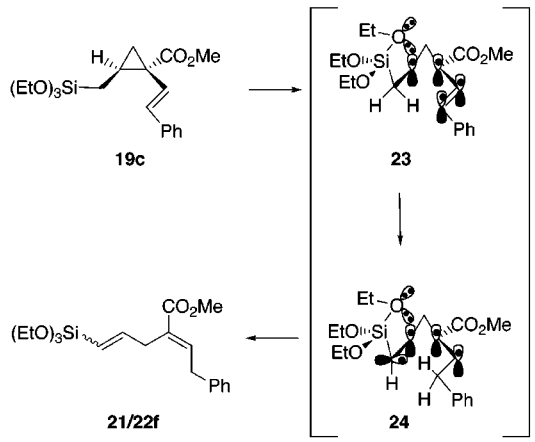
(19) AM1 calculations (CS Chem3D Pro, Version 4.0) indicate that for 1,4-dienes **21** and **22** where R = Ph and R′ = R″ = R‴ = H, the ground state energy of 1*E*,4*Z*-diene **21** is 3.8 kcal/mol lower in energy than that of the 1*Z*,4*Z*-isomer **22**.

(20) (a) Mayr, H.; Pock, R. *Tetrahedron* **1986**, *42*, 4211. (b) Mayr, H.; Hagen, G. *J. Chem. Soc., Chem. Commun.* **1989**, 91. (c) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954. (d) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710. (e) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609. (f) Brook, M. A.; Henry, C.; Jüschke, R.; Modi, P. *Synlett* **1993**, 97. (g) Brook, M. A.; Henry, C.; Jefferson, E.; Jüschke, R.; Sebastian, T.; Tomaszewski, M.; Wenzel, S. *Bull. Soc. Chem. Fr.* **1995**, *132*, 559.

Scheme 6. Conformations of the 1,5-Hydrogen Shift



Scheme 7. Possible Diradical Pathway for 1,5-Hydrogen Migration in Triethoxysilyl Compound 19c



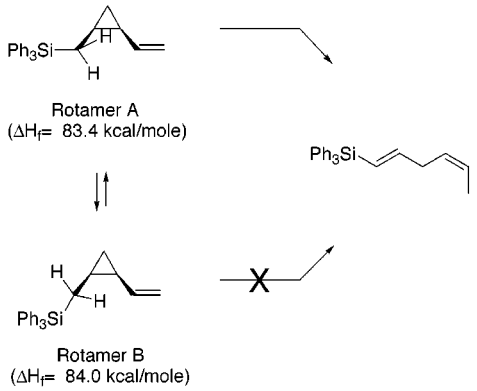
clopropane is a thermally allowed reaction process.[21] Some early studies on the reaction showed that the pentadiene product is formed with exclusive *Z*-geometry at carbons 4 and 5.[4] To rationalize this stereochemistry, Berson proposed a mechanistic model for the rearrangement[22] in which the hydrogen atom transfer preferentially occurs along the face anti to the cyclopropane ring, as depicted in Scheme 6, in a manner which is supported by orbital alignment considerations. Extending the Berson model to these 1-silylmethyl-2-vinylcyclopropane systems, the Si−C_1 bond could be positioned either antiperiplanar or orthogonal to the cleaving carbon−carbon bond of the cyclopropane ring, as shown in Scheme 6 for conformers I and II, respectively. The fact that the reactions of **17a**−**c** and **19a** afford only the *E*-vinylsilane product III indicates that the rearrangement proceeds faster through conformer I.[23] This most likely is the result of the antiperiplanar[24] Si−C_1/C_2−C_3 bond arrangement, which facilitates the hydrogen migration by enabling hyperconjugation of the carbon-silyl σ-bond with the σ^* antibonding orbital of the cleaving carbon−carbon bond. Such behavior is well-precedented for electrophile-promoted ring opening reactions of cyclopropylmethylsilanes.

From the model pictured in Scheme 6, one would expect that the overall stereoselectivity of the hydrogen migration would depend on the severity of the steric interactions in conformer II. Whereas the triphenylsilylmethyl vinylcyclopropane **19a** (R = Ph) gives exclusively the *E*-vinylsilane product III, the 1-trimethylsilylmethyl-2-vinylcylopropane **19b** (R = Me) rearranges to a 5.4:1 mixture of *E*- and *Z*-isomers (III and IV) at 80 °C. Stereoselectivity further decreases to 4:1 at higher temperature (110 °C), indicating that steric congestion is indeed a dominant factor in the rearrangement. The almost complete loss of stereocontrol observed for the trialkoxysilyl system **19c** (R = OEt) may reflect the smaller steric bulk of the ethoxy group compared to methyl or phenyl. We also considered the possibility that this particular rearrangement may proceed through a nonconcerted[25] mechanism via a diradical intermediate such as **23** since it has been suggested that an alkoxy silyl substituent can provide additional stabilization of a β-radical[26] via secondary orbital overlap with the ethoxy oxygen's nonbonding orbital (Scheme 7).[27] Intramolecular hydrogen atom abstraction from **23** would deliver **24**, which could collapse to either diene **21f** or **22f** depending on which direction the C_1−C_2 bond rotates. This scenario is not without support, since diradical intermediates are formed from vinylcyclopropanes during thermal 1,3-alkyl

(21) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(22) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4595.

(23) AM1-level calculations (CS Chem3D Pro, Version 4.0) reveal that the carbon-silyl bond in **17a** strives to be antiperiplanar to one of the cyclopropyl ring bonds, adopting either of the conformations shown below. Rotamer A, which corresponds to structure I in Scheme 6, is about 0.6 kcal/mol more stable than the rotamer B which is not in a proper geometry to undergo the concerted 1,5-hydrogen rearrangement.

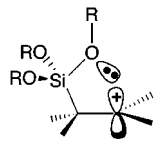


(24) Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, *7*, 999.

(25) (a) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695. (b) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 10621.

