Stereospecific Deconjugation of Alkyl (*E*)- and (*Z*)-3-Trimethylstannyl-2-alkenoates

Edward Piers* and Ashvinikumar V. Gavai

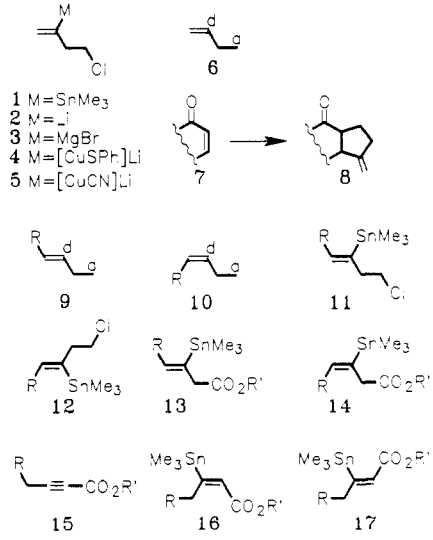
Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Received July 28, 1989

Reaction of the alkyl (*E*)-3-trimethylstannyl-2-alkenoates **16a–e** with lithium diisopropylamide in tetrahydrofuran, followed by protonation of the resultant enolate anions, affords *exclusively* the alkyl (*Z*)-3-trimethylstannyl-3-alkenoates **13a–e**, respectively. In similar fashion, the (*Z*)-2-alkenoates **17a–e** are transformed, completely stereoselectively, into the corresponding (*E*)-3-alkenoates **14a–e**.

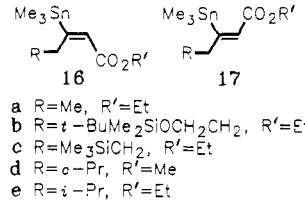
Recent publications[1] from this laboratory have reported that 4-chloro-2-trimethylstannyl-1-butene (**1**), readily prepared[2] by reaction of 4-chloro-1-butyne with $Me_3SnCu{\cdot}Me_2S$,[3] serves as an excellent precursor of reagents (e.g., **2–5**) that are synthetically equivalent to the 1-butene d^2,a^4-synthon[4] **6**. Indeed, reagents **3–5** are very useful for effecting short, efficient methylenecyclopentane annulation sequences that can be represented, in general terms, by the conversion of enones **7** into the annulation products **8**.[1b,e] This type of process has played a key role in the total syntheses of the triquinane sesquiterpenoids (±)-$\Delta^{9(12)}$-capnellene[1c,e] and (±)-pentalenene.[1d,f]

In continuation of our research program regarding the preparation and synthetic uses of bifunctional reagents, we wished to extend the work summarized above to the preparation of reagents that would be synthetically equivalent to the donor–acceptor synthons[4] **9** and **10**. This objective would require initially the synthesis of trimethylstannylalkenes of general structures **11** and **12**, respectively. Presumably, these substances could be obtained readily from the corresponding β,γ-unsaturated esters **13** and **14**.

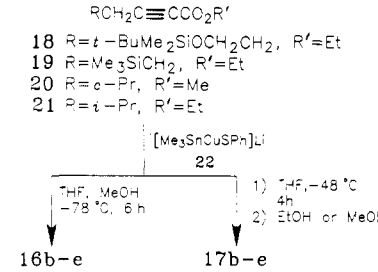


Recent studies[5] concerning the reactions of various (trimethylstannyl)copper(I) reagents[3] with α,β-acetylenic esters **15** have led to the synthetically important discovery that addition of the elements of Me_3Sn–H across the triple bond of the substrates can be stereochemically controlled by judicious choice of reagent and/or experimental conditions. Consequently, isomerically pure β-trimethylstannyl α,β-unsaturated esters of general structures **16** and **17** are readily available.[5] Clearly, the corresponding β,γ-unsaturated substances **13** and **14** required for the present study would be readily procured if one could effect the *stereospecific* deconjugation of **16** and **17**. We report here the results of a study[6] concerning the deconjugation of a number of alkyl (*E*)- and (*Z*)-3-trimethylstannyl-2-alkenoates. This investigation disclosed that these deconjugations are indeed completely stereospecific and that, therefore, substances of general structures **13** and **14** are readily prepared.

Chart I



Scheme I



Results and Discussion

(a) Preparation of the Alkyl 3-Trimethylstannyl-2-alkenoates 16b–e and 17b–e. The substrates chosen for this study were the alkyl (*E*)-3-trimethylstannyl-2-alkenoates **16a–e**, along with the corresponding *Z* isomers **17a–e** (Chart I). Collectively, the R groups present in these substances differ considerably in terms of steric bulk and exhibit a variety of functionality. Consequently, although not large in number, these substrates were expected to provide useful information regarding the scope of the proposed deconjugation reactions.

Compounds **16a** and **17a** have been reported previously.[5] The other required substrates were prepared from the corresponding α,β-acetylenic esters **18–21** (see Scheme I),

(1) Piers, E.; Karunaratne, V. (a) *J. Org. Chem.* **1983**, *48*, 1774. (b) *J. Chem. Soc., Chem. Commun.* **1983**, 935. (c) *Can. J. Chem.* **1984**, *62*, 629. (d) *J. Chem. Soc., Chem. Commun.* **1984**, 959. (e) *Tetrahedron* **1989**, *45*, 1089. (f) *Can. J. Chem.* **1989**, *67*, 160.
(2) Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425.
(3) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78.
(4) Cf. Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.
(5) (a) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. (b) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905. (c) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron* **1989**, *45*, 363.
(6) For a preliminary report regarding a portion of this work, see: Piers, E.; Gavai, A. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1241.

0022-3263/90/1955-2374$02.50/0

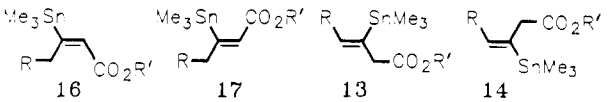
which, in turn, were synthesized as follows. Reaction of the lithium acetylide of 5-*tert*-butyldimethylsiloxy-1-pentyne[7] with ethyl chloroformate gave the ester **18** (89%), while successive addition of cyclopropylmethyl bromide[8] (1.05 equiv) and MeI (4 equiv) to a solution of the dilithio salt of propynoic acid in tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA)[9] provided, after appropriate reaction times, the acetylenic ester **20** (53%). Reaction of 3-methylbutanal and 3-trimethylsilylpropanal[10] with dibromomethylenetriphenylphosphorane[11] in dichloromethane gave the corresponding 1,1-dibromoalkenes. Treatment of each of these substances with MeLi (2 equiv) in THF,[11] followed in each case by addition of ethyl chloroformate, afforded the required esters **21** (70%) and **19** (67%), respectively.

