Regioselective Carboxylation of Silicon-Stabilized Allylic Carbanions and the Synthetic Utility of 2-Silyl-3-butenoates

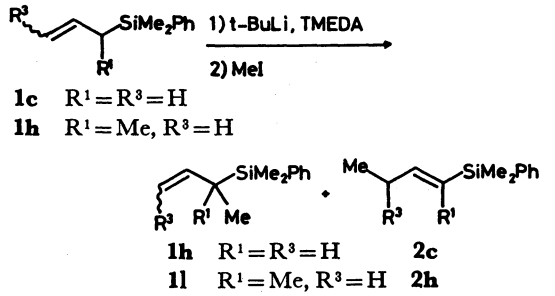
Hidemitsu Uno
Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho 2-5, Matsuyama 790
(Received March 10, 1986)

Carbanions of allylic dimethylphenylsilanes show remarkable regioselectivity toward both carboxylation with carbon dioxide and methylation with methyl iodide. Methylation of these compounds occurred preferentialy at α position, although allyltrimethylsilane and allyltriphenylsilane are known to give γ selectivity toward the same electrophiles. Moreover, their aluminum "ate" complexes react with carbon dioxide regioselectively at the α position irrespective of methyl substitution pattern of the allylic moieties. The α-carboxylated allylic silanes proved to be useful synthons of 3-(methoxycarbonyl)allyl anions after esterification.

Regioselectivity in the reaction of unsymmetrical allylic carbanions with electrophiles has been discussed from both theoretical and synthetic points of view by numerous investigators[1] and is still subtle because it depends upon not only inherent characters of allylic carbanions, i.e. charge densities and HOMO coefficients, but also counter metal cations, solvation, steric effects, and transition states. Many efforts have been made to attain preferable regiochemistry. For example, predominant location of the counter cations was successfully achieved by charge repulsion,[2] intramolecular chelation,[3] and transmetallation[4] including "ate" complexation.[5] Accessibility of electrophiles to the carbanionic centers was well controlled by "hard-soft" interaction,[6] steric effects,[7] and transition state.[7] Although similar methodologies could be generally applied for the regiochemical control of silicon-stabilized allylic carbanions, γ-regioselectivity was frequently realized mainly because of steric factors.[8] Tsai and Matteson[9] have reported an exclusive α selectivity in reactions of 3-trimethylsilyl-2-propenyl-boronate. Similar results[10] have been reported in the reaction of η^3-trimethylsilylallyltitanium(III) compound, $[Ti(\eta^5\text{-cp})_2(\eta^3\text{-1-trimethylsilylallyl})]$. Success of these reactions may be ascribed to location of very bulky counter cations on the γ carbon. While the effects of counter cations at the transition state have been frequently discussed,[8] the roles of substituents on silicon atom have never been considered. We have already reported that aluminates of dimethylphenylsilyl-stabilized allylic carbanions reacted with carbon dioxide regioselectively at α position.[11] In this report, we describe the further results about the effects of substituents on a silicon atom.

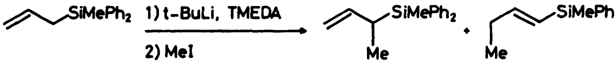
Results and Discussion

Regioselectivity in Nucleophilic Reaction of Silyl-Stabilized Allylic Carbanions. Alkylation of silyl-stabilized carbanions bearing alkali metals as counter cations has been reported to occur preferably at γ position because of the steric hindrance and the large γ charge densities. For example, lithiated allyltriphenylsilane (**1b**) reacted with methyl iodide exclusively at γ position as well as the corresponding trimethylsilyl derivatives.[8a,8f,8l] The lithiated derivative of allyldimethylphenylsilane (**1c**), however, was found to react predominantly at α position to give a mixture of (1-methyl-2-propenyl)dimethylphenylsilane (**1h**) and (1-butenyl)dimethylphenylsilane (**2c**) (**1h**/**2c** =80/20) (Eq. 1). Also, moderate α selectivity was observed in 1-methyl-2-propenylsilane **1h** (**1l**/**2h**= 64/36). Allylmethyldiphenylsilane (**1d**), of which α position could be more hindered than **1c**, still showed α selectivity (**1m**/**2d**=73/27).