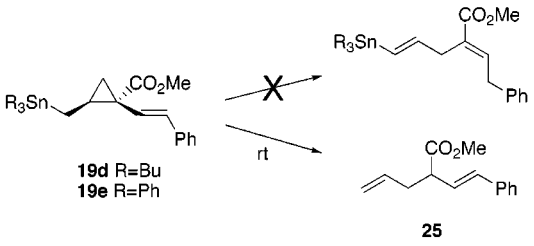
(26) A silyl-carbon σ-bond provides approximately 2.7 kcal/mol of stabilization to a β-alkyl radical. (a) Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979. (b) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (c) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644. (d) Walsh, R. *Pure Appl. Chem.* **1987**, *59*, 69. (e) Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281. (f) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(27) Alkoxy ligands on silicon appear to have an enhanced β-cation stabilizing effect. Brook and Neuy have suggested that this may be due to either a larger electron-releasing effect, or a through-space interaction between the oxygen n-orbital with the empty p-orbital such as in structure **i** (ref 20e).



i

Scheme 8. Thermal Demetalation of 1-Stannylmethyl-2-Vinylcyclopropane Esters 19d,e

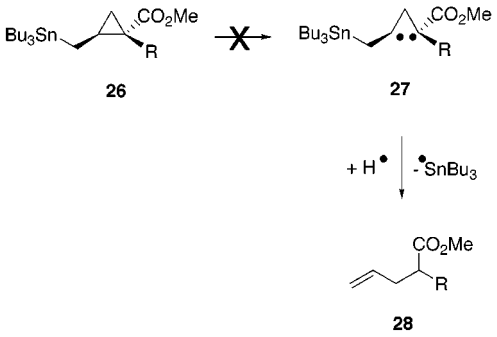


shifts and *cis*−*trans* ring interconversions. However, our experiments indicate that **19c** does not undergo *cis*−*trans* ring isomerization even upon extended heating at 140 °C, nor did we obtain radical trapping products when the thermolyses were carried out in the presence of a large excess of tetracyanoethylene. We believe that the poor stereochemical control during the migration is the result of the smaller effective size of $Si(OEt)_3$ compared to either $SiPh_3$ or $SiMe_3$. Thus, stereoselectivity in the reaction and size of the silyl group both increase together in the order $Si(OEt)_3 < SiMe_3 < SiPh_3$.

The model in Scheme 6 also suggests that the steric demands of the alkene substituents in the vinylcyclopropane would affect the rate of the 1,5-hydrogen shift. Since the *Z*-substituent R‴ is presumably responsible for creating nonbonding interactions with the alkylsilyl group in both conformers I and II, increasing the size of R‴ should diminish the rate of the 1,5-hydrogen shift. This is borne out experimentally as illustrated in the case of *Z*-isomer **17c** (R″ = H; R‴ = Ph), which rearranges more sluggishly than *E*-compound **17c** (R″ = Ph; R‴ = H), as revealed in Table 2. The rate of rearrangement is also retarded when there is an electron-withdrawing substituent at the C_5 terminus of the double bond. We see this in the reactions of the C_5 ester-containing compound **17b** and the C_5 phenyl-bearing derivative **17c**, which both rearrange more slowly that the C_5 unsubstituted vinylcyclopropane **17a**. However, an electron-withdrawing group located at C_3 on the ring *accelerates* the migration, as illustrated in the thermolyses of **19a** versus *E*-**17c**. These opposing substituent effects simply reflect whether π-conjugation is being destroyed or created during the isomerization process.

Thermolyses of 1-Stannylmethyl-2-Vinylcyclopropanes. Earlier studies[20] by Mayr and Brook determined that the ability of silyl and stannyl moieties to stabilize β-cationic charge increases in the order of $Si(OMe)_3 < SiPh_3 < SiMe_3 < SnPh_3 < SnBu_3$. The stronger electron-releasing ability of the carbon-stannyl bond relative to the carbon-silyl bond led us to assume that the 1-stannylmethyl-2-vinylcyclopropanes **19d** and **19e** would undergo thermolytic ring opening with greater facility than the silylated compounds **19a**−**c** described above. This is in fact what we observe, with stannyl compounds **19d** and **19e** undergoing the ring opening at room temperature rather than at 80 °C. However, to our surprise, these reactions afforded the demetalated 1,5-diene **25** rather than the expected 1,5-hydrogen migration product (Scheme 8). Compound **19d** was transformed to **25** within 15 h at room temperature in CH_2Cl_2 and within 5 h in refluxing $CDCl_3$. In the absence of solvent, **19d** suffered demetalation to **25** within 3 h at room temperature. Triphenylstannyl compound **19e** proved to be more resistant to demetalation but slowly gave **25** over a period of 10 days

Scheme 9. Pyrolysis of 1-Stannylmethylcyclopropane Esters 26



in CH_2Cl_2 at room temperature. In no case were products from 1,5-hydrogen migration observed (top pathway, Scheme 8).

We investigated whether this demetalation could be proceeding through a stannyl-stabilized[28,29] diradical intermediate such as **27**. Compound **26** where R = H is thermally stable at 110 °C for more than 48 h, without any indication of *cis*−*trans* ring isomerization or demetalation to **28** (Scheme 9). Thus, formation of a diradical species **27** is highly improbable. Although diradical formation could conceivably occur more readily when R is CH═CHPh, it seems unlikely that ring opening could take place at *room temperature* via this mechanism. Also, when the thermolyses of **26** (R = CH═CHPh) were done in refluxing tetracyanoethylene, we failed to detect any adducts that could be derived from trapping of diradical **27** or from capture of an alkyl or Bu_3Sn radical intermediate produced from **27** (such as $(Bu_3Sn)_2$ dimer). We conclude that the demetalation of **19d** and **19e** must be occurring through a pathway that does not involve a diradical species.

