Evaluation of the Relative Magnitude of the β-Effect of Silicon and the γ-Effect of Tin by Intermolecular Competition

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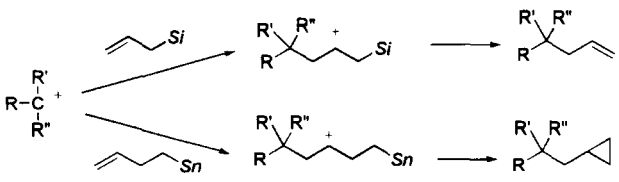
The relative magnitude of the β-effect of silicon and the γ-effect of tin was evaluated by intermolecular competition. An acetal was allowed to react with a 1 : 1 mixture of an allylsilane and a homoallylstannane in the presence of TMSOTf (trimethylsilyl trifluoromethanesulfonate); the former was found to be more reactive than does the latter, indicating that the β-silyl group activates the carbon–carbon double bond more effectively than the γ-stannyl group. This is consistent with the results of molecular-orbital calculations which indicate that the HOMO level of the allylsilane is higher than that of the homoallylstannane. The intermolecular competition between a homoallylstannane and a terminal alkene toward electrophilic reactions with an acetal have revealed that the former is more reactive than the latter. This result indicates that the stannyl group at the γ-position definitely activates the carbon–carbon double bond toward electrophiles.

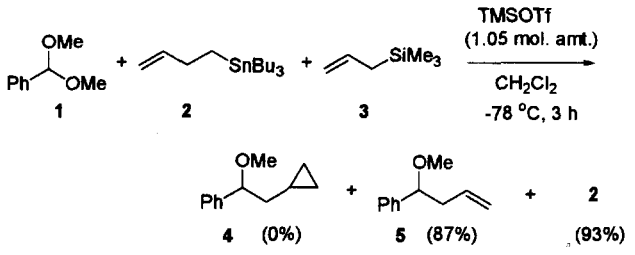
The electronic effects of group-14 elements, such as silicon and tin, have received significant research interests.[1] These studies have uncovered a rich variety of synthetic methodologies based on organo group-14 element compounds. Although the ability of group-14 elements to promote the formation of a positive charge, such as a carbocation at the β-position is known as the β-effect;[2,3] the ability of group-14 elements to promote the formation of a positive charge at the γ-position (the γ-effect) is also quite effective, and is utilized in organic synthesis.[4,5] Extensive experimental and theoretical studies on the origin of β-effects[6] and γ-effects[4a,7] of group-14 elements have revealed that the interaction of the C–M (M = Si, Ge, Sn) σ orbital with a vacant p orbital of the developing carbocation has proved to play a central role, although inductive effects cannot be ignored. Studies on the relative magnitude of these effects have been carried out mainly based on solvolysis experiments; such studies indicate that the magnitude of the effect increases in the order Si < Ge < Sn, and that the β-effect is larger than the γ-effect if we employ the same group-14 element. We have been interested in the relative magnitude of the β-effect and the γ-effect of different elements from the view point of product selectivity.

Previously, we have reported that the γ-elimination of tin is faster than the β-elimination of silicon in intramolecular competition, and that cationic cyclopropanation of "tin carbenoid" with alkenes can be achieved based on the γ-elimination of tin.[8,9] We have also been interested in the relative magnitude of the γ-effect of tin and the β-effect of silicon in cation-forming reactions, such as the addition of electrophiles to carbon–carbon double bonds.[10] In order to obtain insight into this issue, the intermolecular competition of an allylsilane and a homoallylstannane toward an electrophilic reaction was conducted. If the former is more reactive, the reaction leads to a predominant formation of the allylated product, indicating that the β-effect of silicon is stronger than the γ-effect of tin. If the latter is more reactive, the cyclopropylmethylated product is formed, indicating that γ-tin is more effective than β-silicon. In a preliminary study we reported that the allylsilane is more reactive than the homoallylstannane toward acetals, indicating that the β-silyl group activates the carbon–carbon double bond more effectively than the β-stannyl group (Scheme 1).[11] We report herein on the full details of this study.