Conversion of the alkynoates **18–21** into the alkyl (*E*)- and (*Z*)-3-trimethylstannyl-2-alkenoates **16b–e** and **17b–e**, respectively, was achieved via procedures modified somewhat from those reported previously.[5a,c] Thus, reaction (THF, −78 °C, 6 h) of each of the substrates **18–21** with lithium (phenylthio)(trimethylstannyl)cuprate (**22**)[3] (1.4 equiv) *in the presence of methanol* (1.7 equiv) (Scheme I) afforded the *E* alkenoates **16b–e**, respectively. On the other hand, treatment (THF, −48 °C, 4 h) of **18–21** with the cuprate **22** (1.3 equiv) *in the absence of a proton source*, followed by addition of ethanol or methanol, provided the corresponding *Z* alkenoates **17b–e**. In all of these transformations (Scheme I), it was found that the workup was greatly facilitated by addition of petroleum ether to the reaction mixture upon completion of the reaction. Furthermore, all of the conversions were highly stereoselective and, in each case, analysis of the crude product by gas–liquid chromatography (GLC) showed the presence of very little (<5%) of the geometric isomer. In each case, the small amount of the minor isomer was removed from the major desired product by flash chromatography of the mixture on silica gel.

The stereochemistry of each of the substances **16** and **17** was readily determined by ^{1}H NMR spectroscopy. Of particular note in each case was the strength of the coupling between the olefinic proton and the tin atom (^{117}Sn, ^{119}Sn) of the Me_3Sn group. It has been well established[12] that when a trialkylstannyl group and a proton are vicinal on a carbon–carbon double bond, the $^3J_{Sn-H}$ value is considerably larger when these moieties are trans than when they are cis. For compounds **16b–e**, these coupling constants are in the range 73–76 Hz, while, for substances **17b–e**, the $^3J_{Sn-H}$ values are about 120 Hz.

(b) Deconjugation Studies. A summary of the results obtained from a study of the deconjugation of the β-trimethylstannyl α,β-unsaturated esters **16** and **17** is given in Table I. Reaction of the ester **16a** with lithium diisopropylamide (LDA) in THF, followed by protonation of the resultant enolate anion with HOAc, provided *exclusively* ethyl (*Z*)-3-trimethylstannyl-3-pentenoate (**13a**) (Table I, entry 1). In similar fashion (entries 2–4), the conjugated esters **16b–d** were converted cleanly and efficiently into the corresponding β,γ-unsaturated esters **13b–d**. In each of these transformations, careful analysis of the crude product by GLC and ^{1}H NMR spectroscopy showed the complete absence of the geometrically isomeric β,γ-unsaturated ester (**14a–d**, respectively).

Table I. Deconjugation of β-Trimethylstannyl α,β-Unsaturated Esters



a R = Me, R' = Et
b R = *t*-BuMe$_2$SiOCH$_2$CH$_2$, R' = Et
c R = Me$_3$SiCH$_2$, R' = Et
d R = *c*-Pr, R' = Me
e R = *i*-Pr, R' = Et

entry	starting material	method[a]	product	yield,[b] %
1	**16a**	A	**13a**	82
2	**16b**	A	**13b**	83
3	**16c**	A	**13c**	72
4	**16d**	A	**13d**	79
5	**16e**	A[c]	**13e**	63
6	**17a**	B	**14a**	87
7	**17b**	B	**14b**	81
8	**17c**	B	**14c**	78
9	**17d**	B	**14d**	77
10	**17e**	B	**14e**	71

[a] A: Substrate **16** was treated with LDA (2.3 equiv) in THF (−78 °C, 30 min; 0 °C, 1 h); the solution was cooled to −78 °C and added (cannulation) to a cold (−98 °C) solution of HOAc in Et_2O. B: Substrate **17** was treated with LDA (1.5 equiv) in THF containing 1.5 equiv of HMPA. Reaction conditions and enolate quenching as in A. [b] Yield of purified, distilled product. [c] In this case, LDA–HMPA (2.3 equiv) was used (see text).

Attempted deconjugation of ethyl (*E*)-5-methyl-3-trimethylstannyl-2-hexenoate (**16e**) via the procedure outlined above (Table I, method A) was not clean. Although the expected substance **13e** was the major product, minor unidentified side-products were also present. It seemed likely that the formation of the side-products in this case was associatd with the relatively sluggish removal of one of the (hindered) γ protons of **16e** by LDA. Fortunately, deprotonation of **16e** with LDA in THF *in the presence of HMPA* (2.3 equiv), followed by the usual quenching procedure, provided **13e** as a singlet product (entry 5).

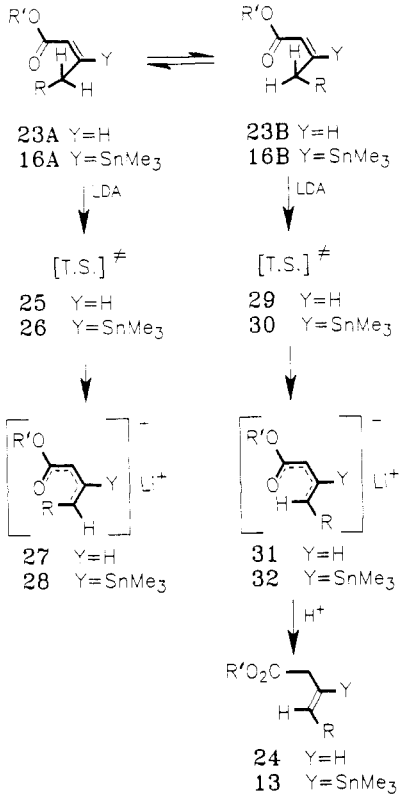
Deconjugation of the *Z* α,β-unsaturated esters **17a–e** also occurred with complete stereoselectivity, producing *exclusively* the alkyl (*E*)-3-trimethylstannyl-3-alkenoates **14a–e**, respectively (Table I, entries 6–10). The procedure employed (Table I, method B) for these conversions was similar to that used for the *E* esters, except that the deprotonation step was done with 1.5 equiv of LDA in THF containing 1.5 equiv of HMPA. The presence of HMPA was found to be necessary, since deprotonation of **17a** with LDA (2.3 equiv) in THF (method A), followed by protonation, gave a mixture containing the starting material **17a** (~14%), the β,γ-unsaturated ester **14a** (~80%), and a number of minor components. On the other hand, subjection of the substrates **17a–e** to the conditions of method B provided the desired products **14a–e** cleanly and efficiently.

The stereochemistry of each of the β,γ-unsaturated esters **13** and **14** was readily assigned on the basis of ^{1}H NMR spectroscopy. In this regard, the magnitude of the coupling constants $^3J_{Sn-H}$ associated with coupling between the olefinic proton and the tin atom was, again, particularly diagnostic.[12] In the *Z* isomers **13** (Me_3Sn and alkene proton in a trans relationship), these $^3J_{Sn-H}$ values are ~130 Hz, while the corresponding coupling constants for the *E* isomers **14** (Me_3Sn and olefinic proton in a cis relationship) are ~74 Hz.