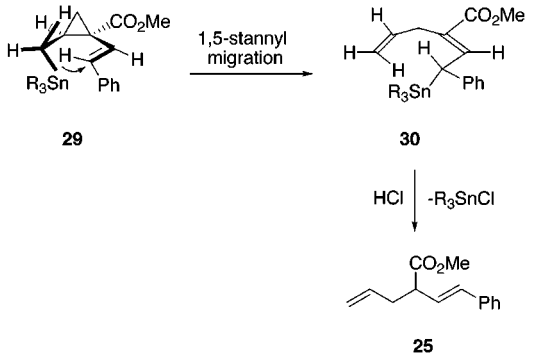
Cyclopropylmethylmetals are notoriously sensitive to ring opening[30] in the presence of electrophilic reagents, and thus it is likely that these destannylations may be caused by trace quantities of acid in the $CDCl_3$ solution. Alternatively, the reactions could be proceeding via 1,5-migration of the stannyl group[31] through an allylstannane intermediate such as **30**, which could then give the product by protodestannylation (Scheme 10). In comparing the bond strength of a C−Sn bond (51.9 kcal/mol in $SnMe_4$)[33] to that of a typical C−H bond (104 kcal/mol in CH_4),[33] the activation energy for the 1,5-stannyl shift would be well below that of the 1,5-hydrogen shift (31 kcal/mol) such that the metal migration would proceed

(28) For examples of β-stannyl alkyl radicals, see (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161. (b) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. (c) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. (d) Kawamura, T.; Meakin, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 8065. (e) Symons, M. C. R. *J. Am. Chem. Soc.* **1972**, *94*, 8589. (f) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6459. (g) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6715. (h) Symons, M. C. R. *Tetrahedron Lett.* **1975**, 793. (i) Stark, T. J.; Nelson, N. T.; Jensen, F. R. *J. Org. Chem.* **1980**, *45*, 420. (j) Curran, D. P. *Synthesis* **1988**, 489.

(29) For comparison, the β-silyl alkyl radical is reportedly stable up to 140 °C without loss of the trialkylsilyl radical (Bennett, S. W.; Eaborn, C.; Jackson, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 573), despite having an exothermicity of 20 kcal/mol.

(30) (a) Grignon-Dubois, M.; Dunoguès, J.; Calas, R. *J. Chem. Res., Synop.* **1979**, 6. (b) Grignon-Dubois, M.; Dunoguès, J.; Calas, R. *Can. J. Chem.* **1981**, *59*, 802. (c) Ochiai, M.; Sumi, K.; Fujita, E. *Chem. Pharm. Bull.* **1983**, *31*, 3931. (d) Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* **1988**, *53*, 4682. (e) Ryu, I.; Hirai, A.; Suzuki, H.; Sonoda, N.; Murai, S. *J. Org. Chem.* **1990**, *55*, 1409. (f) Lucke, A. J.; Young, D. J. *Tetrahedron Lett.* **1991**, *32*, 807.

Scheme 10. 1,5-Stannyl Shift in 1-Stannylmethyl-2-vinylcyclopropane 29 Leading to Demetalated Diene 25



at or near room temperature. By running the reaction in acid-free $CDCl_3$, we were able to isolate allylstannane intermediate **30** from the reaction mixture and to subsequently convert it to diene **25** just by letting it stand in hydrous $CDCl_3$ solution. Thus, at least some of the demetalation could proceed via 1,5-stannyl shift.

Conclusions

Several interesting findings have emerged from these investigations. First, we have shown that a silyl group can enhance *both* the rate and stereoselectivity of 1,5-hydrogen migration in *cis*-disubstituted 1-silylmethyl-2-vinylcyclopropanes. Thermal isomerization of these activated substrates occurs at temperatures at least 100 °C lower than that reported for the nonsilylated systems. The facility of hydrogen atom migration is believed to arise from hyperconjugation of the carbon−silyl bond with the adjacent cyclopropane ring orbitals, which lowers the activation energy for ring cleavage. The substituents on the silyl center further influence the rate of rearrangement, with the relative order of reactivity being triphenylsilyl > trialkoxysilyl > trialkylsilyl. The stereochemistry of the hydrogen shift is influenced by the silyl ligands as well, with the order being triphenylsilyl > trialkylsilyl > trialkoxysilyl. This is reflected directly in the *E*/*Z* product ratios of the vinylsilanes. The vinylcyclopropanes are postulated to isomerize via a concerted mechanism through a transition state having the silyl-carbon bond antiperiplanar to the ring bond that is being cleaved, and the migrating hydrogen *anti* to the cyclopropane ring. The substituents on the vinylcyclopropane can also influence the rate of the rearrangement but not the final geometries of the two double bonds in the diene products. An electron-withdrawing group at the C_5 terminus of the alkene retards the rearrangement, while an electron-withdrawing substituent at C_3 of the vinylcyclopropane ring facilitates the 1,5-hydrogen shift. The retro-ene rearrangement occurs irreversibly under these mild reaction conditions to give 1-silylpenta-1,4-dienes that are stable to thermodynamic equilibration. The vinylsilane products formed in these reactions belong to an important class of synthetic reagents which may be readily accessed by this methodology. The *trans*-vinylcyclopropanes are thermally inert under these reaction conditions. In contrast to the silyl systems, the corresponding *cis*-1-stannylmethyl-2-vinylcyclopropanes are unstable at room temperature and give a ring opened 1,5-diene by expulsion of the metal moiety. These stannylated systems show no tendency to undergo 1,5-hydrogen migration but are susceptible to 1,5-stannyl isomerization that leads to demetalated ring opened product via an allylstannane intermediate.

Experimental Section

General experimental procedures are given in the Supporting Information.

Preparation of Cyclopropyl Esters 15. Ethyl diazoacetate (173 mg, 1.51 mmol) was added dropwise over 5 h to a 1 mL CH_2Cl_2 solution of allyltriphenylsilane (500 mg, 1.66 mmol) and rhodium(II) acetate (3.3 mg, 7.6 μmol) at room temperature under nitrogen. The solution was stirred for 1 h at room temperature and then concentrated. The *cis* and *trans* isomers of **15** were separated by column chromatography with a mixed solvent gradient of petroleum ether and CH_2Cl_2 to give 231 mg (40%) of *cis*-**15** and 323 mg (55%) of *trans*-**15** as white solids. Data for *cis*-**15**: Mp 61−62 °C; ^{1}H NMR (500 MHz) δ 7.55 (6H, dd, J = 7.5, 1.5 Hz), 7.41 (3H, tt, J = 7.5, 1.5 Hz), 7.36 (6H, t, J = 7.5 Hz), 4.09 (1H, dq, J = 10.5, 7.0 Hz), 3.95 (1H, dq, J = 10.5, 7.0 Hz), 1.71 (2H, m), 1.63 (1H, m), 1.41 (1H, m), 1.22 (3H, t, J = 7.0 Hz), 0.95 (1H, m), 0.84 (1H, m); ^{13}C NMR (125 MHz) δ 173.6, 136.5, 135.5, 130.2, 128.6, 61.0, 20.3, 18.4, 16.4, 15.1, 11.5; IR 1723 cm^{-1}; MS (EI) *m*/*z* 386.2 (M^+). Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.80; H, 6.84. Data for *trans*-**15**: Mp 73−74 °C; ^{1}H NMR (500 MHz) δ 7.54 (6H, dt, J = 7.0, 1.0 Hz), 7.42 (3H, tt, J = 7.0, 1.0 Hz), 7.37 (6H, t, J = 7.0 Hz), 4.03 (2H, m), 1.62 (1H, dd, J = 14.5, 6.0 Hz), 1.52 (1H, m), 1.32 (1H, dd, J = 14.5, 7.5 Hz), 1.30 (1H, m), 1.22 (t, 3H, J = 7.0 Hz), 1.10 (1H, m), 0.60 (1H, m); ^{13}C NMR (125 MHz) δ 175.0, 136.5, 135.3, 130.4, 128.7, 61.0, 23.6, 19.3, 18.8, 18.7, 15.1. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.53; H, 6.81.