The intermolecular competition between the γ-effect of tin and the β-effect of silicon was examined using an electrophilic reaction of a homoallylstannane and an allylsilane with an acetal. Thus, benzaldehyde dimethyl acetal (**1**) was allowed to react with a 1 : 1 mixture of tributylhomoallylstannane (**2**) and allyltrimethylsilane (**3**) in dichloromethane in the presence of TMSOTf (trimethylsilyl trifluoromethanesulfonate) (Eq. 1). The cyclopropylmethylated product (**4**), the expected product derived from **1** and **2**, was not detected, and most of **2** was recovered unchanged. The allylated product **5** was obtained in 87% yield.[12]



Scheme 1.

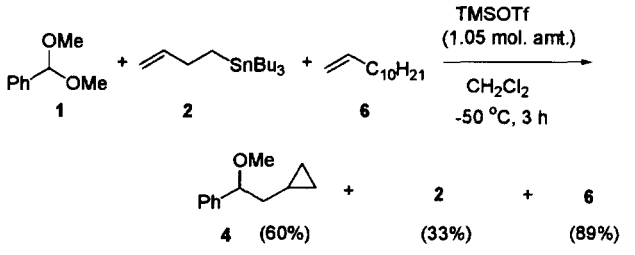


(1)

This result indicates that **3** is much more reactive than **2** toward the oxonium ion ($PhCH{=}OMe^+$) generated from **1**, and suggests that the β-effect of silicon is stronger than the γ-effect of tin in intermolecular competition. In other words, the β-silyl group activates the carbon–carbon double bond more effectively toward the electrophilic reaction than the γ-stannyl group, if we assume that the rate-determining step is the addition of $PhCH = OMe^+$ to the carbon–carbon double bond. This can be explained in terms of the molecular-orbital consideration (Fig. 1). In the case of allylsilane **3**, the energy level of the π orbital of the carbon–carbon double bond is increased by an interaction with the neighboring C–Si σ orbital (σ–π interaction).[1g] Therefore, the reactivity toward electrophiles is increased in comparison with simple carbon–carbon double bonds. In the case of homoallylstannane **2**, however, the energy level of the π orbital seems to be similar to that for normal carbon–carbon double bonds, because the interaction between the π orbital of the carbon–carbon double bond and the C–Sn σ orbital seems to be very weak due to the flexibility of the conformation.[6]

This explanation is supported by the following facts. The oxidation potential of **2** (E_d = 1.43 V vs. Ag/AgCl) is similar to that of tetrabutylstannane (E_d = 1.45 V vs. Ag/AgCl), indicating that the interaction between the C–Sn σ orbital and the π orbital of the carbon–carbon double bond is very small, even if it exists. The oxidation potential of allyltributylstannane (0.97 V) is, however, less positive than that of tetrabutylstannane. In this case the effective interaction between the C–Sn σ orbital and the π orbital increases the HOMO, which in turn favors electron transfer. Likewise, the oxidation potential of **3** (1.53 V) is less positive than those of tetramethylsilane (>2.5 V) and simple terminal alkenes (ca. 2.0 V), indicating the effective interaction between the C–Si σ orbital and the π orbital to increase the HOMO level.[13]

The next question is whether the reactivity of the carbon–carbon double bond of the homoallylstannane is the same as those of simple terminal alkenes or not. Thus, we examined the intermolecular competition between the homoallylstannane and normal terminal alkenes. A 1 : 1 mixture of homoallylstannane (**2**) and 1-dodecene (**6**) was allowed to react with **1** in the presence of TMSOTf. Although it required a slightly higher temperature, the reaction of **1** and **2** took place smoothly to give the cyclopropylmethylated product **4** in 60% yield.[14] Most of **6** was recovered unchanged (Eq. 2).