1c $R^1=R^3=H$
1h $R^1=Me, R^3=H$

1h $R^1=R^3=H$ **2c**
1l $R^1=Me, R^3=H$ **2h** (1)



1d **1m** **2d** (2)

According to MINDO/3 calculation for a carbanion of allylsilane,[12] α selectivity was predicted under orbital control conditions, while γ selectivity under charge control conditions. From orbital cosideration, stabilization of an adjacent carbanion by a silyl group is attributable to p-σ* hyperconjugation.[13] In allyldimethylphenylsilane (**1c**), the energy level of the σ*

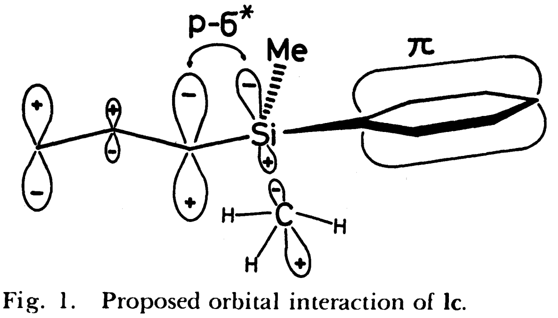


Fig. 1. Proposed orbital interaction of **1c**.

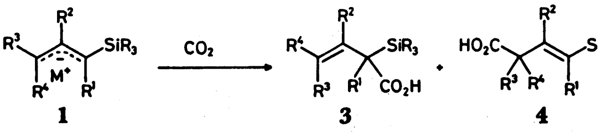
Table 1. Carboxylation of Allylic Carbanions

Entry	Silane 1						3/4 Ratio (Yield/%)[a)]	
	R_3	R^1	R^2	R^3	R^4		M^+=Li^+	M^+=$AlEt_3\cdot Li^+$
1	Me_3	H	H	H	H	(**1a**)	12/88	75 (35)/25
2	Ph_3	H	H	H	H	(**1b**)	20/80 (60)[b)]	70 (55)/30
3	Me_2Ph	H	H	H	H	(**1c**)	20/80 (59)[c)]	100 (85)/—
4	$MePh_2$	H	H	H	H	(**1d**)	23/77 (91)[c)]	100 (60)/—
5	$Me_2(CH=CH_2)$	H	H	H	H	(**1e**)	29/71 (29)[c)]	100 (46)/—
6	Me_2(*p*-Tol)	H	H	H	H	(**1f**)	22/78 (53)[c)]	100 (50)/—
7	Me_2(*t*-Bu)	H	H	H	H	(**1g**)	—[d)]	100 (20)/—
8	Me_2Ph	Me	H	H	H	(**1h**)	45 (35)/55 (44)	100 (75)/—
9	Me_2Ph	H	Me	H	H	(**1i**)	20/80 (50)[c)]	100 (70)/—
10	Me_2Ph	H	H	Me	H	(**1j**)	—/100 (79)	100 (65)/—[e)]
11	Me_2Ph	H	H	Me	Me	(**1k**)	—/100 (25)	—

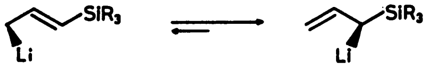
a) Isolated yield. b) Ref. 8b. c) Isolated yield of the regioisomeric mixture. d) Not determined. e) Stereoisomeric ratio was determined to be *Z*/*E*=>10/1 by the ^{1}H NMR (400 MHz) analysis after methylation with diazomethane.

orbital of Si–Me bond would be lowered by the conjugation with a phenyl group (Fig. 1).[14)] Therefore, the interaction between p orbitals of an allylic carbanion moiety and the σ^* antibonding orbital might be increased and larger HOMO coefficient at α carbon was expected than that of allyltrimethylsilane (**1a**). Moreover, the charge density at the α carbon might be increased according to the electron-attracting character of a phenyl group. Allyltriphenylsilane (**1b**) would show the reverse selectivity because of not only large steric hindrance but the lack of the low lying sp^3-σ^* orbital. Indeed, it was reported that methylation of **1b** occurred exclusively at the γ carbon[8a)] and that moderate γ selectivity (α/γ=35/65) was observed in the alkylation of **1a** with alkyl iodides. On the other hand, preferential α methylation was observed if the silicon atom had both methyl and phenyl groups (**1c**: α/γ=80/20, **1d**: α/γ=73/27). Allylic carbanions stabilized by a dimethylphenylsilyl or methyldiphenylsilyl group were no longer γ selective in the reaction with methyl iodide, a "soft" electrophile. In the next, we will focus the discussion on the regioselectivity in the carboxylation of silyl-substituted allylic carbanions with carbon dioxide, which is classified to a "hard" electrophile.