Reduction of Cyclopropyl Esters 15. A solution of ester *cis*-**15** (200 mg, 0.52 mmol) dissolved in 5 mL of anhydrous ether was added dropwise at 0 °C to a stirred suspension of lithium aluminum hydride (33 mg, 0.88 mmol) in 5 mL of anhydrous ether under nitrogen. The mixture was stirred at 0 °C for 30 min, then quenched with saturated ammonium chloride solution (0.4 mL). The salts were filtered and washed with ether (100 mL). The combined organic washings were concentrated to give 134 mg (75%) of the *cis*-alcohol product as a white solid pure enough for further use. Mp 90−91 °C; ^{1}H NMR (360 MHz) δ 7.55 (6H, m), 7.38 (9H, m), 3.22 (1H, dd, J = 11.2, 6.6 Hz), 3.15 (1H, dd, J = 11.2, 6.7 Hz), 1.55 (1H, dd, J = 15.5, 5.4 Hz), 1.32 (1H, dd, J = 15.5, 7.4 Hz), 1.18 (1H, s), 0.74 (2H, m), 0.35 (1H, m), 0.29 (1H, m); ^{13}C NMR (90 MHz) δ 135.9, 135.2, 129.7, 128.1, 67.0, 24.1, 18.2, 12.7, 12.6; IR 3348 cm^{-1}. Anal. Calcd for $C_{23}H_{24}OSi$: C, 80.18; H, 7.02. Found: C, 79.91; H, 7.17.

***trans*-2-(Triphenylsilylmethyl)cyclopropylmethanol.** White solid, 80%, mp: 111−112 °C; ^{1}H NMR (360 MHz) δ 7.56

(31) For sigmatropic rearrangements in organometallic reagents, see (a) Wilson, K. W.; Roberts, J. D.; Young, W. G. *J. Am. Chem. Soc.* **1950**, *72*, 218. (b) Brook, A. G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493. (c) Kwart, H.; Slutsky, J. *J. Am. Chem. Soc.* **1972**, *94*, 2515. (d) Hutchison, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075. (e) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678. (f) Verdone, J. A.; Mangravite, J. A.; Scarpa, N. M.; Kuivila, H. G. *J. Am. Chem. Soc.* **1975**, *97*, 843. (g) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595. (h) Kira, M.; Yoshida, H.; Sakurai, H. *J. Am. Chem. Soc.* **1985**, *107*, 7767. (i) Kobayashi, M.; Kobayashi, M. *Chem. Lett.* **1986**, 385. (j) Fleming, I.; Rowley, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2259. (k) Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem.* **1989**, *54*, 5647. (l) Takuwa, A.; Kanaue, T.; Yamashita, K.; Nishigaichi, Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1309. (m) Jephcote, V. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 429. (n) Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 1948.

(32) Wilkinson, G.; Stone, F. G. A.; Abel, E. W.; Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982, 1, p 5.

(33) This commonly accepted value for the strength of the C−H bond may be an overestimate for that of a C−H bond at a stannyl-substituted center (see ref 30a).

(6H, m), 7.38 (9H, m), 3.64 (1H, dd, J = 11.5, 6.0 Hz), 3.43 (1H, dd, J = 11.5, 7.9 Hz), 1.64 (1H, dd, J = 15.1, 4.7 Hz), 1.31 (1H, s), 1.29 (1H, dd, J = 15.1, 8.3 Hz), 1.05 (2H, m), 0.67 (1H, m), −0.10 (1H, m); ^{13}C NMR (90 MHz) δ 136.0, 135.1, 129.7, 128.1, 63.1, 24.0, 19.2, 12.5, 12.0.

Oxidation of Cyclopropylmethyl Alcohols. A solution of the above *cis*-alcohol (200 mg, 0.58 mmol) dissolved in 5 mL of CH_2Cl_2 containing 4 Å sieves and *N*-methylmorpholine *N*-oxide (NMO) (102 mg, 0.87 mmol) was stirred for 10 min, and *tetra*-*n*-propylammonium perruthenate (TPAP) (2 mg, 5.8 μmol) was added. The progress of the reaction was followed by TLC until the starting material was completely consumed. The initial green-colored mixture darkened as the reaction proceeded. The mixture was diluted with CH_2Cl_2 (50 mL) and then washed with 5% aqueous sodium sulfite solution (12 mL), brine (10 mL), and saturated aqueous copper(II) sulfate solution (12 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to give 179 mg (90%) of aldehyde *cis*-**16** as a colorless oil. ^{1}H NMR (360 MHz) δ 9.24 (1H, d, J = 3.6 Hz), 7.54 (6H, d, J = 6.8 Hz), 7.34 (9H, m), 1.81 (2H, m), 1.65 (3H, m), 1.04 (1H, m); ^{13}C NMR (90 MHz) δ 201.7, 135.9, 134.4, 129.8, 128.1, 28.7, 21.2, 17.1, 12.1; IR 1690 cm^{-1}.