(2)

This result indicates that the homoallylstannane is definitely more reactive toward electrophiles than simple terminal alkenes. Therefore, there seems to exist some interaction between the C–Sn σ orbital and the π orbital of the carbon–carbon double bond, as shown in Fig. 1, **B**, even if it is not very strong.

Ab initio molecular-orbital calculations were carried out in order to examine the HOMO level of the allylsilane, and that of the homoallylstannane. As shown in Fig. 2, the HOMO level of the allylsilane varies dramatically with the torsion angle of C–C–C–Si, and becomes the maximum when the torsion angle is about 90 degrees. The difference between the maximum and the minimum is about 0.4 eV, indicating that the orbital interaction between the π orbital of the carbon–carbon double bond and the carbon–silicon σ orbital is significant. The HOMO level of the homoallylstannane also varies with the torsion angle of C–C–C–C, and becomes the maximum when the torsion angle is about 75 degrees. However, the difference between the maximum and the minimum is not as large as that for the allylsilane. This difference indicates a smaller interaction of the π-orbital of the carbon–carbon double bond and the C–Sn σ orbital. Since the

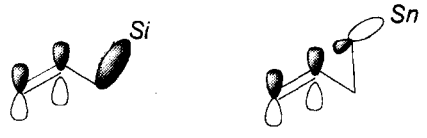


Fig. 1. σ–π Interactions in allylsilane (**A**) and homoallylstannane (**B**).

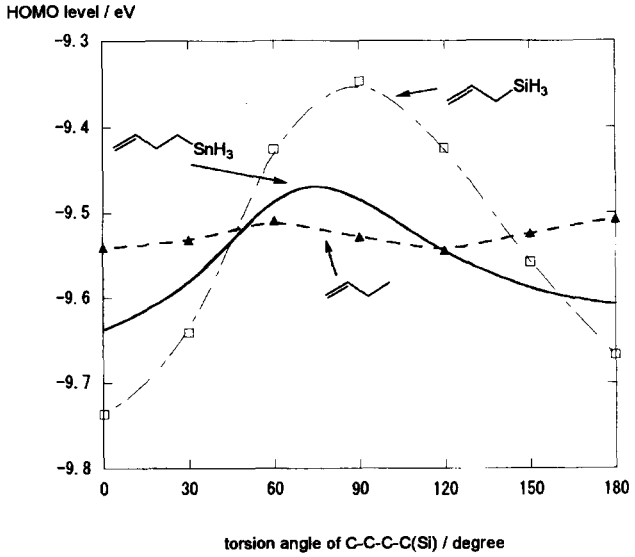


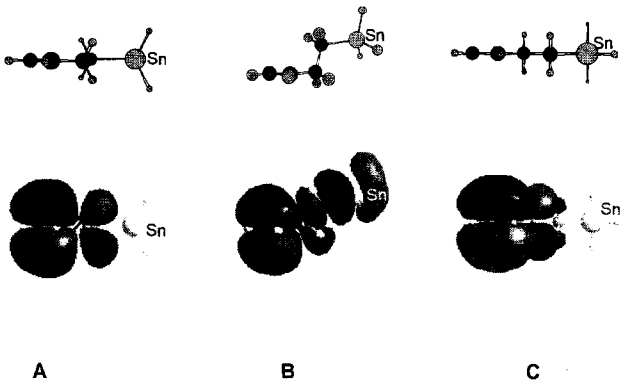
Fig. 2. Variation of HOMO of allylsilane, homoallylstannane, and 1-butene with the torsion angle (MP2/LANL2DZ).

energy match between the C–Sn σ orbital with the π orbital seems to be better than that between the C–Si σ orbital with the π orbital, the smaller interaction seems to be attributed to an unfavorable spatial relationship between two orbitals.