On the basis of the results summarized above, it is evident that the deconjugations of the β-trimethylstannyl α,β-unsaturated esters **16** and **17** are completely stereo-

(7) Lin, C. H.; Stein, S. J. *Synth. Commun.* **1976**, *6*, 503.
(8) Beres, J. A.; Kurlick, N. J.; Shaffer, S. E.; Varner, M. G. *Eur. J. Med. Chem. Chim. Ther.* **1980**, *15*, 571.
(9) Carlson, R. M.; Oyler, A. R.; Peterson, J. R. *J. Org. Chem.* **1975**, *40*, 1610.
(10) Khatuntsev, G. D.; Sheludyakov, V. D.; Mironov, V. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 2111.
(11) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.
(12) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285.

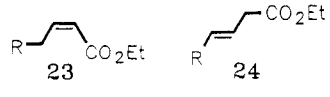
Scheme II



specific. A rationale for this observed stereospecificity is provided in the next section of this paper.

(c) Mechanistic Considerations. Since the initial reports[13,14] on protonative and alkylative deconjugations of α,β-unsaturated esters, these types of reactions have been used quite extensively in organic chemistry.[15] However, studies aimed explicitly at determining the stereochemistry of deconjugation of alkyl 2-alkenoates have been carried out only recently.[16-18] Furthermore, the stereochemical outcome of deconjugation of α,β-unsaturated esters that contain, at C-3, an additional noncarbon substituent had not been investigated prior to our work.

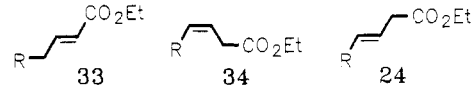
The previous investigations[16,17] had shown that deconjugations (LDA, THF–HMPA; H^+) of ethyl (*Z*)-2-alkenoates **23** provide the corresponding (*E*)-3-alkenoates **24** in a highly stereoselective fashion. For example, conversion of **23** (R = Me, *n*-Pr, *i*-Pr) into the corresponding products **24** could be carried out in yields of 98, 99, and 95%, respectively.[17] Stereochemically, our results on the deconjugation of the (*E*)-β-trimethylstannyl α,β-unsaturated esters **16** (Table I, entries 1–5) are completely analogous to those derived from the *Z* esters **23**.[16,17]



These findings can be rationalized in a qualitative manner by means of the formulations shown in Scheme II. For the kinetically controlled deprotonation of the (*Z*)-2-alkenoates **23**, two ground-state conformations (**23A**, **23B**) must be considered in each case.[17] The transition state **25** derived from **23A** would be destabilized by a notable steric interaction ($A^{1,3}$ strain[19]) between the R group and the CO_2R' function. On the other hand, deprotonation of conformer **23B** would proceed via a transition state **29** in which steric factors do not play a large role. Consequently, one would expect the pathway **23B** → **29** → **31** to be energetically favored over that involving conversion of **23A** into **27** (via **25**). Protonation of the enolate **31** would then produce the (*E*)-3-alkenoate **24**.

A similar argument holds for the deconjugation of the (*E*)-3-trimethylstannyl-2-alkenoates **16**. In each of these cases, the transition state **30** derived from conformer **16B** would be destabilized by $A^{1,2}$ strain[19] between the R and Me_3Sn groups. However, owing to at least partially to the length of the carbon–tin bonds (~0.2 nm[20]), this interaction would be expected to be considerably smaller than the $A^{1,3}$ strain[19] inherent in the transition state **26** between **16A** and **28**. Therefore, again, the pathway **16B** → **30** → **32** would be favored, leading eventually to the stereoselective formation of the (*Z*)-3-alkenoates **13**.

Deconjugation (LDA, THF–HMPA; H^+) of ethyl (*E*)-2-pentenoate (**33**, R = Me) provides the (*Z*)-3-pentenoate **34** (R = Me) in 98% yield.[17] However, in those cases in which R is larger than methyl, the deconjugative process is considerably less stereoselective. For example, subjection of **33** (R = *n*-Pr) to deconjugation provides (94%) a mixture of **34** (R = *n*-Pr) and **24** (R = *n*-Pr), in a ratio of



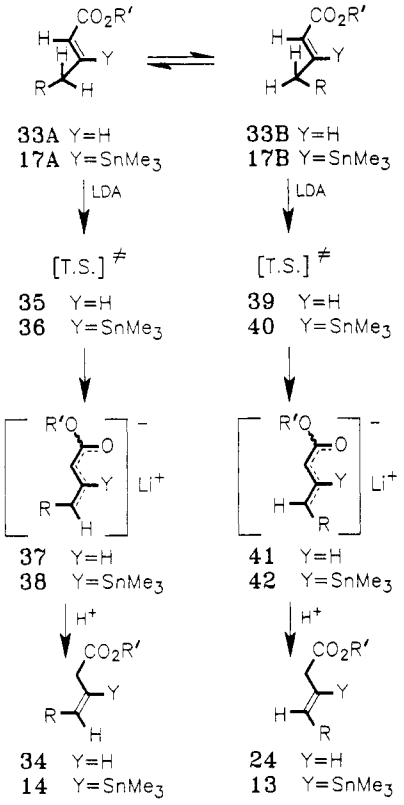
~6:1, respectively.[17] Furthermore, with a substrate containing a still more bulky group (**33**, R = *i*-Pr), the ratio of the products **34** (R = *i*-Pr) and **24** (R = *i*-Pr) is ~1.8:1 (97% yield).[17] Clearly, the deconjugation of ethyl (*E*)-2-alkenoates **33** is, in most cases, considerably less stereoselective than deconjugation of the corresponding (*Z*)-2-alkenoates **23**.[21]

From a synthetic viewpoint, it was important to find that deconjugation of each of the alkyl (*Z*)-3-trimethylstannyl-2-alkenoates **17a–e** is completely stereoselective (Table I, entries 6–10). Even in those cases (**17c–e**) in which the R groups are quite bulky, the only products obtained were the corresponding (*E*)-3-alkenoates **14c–e**. Thus, in contrast to the structurally related ethyl (*E*)-2-alkenoates **33**, the stereoselectivities of the deconjugative transformations involving alkyl (*Z*)-3-trimethylstannyl-2-alkenoates **17** are maintained even when the R groups are quite large.