***trans*-2-(Triphenylsilylmethyl)cyclopropanecarboxaldehyde (*trans*-16).** Colorless oil, 95%; ^{1}H NMR (300 MHz) δ 9.03 (1H, d, J = 5.1 Hz), 7.78 (6H, dt, J = 7.2, 1.6 Hz), 7.55 (9H, m), 1.79 (3H, m), 1.60 (1H, m), 1.41 (1H, m), 0.98 (1H, m); ^{13}C NMR (90 MHz) δ 200.7, 135.5, 134.1, 129.6, 127.9, 32.8, 19.1, 17.5, 17.5.

Conversion of Cyclopropyl Aldehydes 16 to Vinylcyclopropanes 17. Method A. Using ((Methoxycarbonyl)-methylene)triphenylphosphorane. A mixture of aldehyde *cis*-**16** (200 mg, 0.58 mmol) and ((methoxycarbonyl)methylene)triphenylphosphorane (215 mg, 0.64 mmol) CH_2Cl_2 (10 mL) was stirred for 14 h at room temperature and evaporated under reduced pressure. The residue was purified by column chromatography, eluting with a 1:10 CH_2Cl_2-petroleum ether mixture, to give 215 mg (95%) of product *cis*-**17b** as a colorless oil. ^{1}H NMR (300 MHz) δ 7.55 (6H, dd, J = 7.4, 1.4 Hz), 7.36 (9H, m), 6.69 (1H, dd, J = 15.2, 10.2 Hz), 5.80 (1H, d, J = 15.2 Hz), 3.68 (3H, s), 1.70 (1H, d, J = 12.6 Hz), 1.52 (1H, m), 1.38 (2H, m), 1.04 (1H, m), 0.42 (1H, m); ^{13}C NMR (90 MHz) δ 167.0, 150.9, 135.8, 134.7, 129.7, 128.0, 119.7, 51.3, 20.9, 18.0, 17.2, 13.6; IR 1723 cm^{-1}.

Methyl *E*-3-(*trans*-2-(Triphenylsilylmethyl)cyclopropylprop-2-enoate (*trans*-17b). Colorless oil, 93%; ^{1}H NMR (300 MHz) δ 7.52 (6H, m), 7.37 (9H, m), 6.30 (1H, dd, J = 15.4, 9.9 Hz), 5.58 (1H, d, J = 15.4 Hz), 3.68 (3H, s), 1.47 (2H, d, J = 7.0 Hz), 1.22 (1H, m), 1.15 (1H, m), 0.79 (1H, m), 0.70 (1H, m); ^{13}C NMR (90 MHz) δ 167.4, 153.7, 135.9, 134.8, 129.8, 128.1, 117.4, 51.4, 24.8, 19.0, 18.7, 18.5.

Method B. Using Methyltriphenylphosphonium Bromide or Benzyltriphenylphosphonium Chloride. Methyltriphenylphosphonium bromide (229 mg, 0.64 mmol) was suspended in 10 mL of anhydrous THF under nitrogen. *n*-Butyllithium (1.1 mL, 1.6 M in hexanes, 0.70 mmol) was injected into the reaction flask by syringe. The resulting ylide mixture was allowed to stir for 30 min, and the reaction mixture was cooled to −78 °C. A solution of *cis*-**16** (200 mg, 0.58 mmol) in THF (10 mL) was injected dropwise into the cooled reaction mixture, which was then allowed to warm slowly to room temperature. After 24 h, water (50 mL) was added to the mixture and then ether (50 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ether (50 mL) and then with CH_2Cl_2 (50 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude material was purified by column chromatography with CH_2Cl_2 as eluent to afford 203 mg (93%) of product *cis*-**17a** as a colorless oil. ^{1}H NMR (360 MHz): δ 7.55 (6H, dd, J = 6.1, 1.8 Hz), 7.38 (9H, m), 5.55 (1H, ddd, J = 10.4, 10.0, 8.6 Hz), 5.04 (1H, d, J = 10.4 Hz), 4.97 (1H, d, J = 8.6 Hz), 1.65 (1H, d, J = 13.7 Hz), 1.46 (1H, m), 1.19 (2H, m), 0.85 (1H, m), 0.17 (1H, m). ^{13}C NMR (90 MHz) δ 138.4, 136.0, 135.3, 129.6, 128.0, 114.5, 21.1, 15.2, 14.2, 13.0. IR 1631 cm^{-1}.

***trans*-1-Ethenyl-2-(triphenylsilylmethyl)cyclopropane (*trans*-17a).** Colorless oil, 95%; ^{1}H NMR (360 MHz): δ 7.54 (6H, dd, J = 6.3, 1.6 Hz), 7.37 (9H, m), 5.23 (1H, ddd, J = 17.0, 10.2, 10.0 Hz), 4.82 (1H, d, J = 17.0 Hz), 4.74 (1H, d, J = 10.2 Hz), 1.44 (1H, dd, J = 6.9, 5.4 Hz), 1.11 (1H, m), 0.89 (2H, m), 0.56 (1H, m), 0.47 (1H, m); ^{13}C NMR (90 MHz) δ 142.0, 135.0, 135.6, 129.6, 128.0, 111.5, 25.4, 18.7, 16.8, 16.5.

***cis*-1-(2-Phenylethenyl)-2-(triphenylsilylmethyl)cyclopropane (*cis*-17c).** Colorless oil, 92%, E:Z = 2.6:1; ^{1}H NMR (360 MHz) δ 7.56 (Z, 6H, m; E, 6H, m), 7.30 (Z, 13H, m; E, 13H, m), 7.11 (Z, 1H, m; E, 1H, m), 6.45 (Z, 1H, d, J = 11.6 Hz), 6.37 (E, 1H, d, J = 15.7 Hz), 5.92 (E, 1H, dd, J = 15.7, 8.6 Hz), 5.41 (Z, 1H, dd, J = 11.6, 9.4 Hz), 1.83 (Z, 2H, m), 1.69 (E, 1H, dd, J = 14.4, 4.1 Hz), 1.53 (E, 1H, m), 1.27 (Z, 2H, m; E, 2H, m), 0.97 (Z, 1H, m), 0.90 (E, 1H, m), 0.29 (E, 1H, m), 0.19 (Z, 1H, m); ^{13}C NMR (90 MHz) δ 138.0, 135.9, 135.2, 135.2, 134.0, 133.8, 132.4, 130.7, 130.2, 129.9, 129.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.3, 128.1, 126.7, 126.6, 125.9, 20.9, 18.1, 17.4, 16.0, 15.2, 15.0, 13.5, 13.4; IR 1651 cm^{-1}.