Carboxylation of the lithiated derivatives of allyltriorganosilanes was carried out at −78 °C by reverse addition of the carbanion solution to give a regioisomeric mixture in moderate to good yields (Eq 3 and Table 1). In Entries 1—6, moderate γ regioselectivity (**3**/**4**=12/88—29/71) was observed. The γ selectivity could be well explained in terms of the 6-membered cyclic transition state if the equilibrium between the α-lithio allylic silanes and γ-lithio vinylic silanes was assumed to lie to the formers (Eq. 4).



(3)



(4)

This assumption was supported by the fact that carboxylation of butenylsilane **1j** occurred preferably at the carbanion center bearing a methyl substituent to give exclusively γ carboxylated compounds **4j** in good yield, although this position is sterically disadvantageous (Entry 10). On the other hand, the reaction of (1-methyl-2-propenyl)dimethylphenylsilane (**1h**) showed lower regioselectivity (Entry 8, **3h**/**4h**=45/55).[15)] It is known that a methyl substituent increases the charge density on the γ carbon to the methyl group because of its electron-donating character. Therefore, lithium counter cation would tend to be localized at the γ position to the methyl group. Opposite effects between methyl and dimethylphenylsilyl groups described above would be the reason for the low selectivity in 1-methyl-2-propenylsilane **1h**. On the other hand, cooperative effects of both substituents to give the high γ regioselectivity in **1j** and **1k**.

We turned our attention to effects of counter cations. Corriu and his co-workers[8b)] reported that α-carboxylated compound **3b** was preferably obtained (**3b**/**4b**=85/15) in the reaction of the Grignard reagent prepared from 3-bromo-1-triphenylsilylpropene. The similar result (**3c**/**4c**=83/17) was obtained in the carboxylation of the Grignard reagent prepared from 3-bromo-1-(dimethylphenylsilyl)propene.[8b)] As the carboxylation of the Grignard reagents would also be thought to proceed via 6-membered cyclic transition state, the different selectivity between lithio and magnesio derivatives might be interpreted if we would assume that the magnesium counter cation would be localized mainly at the γ position by the electronic repulsion with the silyl group. Though the respective electronegativity values of magnesium and lithium were given as 1.2 and 1.0, a magnesium counter cation might be more positive than a lithium counter cation because the former had another highly polarized magnesium-halogen bond.[16]

In order to obtain the α-carboxylated products in high selectivity, we examined the effects of additives to lithio derivatives of allylic silanes. As high α selectivity was reported in the reaction of lithiated allyltrimethylsilane with acetophenone in the presence of $MgBr_2$,[8f] carboxylation was carried out according to the similar manner to give a regioisomeric mixture (**3a**/**4a**=83/17). In the course of the reaction, it was ambigous whether the actual intermediate was a magnesio derivative or a magnesium "ate" complex, because the magnesium-bromine bond was accounted to undergo transmetallation reaction with alkyllithiums.

As aluminum "ate" complexes were reported to show marked regioselectivity in the reaction with various electrophiles,[5] we attempted to utilize this method to the carboxylation. The allylic aluminum "ate" complex, which was generated in situ by adding triethylaluminum to the lithiated allyltrimethylsilane, reacted smoothly with CO_2 to give a regioisomeric mixture which consisted of **3a** and **4a** (**3a**/**4a**=75/25). By chromatographic separation, pure α-carboxylated compound **3a** was obtained in 35% yield (Table 1). The low isolated yield seemed to be attributable to instability of **3a**. During the isolation and purification, **3a** slowly decomposed to give 2- and 3-butenoic acid. Once **3a** was isolated as solids, it could be stored in a freezer without decomposition for several weeks. Allyltriphenylsilane (**1b**) gave a mixture of α- and γ-carboxylated compounds (**3b**/**4b**=70/30). On the other hand, carboxylation of dimethylphenylsilyl derivative **1c** occurred exclusively at the α position to give 2-(dimethylphenylsilyl)-3-butenoic acid (**3c**) in good yield (Entry 3). Similar high α selectivity was realized in the reaction of "hybrid" allylsilanes (Entries 4—7). Low yields obtained in the reaction of **1e** and **1g** (Entries 5 and 7) could be ascribed to anionic polymerization and poor metallation. A methyl substituent on the allyl moiety proved to have no influence on the regioselectivity if the dimethylphenylsilyl group was employed as an anion-stabilizing group. Silanes **1h**, **1i**, and **1j** were carboxylated regioselectively at α position to give α-silyl β,γ-unsaturated carboxylic acids in good yields (Entries 8, 9, and 10). It is noteworthy that 2-butenylsilane **1j** gave *Z*-isomer of 2-(dimethylphenylsilyl)-3-pentenoic acid (**3j**) in good selectivity (*Z*/*E*=>10/1) (Entry 10). 3-Methyl-2-butenylsilane **1k** (Entry 11) did not show the existence of any carboxylated compounds. Similar results were also obtained in the reactions of (1,2-dimethyl-2-propenyl)-, (2-methyl-2-butenyl)-, and (1-methyl-2-butenyl)dimethylphenylsilanes of which lithiation seemed to occur insufficiently. Though there is some limitation that this method could not be applied for highly-substituted allylic silanes, this method is very useful for the preparation of α-silyl β,γ-unsaturated carboxylic acids.