The results summarized above may be rationalized qualitatively with the help of the formulations shown in Scheme III. For the kinetically controlled deprotonation of **33**, the transition states **35** and **39**, derived from conformers **33A** and **33B**, respectively, would be destabilized by $A^{1,3}$ strain[19] (between the R group and the C-2 olefinic proton) and $A^{1,2}$ strain[19] (between the R group and the C-3 proton, Y = H), respectively. However, as pointed out by

(13) Rathke, M. W.; Sullivan, D. *Tetrahedron Lett.* **1972**, 4249.
(14) Herrmann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2433.
(15) Alcock, S. G.; Baldwin, J. E.; Bohlmann, R.; Harwood, L. M.; Seeman, J. I. *J. Org. Chem.* **1985**, *50*, 3526, and references cited therein.
(16) Krebs, E.-P. *Helv. Chim. Acta* **1981**, *64*, 1023.
(17) Kende, A. S.; Toder, B. H. *J. Org. Chem.* **1982**, *47*, 163.
(18) Ikeda, Y.; Yamamoto, H. *Tetrahedron Lett.* **1984**, *25*, 5181.
(19) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
(20) Pereyere, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987; p 5.
(21) Interestingly, it has been shown[18] that reaction conditions and certain structural features in alkyl (*E*)-2-alkenoates can have a notable effect on the stereochemistry of the deconjugative process. For example, deconjugation (LDA, THF, HMPA, –78 °C; H^+) of ethyl (E)-2-dodecenoate gives, in accord with earlier observations,[16,17] an 84:16 mixture of the corresponding (*Z*)- and (*E*)-3-dodecenoates.[18] On the other hand, treatment (THF, –78 °C) of 2,4-dimethyl-3-pentyl (*E*)-2-dodecenoate with $KN(SiMe_3)_2$, followed by protonation of the resultant enolate anion, affords the corresponding (*Z*)- and (*E*)-3-dodecenoates in a ratio of 97:3.[18]

Scheme III

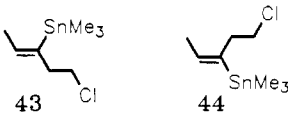


Kende and Toder,[17] the transition state **35** could well experience stabilization from the fact that the (incipient) allylic anion contains a cis R group. Both experimental and theoretical studies[22] have produced strong evidence that allylic anion systems containing terminal cis alkyl groups are more stable than those possessing trans alkyl substituents. Therefore, if the transition states **35** and **39** have (some) allylic anion-type character, one would expect **35** to be stabilized relative to **39**. Consequently, the major product derived from deprotonation of **33** would be expected to be the dienolate anion **37**, which, upon protonation, would give the (*Z*)-3-alkenoate **34**. Indeed, when **33** (R = Me) is deconjugated, **34** (R = Me) is the exclusive product.[17] Apparently, as the R group increases in size, the $A^{1,3}$ strain[19] inherently present in the transition state **35** becomes increasingly important, and, therefore, the alternative pathway **33B** → **39** → **41** begins to compete significantly with the favored route **33A** → **35** → **37**.

With respect to the deconjugation of the alkyl (*Z*)-3-trimethylstannyl-2-alkenoates **17**, it is clear from our studies that the pathway **17A** → **14** (via **36** and **38**) is favored over the alternative route (**17B** → **40** → **42** → **13**), irrespective of the size of the R group. These observations can be rationalized by postulating that the steric interaction ($A^{1,2}$ strain[19]) between the R and Y (=$SnMe_3$)groups in the transition state **40** destabilizes this species significantly. In comparison, the (relatively small) destabilizing steric repulsions ($A^{1,3}$ strain,[19] R–C-2 proton; $A^{1,2}$ strain,[19] Y (=$SnMe_3$)–C-4 proton) in the transition state **36** would be partially offset by the stabilizing influence of a cis R group in the incipient "allylic" anion (vide supra). On balance, deprotonation takes place exclusively from the conformer **17a**, and, therefore, the deconjugative process provides stereoselectively the (*E*)-3-alkenoates **14**.

Conclusion

This investigation showed that deconjugation of alkyl (*E*)- and (*Z*)-3-trimethylstannyl-2-alkenoates (**16** and **17**, respectively) produces exclusively the corresponding alkyl (*Z*)- and (*E*)-3-trimethylstannyl-3-alkenoates (**13** and **14**, respectively). The substances **13** and **14** are structurally novel organotin compounds and should prove to be useful intermediates for organic synthesis. The accompanying paper[23] describes (a) the conversion of **13a** and **14a** into (*Z*)- and (*E*)-5-chloro-3-trimethylstannyl-2-pentene (**43** and



44, respectively), (b) the results of an investigation into the transmetalation of **43** and **44**, and (c) the use of novel bifunctional reagents derived from **43** for effecting synthetically valuable five-membered ring annulation sequences.

Experimental Section

General Procedures. Distillation temperatures, which refer to bulb-to-bulb (Kugelrohr) distillations, are uncorrected. ^1H NMR spectra were recorded on $CDCl_3$ solutions. Signal positions for compounds containing Me_3Sn and/or *t*-$BuMe_2SiO$ groups are given relative to the signal for $CHCl_3$ (δ 7.25). The tin–proton coupling constants (J_{Sn-H}) are given as the average of the ^{117}Sn and ^{119}Sn values. For compounds containing the Me_3Sn group, high resolution molecular mass measurements were determined on the (M^+ - Me) fragment[24] and are based on ^{120}Sn. GLC analyses were performed with instruments equipped with 25 m × 0.21 mm fused silica columns coated with cross-linked SE-54. TLC analyses were carried out with commercial aluminum-backed silica gel plates (E. Merck, Type 5554). Column and flash[25] chromatography were done with 70–230 and 230–400 mesh silica gel (E. Merck), respectively.

All title compounds exhibited one spot on TLC analyses. Furthermore, the purity of each of these substances was judged to be ≥95% by GLC and ^1H NMR spectral analyses.

Ethyl 6-*tert*-Butyldimethylsiloxy-2-hexynoate (18). To a cold (−78 °C), stirred solution of 5-*tert*-butyldimethylsiloxy-1-pentyne[7] (2 g, 10 mmol) in 35 mL of dry THF (argon atmosphere) was added a solution of MeLi in Et_2O (7.1 mL, 10 mmol). The solution was stirred at −78 °C for 15 min and at −20 °C for 1 h. Ethyl chloroformate (1.0 mL, 10 mmol) was added and the yellow solution was stirred at −20 °C for 1 h and at room temperature for 1 h. Saturated aqueous $NaHCO_3$ and Et_2O were added, the phases were separated, and the organic phase was washed (H_2O), dried ($MgSO_4$), and concentrated. Distillaion (105–115 °C (0.3 Torr)) of the residual oil afforded 2.43 g (89%) of the ester **18** as a colorless oil: IR (neat) 2210, 1705, 1250, 1110, 1060, 840 cm^{-1}; ^1H NMR (80 MHz) δ 0.03 (s, 6 H), 0.88 (s, 9 H), 1.28 (t, 3 H, J = 7 Hz), 1.80 (m, 2 H), 2.40 (t, 2 H, J = 7 Hz), 3.65 (t, 2 H, J = 6 Hz), 4.18 (q, 2 H, J = 7 Hz); exact mass calcd for $C_{13}H_{23}O_3Si$ (M^+ - Me) 255.1417, found 255.1419.

Methyl 4-Cyclopropyl-2-butynoate (20). To a cold (−20 °C), stirred solution of *i*-Pr_2NH (140 μL, 1 mmol) and propynoic acid (616 μL, 10 mmol) in 7.5 mL of dry THF (argon atmosphere) was added a solution of *n*-BuLi in hexane (14.5 mL, 21 mmol). After the light yellow solution had been stirred at −20 °C for 10 min, 15 mL of dry HMPA was added and stirring was continued at −20 °C for 15 min and at −10 °C for 1.5 h. Cyclopropylmethyl bromide[8] (1.42 g, 10.5 mmol) was added and the mixture was

(22) Bank, S.; Schriesheim, A.; Rowe, C. A., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3244. Hoffmann, R.; Olofson, R. A. *Ibid.* **1966**, *88*, 943. Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567. Bates, R. B.; Beavers, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 5001. Schlosser, M.; Hartmann, J. *Ibid.* **1976**, *98*, 4674. Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497. Boerth, D. W.; Streitwiesser, A., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 750.