***trans*-1-(2-Phenylethenyl)-2-(triphenylsilylmethyl)cyclopropane (*trans*-17c).** Colorless oil, 94%, E:Z = 4.2:1; ^{1}H NMR (360 MHz) δ 7.54 (E, 6H, m; Z, 6H, m), 7.31 (E, 9H, m; Z, 9H, m), 7.21 (E, 4H, m; Z, 4H, m), 7.11 (E, 1H, m; Z, 1H, m), 6.23 (Z, 1H, d, J = 11.5 Hz), 6.14 (E, 1H, d, J = 15.5 Hz), 5.58 (E, 1H, dd, J = 15.5, 9.0 Hz), 4.94 (Z, 1H, dd, J = 11.5, 10.1 Hz), 1.68 (Z, 2H, m), 1.48 (E, 2H, m), 1.24 (E, 2H, m; Z, 2H, m), 0.87 (Z, 1H, m), 0.67 (E, 1H, m), 0.57 (E, 1H, m; Z, 1H, m); ^{13}C NMR (90 MHz) δ 138.1, 138.0, 136.3, 136.0, 135.9, 135.14, 135.11, 134.3, 129.6, 128.8, 128.6, 128.3, 128.0, 127.4, 127.0, 126.6, 126.4, 125.9, 125.7, 125.2, 25.2, 21.7, 18.8, 18.4, 18.0, 17.8, 17.3, 17.1.

Procedure for the Vinylcyclopropanation of Allylsilanes and Allylstannanes 18. A solution of methyl 4-phenyl-2-diazobutenoate (483 mg, 2.39 mmol) dissolved in 1 mL of CH_2Cl_2 was added dropwise over 5 h into a 1 mL CH_2Cl_2 solution of allyltrimethylsilane (300 mg, 2.63 mmol) and rhodium(II) acetate (5.3 mg, 11.9 μmol) at room temperature under nitrogen. The solution was stirred for 1 h at room temperature and then concentrated. The residue was triturated with 5 mL of hexanes and filtered, and the solvent was removed under reduced pressure. The products were purified by column chromatography with a mixed solvent gradient of petroleum ether and CH_2Cl_2 to afford 616 mg (89%) of **19b** and 46 mg (7%) of **20b** as colorless oils. Data for **19b**: ^{1}H NMR (500 MHz) δ 7.43 (2H, d, J = 7.5 Hz), 7.33 (2H, t, J = 7.5 Hz), 7.24 (1H, t, J = 7.5 Hz), 6.66 (1H, d, J = 16.0 Hz), 6.31 (1H, d, J = 16.0 Hz), 3.71 (3H, s), 1.69 (2H, m), 1.04 (1H, m), 0.76 (1H, dd, J = 16.0, 4.0 Hz), 0.33 (1H, m), 0.03 (9H, s); ^{13}C NMR (90 MHz) δ 175.2, 137.3, 132.0, 128.7, 127.6, 126.5, 125.2, 52.3, 31.0, 28.8, 21.1, 15.7, −1.3; IR 1749 cm^{-1}; MS (CI, isobutane) m/z 289.2 (M + 1). HRMS (CI, isobutane) Calcd for $C_{17}H_{25}O_2Si$ (M + 1): 289.1625. Found: 289.1599. Data for **20b**: ^{1}H NMR (500 MHz) δ 7.36 (2H, d, J = 7.0 Hz), 7.30 (2H, t, J = 7.0 Hz), 7.21 (1H, tt, J = 7.5, 1.5 Hz), 6.90 (1H, d, J = 16.5 Hz), 6.19 (1H, d, J = 16.5 Hz), 3.75 (3H, s), 1.50 (2H, m), 1.33 (1H, m), 0.91 (1H, dd, J = 15.0, 5.0 Hz), 0.73 (1H, dd, J = 15.0, 10.5 Hz), 0.05 (9H, s); ^{13}C NMR (90 MHz) δ 172.6, 137.5, 130.0, 128.7, 127.3, 126.5, 126.3, 52.16, 32.1, 32.0, 22.5, 15.4, −1.3.

Methyl (1R*,2R*)-1-(*E*-2-Phenylethenyl)-2-triphenylsilylmethyl)cyclopropanecarboxylate (19a). Colorless oil, 81%; ^{1}H NMR (500 MHz) δ 7.52 (6H, dd, J = 8.0, 1.0 Hz), 7.44 (3H, tt, J = 8.0, 1.5 Hz), 7.37 (11H, m), 6.28 (1H, d, J = 16.0 Hz), 6.24 (1H, d, J = 16.0 Hz), 3.64 (3H, s), 1.92 (1H, m), 1.55 (1H, dd, J = 9.0, 5.0 Hz), 1.52 (1H, dd, J = 15.0, 6.0 Hz), 1.37 (1H, dd, J = 15.0, 8.0 Hz), 0.99 (1H, dd, J = 6.5, 5.0 Hz); ^{13}C NMR (125 MHz) δ 175.5, 137.6, 136.4, 135.1, 132.8, 130.3, 129.2, 128.6, 128.2, 127.1, 125.4, 52.8, 32.3, 28.3, 21.9, 13.0; IR 1723 cm^{-1}.

Methyl (1S*,2R*)-1-(*E*-2-Phenylethenyl)-2-triphenylsilylmethyl)cyclopropanecarboxylate (19a). Colorless oil, 9%; ^{1}H NMR (360 MHz) δ 7.55 (6H, m), 7.38 (9H, m), 7.18 (1H, m), 6.72 (1H, d, J = 16.1 Hz), 6.04 (1H, d, J = 16.1 Hz), 3.65 (3H, s), 1.82 (1H, dd, J = 14.8, 4.8 Hz), 1.66 (1H, dd, J = 14.8, 8.9 Hz), 1.49 (1H, m), 1.39 (2H, m); ^{13}C NMR (90 MHz)

δ 172.5, 137.4, 136.0, 134.7, 129.8, 129.6, 128.7, 128.1, 127.4, 126.9, 126.3, 52.3, 32.6, 30.9, 23.2, 12.1.