It is important to note, however, that there is a definite effect of γ-Sn, because the HOMO level at about 75 degrees, although this conformer is not energetically most favorable, is higher than the HOMO of simple alkenes, such as 1-butene, the energy of which does not significantly vary with the torsion angle. In a conformation where the HOMO level of the homoallylstannane becomes the maximum, the percaudal interaction between the C–Sn σ orbital and the π-orbital of the carbon–carbon double bond can be attained effectively, as demonstrated in Fig. 3, **B**. The back lobe of the C–Sn σ orbital interacts with the p orbital of the carbon–carbon double bond in an anti-bonding fashion. When the torsion angle is around 0 and 180 degrees, such an interaction cannot be attained, because two orbitals are perpendicular to each other and the HOMO is localized to the carbon–carbon double bond (Fig. 3, **A** and **B**).

Therefore, the results of the molecular-orbital calculations are consistent with the experimental results, although it is rather difficult to know from which conformer the reaction takes place.

The intermolecular competition revealed that the β-silyl group activates the carbon–carbon double bond toward electrophiles more effectively than the γ-stannyl group. The γ-stannyl group, however, definitely activates the carbon–carbon double bond in comparison with alkyl groups, although the magnitude of the γ-effect of tin is much smaller than the β-effect of silicon. The ab initio molecular-orbital calculations indicate that the C–Si σ orbital at the β position interacts with the neighboring π orbital of the carbon–carbon double bond more effectively than the C–Sn σ orbital at γ position. But the calculations also indicate that there is a definite interaction between the C–Sn σ orbital and the π orbital, which is consistent with the experimental fact that the homoallylstannane is more reactive than simple terminal alkenes. The present work provides significant information about the relative magnitude of the β-effect of silicon and the γ-effect of tin, which serve as an effective base to design reactions of organo group-14 element compounds.



A B C

Fig. 3. HOMO of the conformers of homoallylstannane (MP2/LANL2DZ).

Experimental

General Remarks. Glass-support precoated (Merk silica gel 60 F254, 0.25 mm) plates were employed for analytical TLC. Flash chromatography was carried out using Wako-Gel C-300 or Kanto 60N. Gas-phase chromatography (GPC) was performed on a Shimadzu gas chromatograph equipped with a 2 m×3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS (3 mm×2 m) or a capillary column (OV-1, 25 m). Proton NMR spectra were determined on a Varian Gemini 2000 spectrometer (300 MHz). Carbon NMR spectra were determined on a Varian Gemini 2000 spectrometer (75 MHz). Infrared (IR) spectra were determined on a Shimadzu FTIR-8200 spectrophotometer. Mass spectra were obtained on a JEOL IMS-300 spectrometer. Preparative GPC was carried out with Japan Analytical Industry LC-908 (JAIGEL-1H, 2H).

Competition between Allylsilane and Homoallylstannane. To a solution of benzaldehyde dimethyl acetal (30.5 mg, 0.200 mmol), allyltrimethylsilane (22.2 mg, 0.194 mmol) and 3-butenyltributylstannane (68.5 mg, 0.198 mmol) in CH_2Cl_2(0.60 mL) was added TMSOTf (37.0 μL, 0.204 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 3.0 h. The reaction was quenched by the addition of Et_3N (50 μL). The mixture was passed through a silica-gel short column to remove insoluble materials. After removal of the solvent, the products were analyzed. The yields of each compound were determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2,-tetrachloroethane as an internal standard. The allylated product **5** was identified by a comparison of its spectrum data with an authentic sample.

Competition between Homoallylstannane and 1-Dodecene. The reaction was performed by the addition of TMSOTf (37.0 μL, 0.204 mmol) to a solution of benzaldehyde dimethyl acetal (30.5 mg, 0.200 mmol), 1-dodecene (48 μL, 0.198 mmol) and 3-butenyltributylstannane (68.5 mg, 0.198 mmol) in CH_2Cl_2 (0.60 mL) at −52 °C. The cyclopropylmethylated product **4** was identified by a comparison of its spectral data with an authentic sample prepared by the reaction of benzaldehyde dimethyl acetal and 3-butenyltributylstannane.