(23) Piers, E.; Gavai, A. V. *J. Org. Chem.*, following paper in this issue.

(24) Occolowitz, J. L. *Tetrahedron Lett.* **1966**, 5291. Kuivila, H. G.; Tsai, K.-H.; Kingston, D. G. I. *J. Organomet. Chem.* **1970**, *23*, 129.

(25) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

stirred at room temperature for 24 h. Methyl iodide (2.5 mL, 40 mmol) was added and stirring was continued for a further 24 h. Cold water and Et_2O were added and the aqueous layer was extracted thoroughly with Et_2O. The combined organic extracts were washed (water, brine), dried ($MgSO_4$), and concentrated. Flash chromatography of the residual yellow oil on silica gel (30 g, 25:1 petroleum ether–Et_2O), followed by distillation (50–65 °C (0.3 Torr)) of the oil thus obtained, gave 735 mg (53%) of the ester **20**, a colorless oil: IR (neat) 3050, 2210, 1710, 1260 cm^{-1}; ^1H NMR (80 MHz) δ 0.50–1.50 (m, 5 H), 2.30 (d, 2 H, J = 7 Hz), 3.78 (s, 3 H); exact mass calcd for $C_8H_{10}O_2$ 138.0681, found 138.0680.

Ethyl 5-Methyl-2-hexynoate (21). To a reagent[11] prepared by stirring a mixture of Zn dust (3.3 g, 50 mmol), Ph_3P (13.1 g, 50 mmol), CBr_4 (16.6 g, 50 mmol), and 80 mL of dry CH_2Cl_2 (argon atmosphere) at room temperature for 24 h was added 3-methylbutanal (2.7 mL, 25 mmol). The resulting tan suspension was stirred at room temperature for 2 h. Petroleum ether (400 mL) was added and the supernatant solution was decanted from the heavier oil. The oil was dissolved in 80 mL of CH_2Cl_2, petroleum ether (400 mL) was added, and the supernatant solution was again decanted. Concentration of the combined supernatant solutions, followed by rapid distillation (<50 °C (0.1 Torr), receiving bulb cooled to −78 °C) of the remaining oil, gave 5.68 g (94%) of 1,1-dibromo-4-methyl-1-pentene [IR (neat) 1610, 1460, 1380, 1365, 860, 790 cm^{-1}; ^1H NMR (80 MHz) δ 0.93 (d, 6 H, J = 7 Hz), 1.50–1.85 (m, 1 H), 2.00 (t, 2 H, J = 7 Hz), 6.41 (t, 1 H, J = 7 Hz)], which was used directly for the next step.

A cold (−78 °C), stirred solution of the dibromo alkene (5.68 g, 23.5 mmol) in 60 mL of dry THF (argon atmosphere) was treated with a solution of MeLi in Et_2O (30.9 mL, 48 mmol). The solution was stirred at −78 °C for 1 h, at room temperature for 1 h, and then was cooled to −20 °C. Ethyl chloroformate (3.1 mL, 32.2 mmol) was added, and the mixture was stirred at −20 °C for 1 h and at room temperature for 1 h. Saturated aqueous $NaHCO_3$ and Et_2O were added and the phases were separated. The organic phase was washed (water, brine), dried ($MgSO_4$), and concentrated. Distillation (85–100 °C (20 Torr)) of the remaining oil gave 2.67 (74%) of the ester **21**, a colorless oil: IR (neat) 2234, 1713, 1388, 1367, 1251 cm^{-1}; ^1H NMR (80 MHz) δ 1.00 (d, 6 H, J = 7 Hz), 1.32 (t, 3 H, J = 7 Hz), 1.60–2.10 (m, 1 H), 2.23 (d, 2 H, J = 6 Hz), 4.20 (q, 2 H, J = 7 Hz); exact mass calcd for $C_8H_{11}O_2$ (M^+ − Me) 139.0759, found 139.0757.

Ethyl 5-Trimethylsilyl-2-pentynoate (19). This ester was prepared via a procedure identical with that described above. 3-Trimethylsilylpropanal[10] (3.25 g, 25 mmol) was converted into 6.60 g (92%) of 1,1-dibromo-4-trimethylsilyl-1-butene, which, upon successive treatment with MeLi and EtO_2CCl, afforded 3.33 g (73%) of the ester **19**, a colorless oil: distillation temperature 70–85 °C (19 Torr); IR (neat 2239, 1713, 1251, cm^{-1}; ^1H NMR (270 MHz) δ 0.24 (s, 9 H), 1.05 (t, 2 H, J = 7 Hz), 1.48 (t, 3 H, J = 7 Hz, 2.53 (t, 2 H, J = 7 Hz), 4.40 (q, 2 H, J = 7 Hz); exact mass calcd for $C_9H_{15}O_2Si$ (M^+ − Me) 183.0842, found 183.0848.

Conversion of the α,β-Acetylenic Esters 18–21 into the Alkyl (*E*)-3-Trimethylstannyl-2-alkenoates 16b–e. To a cold (−98 °C), stirred solution of lithium (phenylthio)(trimethylstannyl)cuprate (22)[3] (1.4 mmol) in 14 mL of dry THF (argon atmosphere) was added dropwise a solution of the α,β-acetylenic ester (1.0 mmol) in 1.0 mL of dry THF containing 1.7 mmol of dry methanol. The mixture was stirred at −98 °C for 20 min and at −78 °C for 6 h. After successive addition of 2 mL of ethanol (substrates **18**, **19**, **21**) or methanol (substrate **20**) and 30 mL of petroleum ether (bp 30–60 °C), the vigorously stirred mixture was allowed to warm to room temperature. The resulting yellow slurry was filtered through a short column of Florisil. The column was washed with 30 mL of petroleum ether and the combined eluate was concentrated. Flash chromatography of the residue on silica gel (18 g, elution with diethyl ether–petroleum ether mixtures), followed by distillation of the oil thus obtained, afforded the required (*E*)-2-alkenoate. The following substances were prepared via this general procedure.

Ethyl (*E*)-6-*tert*-butyldimethylsiloxy-3-trimethylstannyl-2-hexenoate (16b), 310 mg (71%) from 270 mg (1 mmol) of **18**; flash chromatography with 1:30 Et_2O–petroleum ether; distillation temperature 150–160 °C (0.3 Torr); IR (neat) 1695, 1580, 1175, 840, 770, cm^{-1}; ^1H NMR (400 MHz) δ 0.04 (s, 6 H), 0.20 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.89 (s, 9 H), 1.27 (t, 3 H, J = 7 Hz), 1.60–1.66 (m, 2 H), 2.89–2.94 (m, 2 H), 3.64 (t, 2 H, J = 6 Hz), 4.15 (q, 2 H, J = 7 Hz), 5.96 (br s, 1 H, $^3J_{Sn-H}$ = 73 Hz); exact mass calcd for $C_{16}H_{33}O_3SiSn$ (M^+ − Me) 421.1221, found 421.1218.