Procedure for the Preparation of Vinylcyclopropanes 19c−e. A solution of methyl 4-phenyl-2-diazobutenoate (180 mg, 0.89 mmol) dissolved in 1 mL of CH_2Cl_2 was added dropwise over 5 h into a 1 mL CH_2Cl_2 solution of allyltriethoxysilane (536 mg, 0.98 mmol) and rhodium(II) acetate (5.3 mg, 11.9 μmol) at room temperature under nitrogen. The solution was stirred for 1 h at room temperature and then concentrated. The residue was triturated with 5 mL of hexanes and filtered, and the solvent was removed under reduced pressure to give 313 mg (93%) of product **19c** as a yellow oil which proved to be unstable to column chromatography and was used without further purification. ^{1}H NMR (400 MHz) δ 7.39 (2H, d, J = 7.6 Hz), 7.30 (2H, t, J = 7.6 Hz), 7.22 (1H, t, J = 7.6 Hz), 6.66 (1H, d, J = 16.0 Hz), 6.30 (1H, d, J = 16.0 Hz), 3.81 (6H, q, J = 7.2 Hz), 3.68 (3H, s), 1.77 (1H, m), 1.67 (1H, dd, J = 9.2, 4.8 Hz), 1.21 (3H, t, J = 7.2 Hz), 1.11 (1H, dd, J = 6.8, 4.4 Hz), 0.83 (1H, dd, J = 15.2, 5.6 Hz), 0.49 (1H, dd, J = 15.2, 10.0 Hz); ^{13}C NMR (90 MHz) δ 174.7, 137.0, 132.0, 128.4, 127.3, 126.2, 124.7, 58.4, 52.0, 31.1, 26.5, 20.6, 18.2, 9.7; IR 1718 cm^{-1}.

Methyl (1R*,2R*)-1-(*E*-2-Phenylethenyl)-2-tributylstannylmethyl)cyclopropanecarboxylate (19d). Colorless oil, 93%; ^{1}H NMR (360 MHz) δ 7.42 (2H, d, J = 7.6 Hz), 7.31 (2H, t, J = 7.6 Hz), 7.23 (1H, d, J = 7.6 Hz), 6.67 (1H, d, J = 16.0 Hz), 6.31 (1H, d, J = 16.0 Hz), 3.69 (3H, s), 1.84 (1H, m), 1.70 (1H, dd, J = 9.0, 4.3 Hz), 1.46 (6H, m), 1.28 (9H, m), 1.03 (1H, dd, J = 6.8, 4.7 Hz), 1.92 (1H, m), 0.87 (12H, m), 0.69 (1H, dd, J = 12.6, 10.8 Hz); ^{13}C NMR (90 MHz) δ 174.6, 131.8, 128.6, 127.4, 126.3, 126.1, 124.8, 52.5, 33.1, 32.0, 29.2, 27.1, 22.0, 13.8, 9.2, 7.8; IR 1723 cm^{-1}.

Methyl (1R*,2R*)-1-(*E*-2-Phenylethenyl)-2-triphenylstannylmethyl)cyclopropanecarboxylate (19e). Colorless oil, 92%; ^{1}H NMR (360 MHz) δ 7.50 (6H, m), 7.31 (14H, m), 6.49 (1H, d, J = 16.2 Hz), 6.29 (1H, d, J = 16.2 Hz), 3.59 (3H, s), 2.04 (1H, m), 1.59 (2H, m), 1.51 (1H, dd, J = 8.3, 6.2 Hz), 1.09 (1H, dd, J = 6.2, 4.8 Hz); ^{13}C NMR (90 MHz) δ 174.5, 138.4, 137.2, 132.4, 129.2, 129.0, 128.8, 127.6, 126.6, 124.4, 52.2, 33.0, 30.3, 22.2, 10.6; IR 1723 cm^{-1}.

Procedure for the Pyrolysis of Silylmethyl Vinylcyclopropanes. A solution of vinylcyclopropane **17b** (200 mg, 0.5 mmol) in toluene (25 mL) was heated to reflux until TLC indicated that the starting compound was completely consumed. Alternatively, 0.5 mL aliquots were removed periodically, evaporated, and analyzed by ^{1}H NMR spectroscopy. When the reaction was complete, the solution was evaporated under reduced pressure and the residue was purified by column chromatography to give 193 mg (97%) of methyl (3*Z*,6*E*)-7-triphenylsilylhepta-3,6-dienoate (**21b**) as a colorless oil. ^{1}H NMR (360 MHz) δ 7.50 (6H, m), 7.34 (9H, m), 6.24 (1H, dt, J = 18.4, 1.4 Hz), 6.14 (1H, dt, J = 18.4, 5.4 Hz), 5.76 (2H, m), 3.64 (3H, s), 3.10 (2H, d, J = 5.4 Hz), 2.99 (2H, t, J = 5.4 Hz); ^{13}C NMR (90 MHz) δ 172.4, 149.8, 136.1, 134.9, 129.8, 129.7, 128.0, 124.7, 122.9, 52.0, 34.7, 33.0; IR 1743 cm^{-1}.

(1*E*,4*Z*)-1-Triphenylsilylhexa-1,4-diene (21a). Colorless oil, 96%; ^{1}H NMR (360 MHz) δ 7.51 (6H, m), 7.37 (9H, m), 6.23 (1H, d, J = 18.4 Hz), 6.16 (1H, dd, J = 18.4, 4.7 Hz), 5.57 (1H, m), 5.46 (1H, m), 2.98 (2H, t, J = 5.4 Hz), 1.62 (3H, d, J = 6.8 Hz); ^{13}C NMR (90 MHz) δ 150.1, 136.2, 135.2, 129.6, 128.0, 127.2, 125.8, 123.8, 34.4, 13.0; IR 1611 cm^{-1}.