2-Cyclopropyl-1-methoxy-1-phenylethane (4). To a solution of benzaldehyde dimethylacetal (75 μL, 0.50 mmol) and 3-butenyltributylstannane (219.5 mg, 0.64 mmol) in CH_2Cl_2 (1.8 mL) was added TMSOTf (100 μL, 0.55 mmol) at −40 °C. The reaction mixture was stirred at the same temperature for 3.0 h. The reaction was quenched by the addition of sat. aq $NaHCO_3$. The mixture was warmed to room temperature. The organic materials were extracted with ether, and the organic phase was washed with brine, and dried over $MgSO_4$. After removal of the solvent, the residue was purified via flash chromatography to obtain the title compound (73.1 mg, 83%). TLC R_f 0.27 (hexane/EtOAc = 20/1), ^{1}H NMR (300 MHz, $CDCl_3$) δ = −0.02 (ddd, J = 14.4, 9.0, 5.1 Hz, 1 H), 0.06 (ddd, J = 14.4, 9.6, 5.4 Hz, 1 H), 0.30—0.50 (m, 2 H), 0.60—0.70 (m, 1 H), 1.47 (ddd, J = 13.8, 6.9, 6.9 Hz, 1 H), 1.77 (ddd, J = 13.8, 6.9, 6.9 Hz, 1 H), 3.23 (s, 3 H), 4.18 (t, J = 6.9 Hz, 1 H), 7.20—7.40 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 4.26, 7.56, 43.10, 56.53, 84.44, 126.89, 127.51, 128.35, 142.47; IR (neat) 1455, 1102, 700 cm^{-1}. Anal. Found: C, 81.33; H, 9.10%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

Molecular Orbital Calculations. The ab initio calculations were carried out using the GAUSSIAN 98 program (G98W)[15] at the MP2/LANL2DZ level.

The total energies of the conformers of homoallylstannane are given in Table 1.

Table 1. Conformational Energy of Homoallylstannane (MP2/LANL2DZ)

Torsion angle / degrees	Relative energy / kcal mol^{-1}
0	0.765
30	1.523
60	2.068
70	1.791
75	1.578
80	1.333
90	0.814
118	0
120	0.004
150	1.036
180	2.205

Rotating Disk Electrode Voltammetry. In order to determine the oxidation potentials, rotating-disk electrode voltammetry was carried out with a Hokuto HA-301 and a Nikko Keisoku RRDE-1 using a glassy carbon working electrode, a platinum-wire counter electrode, and a Ag/AgCl (saturated aq KCl) reference electrode in 0.1 M $LiClO_4/CH_3CN$ (1 M = 1 mol dm^{-3}) at 1000 rpm. The sweep rate was 10 mV s^{-1}.

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References

1 For example: a) J. B. Lambert, Y. Zhao, R. W. Emblide, L. A. Salvador, X. Liu, J.-H. So, and E. C. Chelius, *Acc. Chem. Res.*, **32**, 183 (1999). b) J. Yoshida and K. Nishiwaki, *J. Chem. Soc., Dalton Trans.*, **1998**, 2589. c) J. M. White, *Aust. J. Chem.*, **48**, 1227 (1995). d) J. R. Hwu, B.-L. Chen, and S.-S. Shiao, *J. Org. Chem.*, **60**, 2448 (1995). e) J. Yoshida, T. Murata, S. Matsunaga, T. Maekawa, S. Shiozawa, and S. Isoe, *Rev. Heterotaom. Chem.*, **5**, 193 (1991). f) J. B. Lambert, *Tetrahedron*, **46**, 2677 (1990). g) Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, Chichester (1989), p. 57. h) J. C. Giordan, *J. Am. Chem. Soc.*, **105**, 6544 (1983).

2 Synthetic applications of the β-effect of silicon: For example: a) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin and Heidelberg (1983). b) E. W. Colvin, "Silicon Reagents in Organic Synthesis," Academic Press, London (1988). c) I. Fleming, in "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and L. A. Paquette, Pergamon Press, Oxford (1991), Vol. 2, p. 563. d) I. Fleming, J. Dunoguès, and R. Smithers, *Org. React.*, **37**, 57 (1989).