Ethyl (*E*)-5-trimethylsilyl-3-trimethylstannyl-2-pentenoate (16c), 266 mg (73%) from 198 mg (1 mmol) of **19**; flash chromatography with 1:40 Et_2O–petroleum ether; distillation temperature 85–95 °C (0.2 Torr); IR (neat) 1710, 1600, 1240, 1180, 840, 760 cm^{-1}; ^1H NMR (400 MHz) δ 0.03 (s, 9 H), 0.20 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.55–0.60 (m, 2 H), 1.28 (t, 3 H, J = 7 Hz), 2.80–2.88 (m, 2 H), 4.16 (q, 2 H, J = 7 Hz), 5.87 (t, 1 H, J = 1 Hz, $^3J_{Sn-H}$ = 73 Hz); exact mass calcd for $C_{12}H_{25}O_2SiSn$ (M^+ − Me) 349.0645, found 349.0634.

Methyl (*E*)-4-cyclopropyl-3-trimethylstannyl-2-butenoate (16d), 225 mg (74%) from 138 mg (1 mmol) of **20**; flash chromatography with 1:50 Et_2O–petroleum ether; distillation temperature 60–75 °C (0.3 Torr); IR (neat) 3050, 1710, 1590, 1170, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.23 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.15–0.20, 0.45–0.50 (m, m, 2 H each), 0.73–0.82 (m, 1 H), 2.83 (dd, 2 H, J = 1, 7 Hz), 3.68 (s, 3 H), 5.99 (t, 1 H, J = 1 Hz, $^3J_{Sn-H}$ = 76 Hz); exact mass calcd for $C_{10}H_{17}O_2Sn$ (M^+ − Me) 289.0250, found 289.0238.

Ethyl (*E*)-5-methyl-3-trimethylstannyl-2-hexenoate (16e), 237 mg (74%) from 154 mg (1 mmol) of **21**; flash chromatography with 3:200 Et_2O–petroleum ether; distillation temperature 85–95 °C (0.3 Torr); IR (neat) 1719, 1597, 1385, 1367, 1177, 771 cm^{-1}; ^1H NMR (270 MHz) δ 0.16 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.89 (d, 6 H, J = 7 Hz), 1.27 (t, 3 H, J = 7 Hz), 1.60–1.72 (m, 1 H), 2.80 (dd, 2 H, J = 1, 7 Hz), 4.13 (q, 2 H, J = 7 Hz), 6.00 (t, 1 H, J = 1 Hz, $^3J_{Sn-H}$ = 75 Hz); exact mass calcd for $C_{11}H_{21}O_2Sn$ (M^+ − Me) 305.0563, found 305.0566.

Conversion of the α,β-Acetylenic Esters 18–21 into the Alkyl (*Z*)-3-Trimethylstannyl-2-alkenoates 17b–e. To a cold (−78 °C), stirred solution of lithium (phenylthio)(trimethylstannyl)cuprate (22)[3] (1.3 mmol) in 13 mL of dry THF (argon atmosphere) was added a solution of the α,β-acetylenic ester (1.0 mmol) in 1 mL of dry THF. The mixture was stirred at −78 °C for 15 min and at −48 °C for 4 h. After successive addition of 2 mL of ethanol (substrates **18**, **19**, **21**) or methanol (substrate **20**) and 30 mL of petroleum ether, the vigorously stirred mixture was allowed to warm to room temperature. The yellow slurry was filtered through a short column of Florisol (elution with 30 mL of petroleum ether), and the eluate was concentrated. Purification of the remaining oil by flash chromatography (18 g of silica gel) and distillation provided the required (*Z*)-2-alkenoate. This general procedure was used to prepare the following compounds.

Ethyl (*Z*)-6-*tert*-butyldimethylsiloxy-3-trimethylstannyl-2-hexenoate (17b), 345 mg (79%) from 270 mg (1 mmol) of **18**; flash chromatography with 1:50 Et_2O–petroleum ether; distillation temperature 145–155 °C (0.3 Torr); IR (neat) 1695, 1585, 1200, 835, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.05 (s, 6 H), 0.19 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.91 (s, 9 H), 1.29 (t, 3 H, J = 7 Hz), 1.57–1.64 (m, 2 H), 2.46–2.51 (m, 2 H), 3.61 (t, 2 H, J = 6 Hz), 4.18 (q, 2 H, J = 7 Hz), 6.37 (br s, 1 H, $^3J_{Sn-H}$ = 120 Hz); exact mass calcd for $C_{16}H_{33}O_3SiSn$ (M^+ − Me) 421.1221, found 421.1230.

Ethyl (*Z*)-5-trimethylsilyl-3-trimethylstannyl-2-pentenoate (17c), 284 mg (78%) from 198 mg (1 mmol) of **19**; flash chromatography with 1:50 Et_2O–petroleum ether; distillation temperature 70–80 °C (0.2 Torr); IR (neat) 1703, 1600, 1201, 861, 769 cm^{-1}; ^1H NMR (270 MHz) δ 0.01 (s, 9 H), 0.16 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.50–0.58 (m, 2 H), 1.28 (t, 3 H, J = 7 Hz), 2.33–2.40 (m, 2 H), 4.15 (q, 2 H, J = 7 Hz), 6.33 (t, 1 H, J = 1 Hz, $^3J_{Sn-H}$ = 120 Hz); exact mass calcd for $C_{12}H_{25}O_2SiSn$ (M^+ − Me) 349.0645, found 349.0644.

Methyl (*Z*)-4-cyclopropyl-3-trimethylstannyl-2-butenoate (17d), 204 mg (67%) from 138 mg (1 mmol) of **20**; flash chromatography with 3:200 Et_2O–petroleum ether; distillation temperature 70–80 °C (0.3 Torr); IR (neat) 3060, 1705, 1600, 1200, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.19 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.06–0.12 and 0.46–0.53 (m, m, 2 H each), 0.77–0.85 (m, 1 H), 2.34 (dd, 2 H, J = 1, 7 Hz), 3.73 (s, 3 H), 6.53 (t, 1 H, J = 1 Hz, $^3J_{Sn-H}$ = 120 Hz); exact mass calcd for $C_{10}H_{17}O_2Sn$ (M^+ − Me) 289.0250, found 289.0250.