(1*E*,4*Z*)-6-Phenyl-1-(triphenylsilyl)hexa-1,4-diene (21c). Colorless oil, 96%; ^{1}H NMR (360 MHz) δ 7.58 (5H, m), 7.43 (10H, m), 7.25 (4H, m), 7.04 (1H, m), 6.35 (1H, d, J = 18.7 Hz), 6.27 (1H, dd, J = 18.7, 4.7 Hz), 5.75 (1H, m), 5.65 (1H, m), 3.46 (2H, d, J = 7.2 Hz), 3.15 (2H, dd, J = 6.1, 5.0 Hz); ^{13}C NMR (90 MHz) δ 150.7, 140.9, 136.2, 135.0, 130.2, 129.6, 128.64, 128.59, 128.5, 128.0, 127.1, 126.1, 124.3, 37.7, 33.8; IR 1670 cm^{-1}.

(4*E*)-Methyl 2-((*E*)-2-Phenylethylidene)-5-(triphenylsilyl)pent-4-enoate (21d). Colorless oil, 98%; ^{1}H NMR (360 MHz) δ 7.48 (6H, dd, J = 7.5, 1.0 Hz), 7.40 (3H, tt, J = 7.5, 1.0 Hz), 7.34 (6H, tt, J = 7.5, 1.0 Hz), 7.21 (3H, m), 7.12 (2H, dd, J = 7.9, 2.2 Hz), 7.04 (1H, t, J = 7.6 Hz), 6.21 (2H, m), 3.71 (3H, s), 3.52 (2H, d, J = 7.6 Hz), 3.38 (2H, d, J = 2.2 Hz); ^{13}C NMR (90 MHz) δ 168.1, 148.9, 142.8, 138.8, 136.1, 134.9, 129.8, 129.7, 128.9, 128.8, 128.0, 126.7, 124.7, 52.1, 35.2, 33.9; IR 1716 cm^{-1}.

(*E*)-Methyl 2-((*E*)-2-Phenylethylidene)-5-(trimethylsilyl)pent-4-enoate (21e). Colorless oil, 96%; ^{1}H NMR (360 MHz) δ 7.26 (2H, tt, J = 6.8, 1.5 Hz), 7.19 (1H, dt, J = 7.2, 1.5 Hz), 7.15 (2H, m), 6.97 (1H, t, J = 7.6 Hz), 6.01 (1H, dt, J = 18.7, 5.4 Hz), 5.65 (1H, dt, J = 18.4, 1.8 Hz), 3.69 (3H, s), 3.48 (2H, d, J = 7.6 Hz), 3.23 (2H, dd, J = 5.8, 1.4 Hz), 0.01 (9H, s); ^{13}C NMR (90 MHz) δ 168.2, 142.9, 142.4, 138.9, 130.9, 130.1, 128.8, 128.8, 126.6, 52.0, 35.1, 33.8, −1.1; IR 1723 cm^{-1}.

Methyl 2-((*E*)-2-Phenylethylidene)-5-(triethoxysilyl)-pent-4-enoates (21f and 22f). Colorless oil, 94%, 4*E*,4*Z* = 1.3:1; ^{1}H NMR (300 MHz) δ 7.32 (4*E*, 5H, m; 4*Z*, 5H, m), 7.11 (4*E*, 1H, t, J = 7.6 Hz), 7.04 (4*Z*, 1H, t, J = 7.7 Hz), 6.56 (4*E*, 1H, m), 6.51 (4*Z*, 1H, m), 5.54 (4*E*, 1H, dt, J = 18.9, 1.5 Hz), 5.53 (4*E*, 1H, dt, J = 14.4, 1.8 Hz), 3.92 (4*Z*, 6H, q, J = 7.0 Hz), 3.88 (4*E*, 6H, q, J = 7.0 Hz), 3.80 (4*E*, 2H, d, J = 5.4 Hz), 3.71 (4*Z*, 2H, d, J = 7.8 Hz), 3.59 (4*E*, 2H, d, J = 8.0 Hz), 3.39 (4*Z*, 2H, dd, J = 5.6, 1.2 Hz), 1.30 (4*Z*, 9H, t, J = 7.0 Hz), 1.29 (4*E*, 9H, t, J = 7.0 Hz); ^{13}C NMR (63 MHz) δ 151.1 (4*Z*), 149.4 (4*E*), 142.7 (4*Z*), 142.6 (4*E*), 138.6 (4*Z*), 138.5 (4*E*), 130.4 (4*Z*), 129.5 (4*E*), 128.7 (4*Z*), 128.6 (4*E*), 126.6 (4*E*), 126.5 (4*Z*), 120.3 (4*Z*), 119.3 (4*E*), 58.6 (4*E*), 58.5 (4*Z*), 51.9 (4*E* and 4*Z*), 34.9 (4*E*), 34.8 (4*Z*), 33.6 (4*E*), 31.2 (4*Z*), 18.3 (4*E*; 4*Z*); IR 1716 cm^{-1}.

Procedure for the Pyrolysis of Stannylmethyl Vinylcyclopropanes 19d and 19e. A solution of vinylcyclopropane **19d** (200 mg, 0.39 mmol) or **19e** (223 mg, 0.39 mmol) was refluxed in $CDCl_3$ (25 mL) until TLC indicated that the reaction was complete. The solution was evaporated under reduced pressure and the residue was purified by column chromatography to give 83 mg (98%) of diene **25** as a colorless oil. ^{1}H NMR (360 MHz) δ 7.36 (2H, d, J = 7.6 Hz), 7.30 (2H, t, J = 7.6 Hz), 7.22 (1H, t, J = 7.6 Hz), 6.49 (1H, d, J = 15.8 Hz), 6.20 (1H, dd, J = 15.8, 8.6 Hz), 5.77 (1H, m), 5.08 (2H, m), 3.70 (3H, s), 3.27 (1H, dd, J = 15.8, 7.6 Hz), 2.59 (1H, m), 2.41 (1H, m); ^{13}C NMR (90 MHz) δ 174.1, 136.9, 135.0, 132.7, 128.8, 127.8, 127.0, 126.6, 117.4, 52.0, 49.5, 37.1; IR 1736 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.79; H, 7.40. Found: C, 77.59; H, 7.32.

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Supporting Information Available: One-dimensional and two-dimensional NMR spectra for the vinylcyclopropanes and diene products. This material is available free of charge via the Internet at http://pubs.acs.org.

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