3 Synthetic applications of the β-effect of tin: For example: a) M. Pereyre, J.-B. Quintard, and A. Rahm, "Tin in Organic Synthesis," Butterworth & Co., London (1987). b) Y. Yamamoto, *Aldrichimica Acta*, **20**, 45 (1987).

4 Synthetic applications of the γ-effect of silicon: For example: a) H. Sakurai, T. Imai, and A. Hosomi, *Tetrahedron Lett.*, **1977**, 4045. b) Y. Hatanaka and I. Kuwajima, *Tetrahedron Lett.*, **27**, 719 (1986).

5 Synthetic applications of the γ-effect of tin: a) D. D. Davis, R. L. Chambers, and H. T. Johnson, *J. Organomet. Chem.*, **25**, C13 (1970). b) T. Sato, *Synthesis*, **1990**, 259. c) L. Plamondon and J. D. Wuest, *J. Org. Chem.*, **56**, 2066 and 2076 (1991). d) J. A. Marshall, J. A. Jablonowski, and G. P. Luke, *J. Org. Chem.*, **59**, 7825 (1994). e) T. Sato and S. Nagatsuka, *Synlett*, 653 (1995). f) R. L. Beddoes, M. L. Lewis, P. Quayle, and S. Johal, *Tetrahedron Lett.*, **36**, 471 (1995). g) N. Isono and M. Mori, *J. Org. Chem.*, **61**, 7867 (1996). h) H. Wakamatsu, N. Isono, and M. Mori, *J. Org. Chem.*, **62**, 8917 (1997). i) A. Krief and L. Provins, *Tetrahedron Lett.*, **39**, 2017 (1998).

6 a) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organomet. Chem.*, **66**, 249 (1974). b) J. B. Lambert and R. B. Finzel, *J. Am. Chem. Soc.*, **104**, 2020 (1982). c) S. G. Wierschke, J. Chandrasekhar, and W. L. Jorgensen, *J. Am. Chem. Soc.*, **107**, 1496 (1985). d) N. Auner, R. Walsh, and J. Westrup, *J. Chem. Soc., Chem. Commun.*, **1986**, 207. e) P. Magnus, P. M. Cairns, and J. Moursounidis, *J. Am. Chem. Soc.*, **109**, 2469 (1987). f) J. B. Lambert, G. Wang, R. B. Finzel, and D. H. Teramura, *J. Am. Chem. Soc.*, **109**, 7838 (1987). g) D. Hajdasz and R. Squires, *J. Chem. Soc., Chem. Commun.*, **1988**, 1212. h) J. B. Lambert, G. Wang, and D. H. Teramura, *J. Org. Chem.*, **53**, 5422 (1988). i) X. Li and J. A. Stone, *J. Am. Chem. Soc.*, **111**, 5586 (1989). j) J. B. Lambert and E. C. Chelius, *J. Am. Chem. Soc.*, **112**, 8120 (1990). k) M. A. Brook and A. Neuy, *J. Org. Chem.*, **55**, 3609 (1990). l) J. Yoshida, T. Maekawa, T. Murata, S. Matsunaga, and S. Isoe, *J. Am. Chem. Soc.*, **112**, 1962 (1990). m) H.-U. Siehl, F.-P. Kaufmann, Y. Apeloig, V. Braude, D. Danovich, A. Berndt, and N. Stamatis, *Angew. Chem., Int. Ed. Engl.*, **30**, 1479 (1991). n) G. Hage and H. Mayr, *J. Am. Chem. Soc.*, **113**, 4954 (1991). o) J. M. White and G. B. Robertson, *J. Org. Chem.*, **57**, 4638 (1992). p) J. B. Lambert, R. W. Emblidge, and S. Malany, *J. Am. Chem. Soc.*, **115**, 1317 (1993). q) V. Gabelica and A. J. Kresge, *J. Am. Chem. Soc.*, **118**, 3838 (1996). r) V. Y. Chan, C. I. Clark, J. Giordano, A. J. Green, A. Karalis, and J. M. White, *J. Org. Chem.*, **61**, 5227 (1996).