Ethyl (*Z*)-5-methyl-3-trimethylstannyl-2-hexenoate (17e), 243 mg (76%) from 154 mg (1 mmol) of **21**; flash chromatography with 1:100 Et_2O–petroleum ether; distillation temperature 70–80 °C (3 Torr); IR (neat) 1704, 1599, 1385, 1369, 1196, 772 cm^{-1}; ^1H

NMR (270 MHz) δ 0.15 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.87 (d, 6 H, *J* = 7 Hz), 1.27 (t, 3 H, *J* = 7 Hz), 1.60–1.72 (m, 1 H), 2.27 (dd, 2 H, *J* = 1, 7 Hz), 4.16 (q, 2 H, *J* = 7 Hz), 6.28 (t, 1 H, *J* = 1 H, $^3J_{Sn-H}$ = 121 Hz); exact mass calcd for $C_{11}H_{21}O_2Sn$ (M^+ – Me) 305.0563, found 305.0554.

Deconjugation of the Alkyl (*E*)-3-Trimethylstannyl-2-alkenoates 16a–d. Preparation of the Alkyl (*Z*)-3-Trimethylstannyl-3-alkenoates 13a–d. To a cold (–78 °C), stirred solution of LDA (1.15 mmol) in 5 mL of dry THF (argon atmosphere) was added a solution of the α,β-unsaturated ester (0.5 mmol) in 0.5 mL of dry THF. The bright yellow solution was stirred at –78 °C for 30 min and at 0 °C for 1 h. After the solution had been cooled to –78 °C, it was transferred via cannulation to a vigorously stirred, cold (–98 °C) solution of acetic acid (0.3 mL) in 5 mL of dry diethyl ether. The mixture was warmed to room temperature, and saturated aqueous sodium bicarbonate and diethyl ether were added. The organic phase was separated and the aqueous layer was washed twice with diethyl ether. The combined organic extracts were washed (water, brine), dried ($MgSO_4$), and concentrated. Analysis of the crude product by GLC showed the presence of only one of the two possible geometrically isomeric β,γ-unsaturated esters. Distillation of this material provided the pure product. The following substances were prepared via this general procedure.

Ethyl (*Z*)-3-trimethylstannyl-3-pentenoate (13a), 119 mg (82%) from 145 mg (0.5 mmol) of **16a**; distillation temperature 65–80 °C (0.2 Torr); IR (neat) 1720, 1160, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.20 (s, 9 H, $^2J_{Sn-H}$ = 54 Hz), 1.26 (t, 3 H, *J* = 7 Hz), 1.76 (d, 3 H, *J* = 6 Hz), 3.20 (d, 2 H, *J* = 1 Hz), 4.12 (q, 2 H, *J* = 7 Hz), 6.16 (tq, 1 H, *J* = 1, 6 Hz, $^3J_{Sn-H}$ = 131 Hz); exact mass calcd for $C_9H_{17}O_2Sn$ (M^+ – Me) 277.0250, found 277.0246.

Ethyl (*Z*)-6-*tert*-butyldimethylsiloxy-3-trimethylstannyl-3-hexenoate (13b), 180 mg (83%) from 217 mg (0.5 mmol) of **16b**; distillation temperature 155–165 °C (0.3 Torr); IR (neat) 1720, 1110, 840, 775 cm^{-1}; ^1H NMR (400 MHz) δ 0.04 (s, 6 H), 0.16 (s, 9 H, $^2J_{Sn-H}$ = 54 Hz), 0.91 (s, 9 H), 1.20 (t, 3 H, *J* = 7 Hz), 2.24 (q, 2 H, *J* = 7 Hz), 3.17 (s, 2 H), 3.51 (t, 2 H, *J* = 7 Hz), 4.10 (q, 2 H, *J* = 7 Hz), 6.05 (t, 1 H, *J* = 7 Hz, $^3J_{Sn-H}$ = 129 Hz); exact mass calcd for $C_{16}H_{33}O_3SiSn$ (M^+ – Me) 421.1221, found 421.1214.

Ethyl (*Z*)-5-trimethylsilyl-3-trimethylstannyl-3-pentenoate (13c), 130 mg (72%) from 181 mg (0.5 mmol) of **16c**; distillation temperature 85–95 °C (0.2 Torr); IR (neat) 1730, 1615, 1245, 1170, 845, 760 cm^{-1}; ^1H NMR (400 MHz) δ 0.02 (s, 9 H), 0.18 (s, 9 H, $^2J_{Sn-H}$ = 54 Hz), 1.25 (t, 3 H, *J* = 7 Hz), 1.54 (d, 2 H, *J* = 8 Hz), 3.17 (s, 2 H), 4.11 (q, 2 H, *J* = 7 Hz), 6.10 (t, 1 H, *J* = 8 Hz, $^3J_{Sn-H}$ = 131 Hz); exact mass calcd for $C_{12}H_{25}O_2SiSn$ 349.0645, found 349.0651.

Methyl (*Z*)-4-cyclopropyl-3-trimethylstannyl-2-butenoate (13d), 120 mg (79%) from 151 mg (0.5 mmol) of **16d**; distillation temperature 60–75 °C (0.3 Torr); IR (neat) 3060, 1730, 1615, 1180, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.22 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.38–0.44, 0.72–0.78 (m, m, 2 H each), 1.26–1.36 (m, 1 H), 3.18 (s, 2 H), 3.66 (s, 3 H), 5.42 (d, 1 H, *J* = 8 Hz, $^3J_{Sn-H}$ = 128 Hz); exact mass calcd for $C_{10}H_{17}O_2Sn$ (M^+ – Me) 289.0250, found 289.0253.

Deconjugation of Ethyl (*E*)-5-Methyl-3-trimethylstannyl-2-hexenoate (16e). Preparation of Ethyl (*Z*)-5-Methyl-3-trimethylstannyl-3-hexenoate (13e). To a cold (–78 °C), stirred solution of LDA (0.14 mmol) in 0.5 mL of dry THF (argon atmosphere) were added successively 24 μL (0.14 mmol) of dry HMPA and a solution of 19 mg (0.06 mmol) of the ester **16e** in 0.5 mL of dry THF. After the mixture had been stirred at –78 °C for 30 min and at 0 °C for 1 h, it was cooled to –78 °C and then transferred with a syringe into a cold (–98 °C), vigorously stirred solution of acetic acid (0.1 mL) in 1 mL of dry diethyl ether. Workup as described above (preparation of **13a–d**) gave yellow oil that was passed through a short column of silica gel (3 g, elution with 1:100 Et_2O–petroleum ether). Distillation (85–95 °C (0.3 Torr)) of the oil obtained by concentration of the eluate gave 12 mg (63%) of the β,γ-unsaturated ester **13e**: IR (neat) 1731, 1584, 1399, 1369, 1180, 760 cm^{-1}; ^1H NMR (400 MHz) δ 0.20 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.98 (d, 6 H, *J* = 7 Hz), 1.25 (t, 3 H, *J* = 7 Hz), 2.16–2.26 (m, 1 H), 3.16 (s, 2 H), 4.12 (q, 2 H, *J* = 7 Hz), 5.84 (d, 1 H, *J* = 9 Hz, $^3J_{Sn-H}$ = 128 Hz); exact mass calcd for $C_{11}H_{21}O_2Sn$ (M^+ – Me) 305.0563, found 305.0559.

Deconjugation of the Alkyl (*Z*)-3-Trimethylstannyl-2-alkenoates 17a–e. Preparation of the Alkyl (*E*)-3-Trimethylstannyl-3-alkenoates 14a–e. To a cold (–78 °C), stirred solution of LDA (0.75 mmol) and HMPA (0.75 mmol) in 5 mL of dry THF (argon atmosphere) was added, dropwise, a solution of the α,β-unsaturated ester (0.5 mmol) in 0.5 mL of dry THF. After this stage, the procedure was identical with that described above (preparation of **13a–d**). Analysis (GLC) of the crude, undistilled product showed the presence of only one of the two possible geometrically isomeric β,γ-unsaturated esters. Distillation of this material gave the pure product. The following compounds were prepared via this procedure.

Ethyl (*E*)-3-trimethylstannyl-3-pentenoate (14a), 126 mg (87%) from 145 mg (0.5 mmol) of **17a**; distillation temperature 60–70 °C (0.2 Torr); IR (neat) 1725, 1125, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.14 (s, 9 H, $^2J_{Sn-H}$ = 54 Hz), 1.27 (t, 3 H, *J* = 7 Hz), 1.75 (d, 3 H, *J* = 7 Hz), 3.24 (d, 2 H, *J* = 2 Hz), 4.13 (q, 2 H, *J* = 7 Hz), 5.84 (tq, 1 H, *J* = 2, 7 Hz, $^3J_{Sn-H}$ = 72 Hz); exact mass calcd for $C_9H_{17}O_2Sn$ (M^+ – Me) 277.0250, found 277.0250.

Ethyl (*E*)-6-*tert*-butyldimethylsiloxy-3-trimethylstannyl-3-hexenoate (14b), 176 mg (81%) from 217 mg (0.5 mmol) of **17b**; distillation temperature 150–160 °C (0.3 Torr); IR (neat) 1720, 1100, 840, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.05 (s, 6 H), 0.12 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.89 (s, 9 H), 1.25 (t, 3 H, *J* = 7 Hz), 2.38 (q, 2 H, *J* = 7 Hz), 3.29 (d, 2 H, *J* = 1.5 Hz), 3.65 (t, 2 H, *J* = 7 Hz), 4.12 (q, 2 H, *J* = 7 Hz), 5.77 (tt, 1 H, *J* = 1.5, 7 Hz, $^3J_{Sn-H}$ = 73 Hz); exact mass calcd for $C_{16}H_{33}O_3SiSn$ (M^+ – Me) 421.1221, found 421.1218.

Ethyl (*E*)-5-trimethylsilyl-3-trimethylstannyl-3-pentenoate (14c), 141 mg (78%) from 181 mg (0.5 mmol) of **17c**; distillation temperature 85–95 °C (0.2 Torr); IR (neat) 1733, 1601, 1249, 1178, 855, 766 cm^{-1}; ^1H NMR (400 MHz) δ 0.02 (s, 9 H), 0.12 (s, 9 H, $^2J_{Sn-H}$ = 52 Hz), 1.22 (t, 3 H, *J* = 7 Hz), 1.67 (d, 2 H, *J* = 8 Hz), 3.23 (d, 2 H, *J* = 1.5 Hz), 4.12 (q, 2 H, *J* = 7 Hz), 5.77 (tt, 1 H, *J* = 1.5, 8 Hz, $^3J_{Sn-H}$ = 75 Hz); exact mass calcd for $C_{12}H_{25}O_2SiSn$ (M^+ – Me) 349.0645, found 349.0642.

Methyl (*E*)-4-cyclopropyl-3-trimethylstannyl-3-butenoate (14d), 116 mg (77%) from 151 mg (0.5 mmol) of **17d**; distillation temperature 70–80 °C (0.3 Torr); IR (neat) 3060, 1730, 1605, 1170, 770 cm^{-1}; ^1H NMR (400 MHz) δ 0.11 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.37–0.45, 0.75–0.83 (m, m, 2 H each), 1.60–1.70 (m, 1 H), 3.43 (d, 2 H, *J* = 2 Hz), 3.68 (s, 3 H), 6.04 (td, 1 H, *J* = 2, 9 Hz, $^3J_{Sn-H}$ = 72 Hz); exact mass calcd for $C_{10}H_{17}O_2Sn$ (M^+ – Me) 289.0250, found 289.0253.

Ethyl (*E*)-5-methyl-3-trimethylstannyl-3-hexenoate (14e), 113 mg (71%) from 159 mg (0.5 mmol) of **17e**; distillation temperature 70–80 °C (0.2 Torr); IR (neat) 1734, 1369, 1327, 1180, 769 cm^{-1}; ^1H NMR (400 MHz) δ 0.10 (s, 9 H, $^2J_{Sn-H}$ = 56 Hz), 0.95 (d, 6 H, *J* = 7 Hz), 1.25 (t, 3 H, *J* = 7 Hz), 2.66–2.74 (m, 1 H), 3.26 (d, 2 H, *J* = 1.5 Hz), 4.10 (q, 2 H, *J* = 7 Hz), 5.50 (td, 1 H, *J* = 1.5, 9 Hz, $^3J_{Sn-H}$ = 75 Hz); exact mass calcd for $C_{11}H_{21}O_2Sn$ (M^+ – Me) 305.0563, found 305.0568.

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada, Merck Frosst Canada, Inc., and Merck and Co., Inc., for financial support and the University of British Columbia for a University Graduate Fellowship (to A. V.G.).

Registry No. **13a**, 101849-61-0; **13b**, 101849-62-1; **13c**, 125735-20-8; **13d**, 101849-63-2; **13e**, 125735-21-9; **14a**, 101849-64-3; **14b**, 101849-65-4; **14c**, 125735-22-0; **14d**, 125735-23-1; **14e**, 125735-24-2; **16a**, 74854-50-5; **16b**, 101849-57-4; **16c**, 125735-25-3; **16d**, 101849-58-5; **16e**, 125735-26-4; **17a**, 74854-53-8; **17b**, 101849-59-6; **17c**, 125735-28-6; **17d**, 101849-60-9; **17e**, 125735-29-7; **18**, 101849-55-2; **19**, 125735-27-5; **20**, 101849-56-3; **21**, 65236-42-2; **22**, 69608-62-4; 5-(*tert*-butyldimethylsiloxy)-1-pentyne, 61362-77-4; ethyl chloroformate, 541-41-3; propynoic acid, 471-25-0; cyclopropylmethyl bromide, 7051-34-5; 3-methylbutanal, 590-86-3; 1,1-dibromo-4-methyl-1-pentene, 90701-59-0; 1,1-dibromo-4-(trimethylsilyl)-1-butene, 125735-30-0; 3-(trimethylsilyl)propanal, 18146-03-7.

Supplementary Material Available: ^1H NMR spectra of compounds **13a–e**, **14a–e**, **16b–e**, **17b–e**, and **18–21** (40 pages). Ordering information is given on any current masthead page.