7 a) H. G. Kuivila and N. M. Scarpa, *J. Am. Chem. Soc.*, **92**, 6990 (1970). b) H. C. Clark and R. C. Poller, *Can. J. Chem.*, **48**, 2670 (1970). c) D. D. Davis and H. T. Johnson, *J. Am. Chem. Soc.*, **96**, 7576 (1974). d) D. C. McWilliam, T. R. Balasubramanian, and H. G. Kuivila, *J. Am. Chem. Soc.*, **100**, 6407 (1978). e) V. J. Shiner, Jr., M. W. Ensinger, and G. S. Kriz, *J. Am. Chem. Soc.*, **108**, 842 (1986). f) E. R. Davidson and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **108**, 3135 (1986). g) J. Cooper and V. J. Shiner, Jr., *J. Org. Chem.*, **54**, 4270 (1989). h) I. Fleming, S. K. Patel, and C. J. Urch, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 115. i) V. J. Shiner, Jr., and M. W. Ensinger, *J. Org. Chem.*, **55**, 653 (1990). j) J. Cooper, V. J. Shiner, Jr., and M. W. Ensinger, *J. Am. Chem. Soc.*, **112**, 2834 (1990). k) J. B. Lambert, L. A. Salvador, and J.-H. So, *Organometallics*, **12**, 697 (1993). l) A. J. Green, T. Pigdon, J. M. White, and J. Yamen, *J. Org. Chem.*, **63**, 3943 (1998). m) T. Nakashima, R. Fujiyama, M. Fujio, and Y. Tsuno, *Tetrahedron Lett.*, **40**, 539 (1999). n) T. Nakashima, R. Fujiyama, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **72**, 1043 (1999). o) T. Nakashima, R. Fujiyama, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **72**, 741 (1999).

8 M. Sugawara and J. Yoshida, *J. Am. Chem. Soc.*, **119**, 11986 (1997).

9 a) M. Sugawara and J. Yoshida, *Synlett*, **1998**, 1057. b) M. Sugawara and J. Yoshida, *Tetrahedron Lett.*, **40**, 1717 (1999).

10 Reactivity of group 14 elements substituted olefins toward electrophiles: a) J. Bartl, S. Steenken, and H. Mayr, *J. Am. Chem. Soc.*, **113**, 7710 (1991). b) H. Mayr and M. Patz, *Angew. Chem., Int. Ed. Engl.*, **33**, 938 (1994). c) H. Mayr, O. Kuhn, M. F. Gotta, and M. J. Patz, *Phys. Org. Chem.*, **11**, 642 (1998).

11 Sugawara and J. Yoshida, *J. Chem. Soc., Chem. Commun.*, **1999**, 505.

12 A. Hosomi, M. Endo, and H. Sakurai, *Chem. Lett.*, **1976**, 941.

13 Oxidation potential of allylsilanes. See: J. Yoshida, T. Murata, and S. Isoe, *Tetrahedron Lett.*, **27**, 3373 (1986).

14 Reactions of homoallylstannanes with hetero electrophiles have been reported. a) D. J. Peterson and M. D. Robbins, *Tetrahedron Lett.*, **1972**, 2135. b) D. J. Paterson, M. D. Robbins, and J. R. Hansen, *J. Organomet. Chem.*, **73**, 237 (1974). c) K. C. Nicolaou, D. A. Claremon, W. E. Barnette, and S. P. Seitz, *J. Am. Chem. Soc.*, **101**, 3704 (1979). d) Y. Ueno, M. Ohta, and M. Okawara, *Tetrahedron Lett.*, **23**, 2577 (1982). e) J. W. Herndon and J. J. Harp, *Tetrahedron Lett.*, **33**, 6243 (1992).

15 "Gaussian 98 (Revision, A. 6)," M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA (1998).