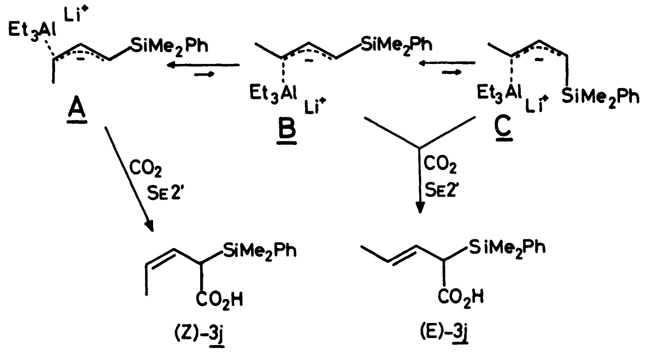
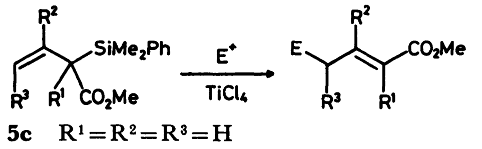


Fig. 2. Proposed carboxylation mechanism.

The remarkable α regioselectivity and stereoselectivity may be interpreted by applying the similar postulation described in the alkylation except for the case of **1g**. The reaction mechanism is discussed about 2-butenyldimethylphenylsilane (**1j**) as a representative case including both problems. There might be a conformational equilibrium of the allylic aluminate generated by adding Et_3Al to the lithiated derivative of 2-butenylsilane **1j** (Fig. 2). In the equilibrium, triethylaluminum would be localized at γ position by steric and/or electrostatic repulsions with the silyl group. Since 2-butenyllithium was reported to exist preferably as an "S"-shape conformer in a THF solution,[17] the conformer **A** would be more faborable than the "W"-shape conformer **B**. Another "S"-shape conformer **C** seemed to be disadvantageous because of the steric interaction between the bulky silyl group and a γ-allylic proton. Indeed, all vinylic silanes obtained in the reaction at γ position had trans geometry and no generation of cis vinylic silanes was observed in all cases irrespective of the species of counter cations. As aluminum "ate" complexes were considered to be in a saturated coordination state, 6-membered cyclic transition state might not participate even in the reaction of carbon dioxide. Therefore, it is suitable to consider that SE2′ type reaction via the conformer **A** would occur on the α carbon which had the large HOMO coefficient to afford *cis*-2-(dimethylphenylsilyl)-3-pentenoic acid (**3j**).

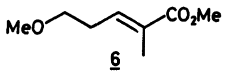
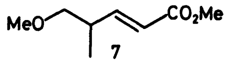
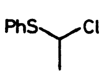
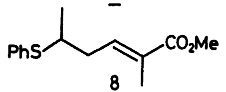
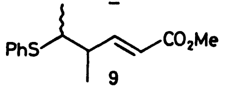
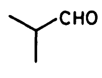
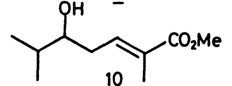
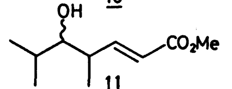
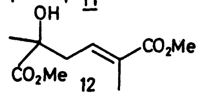
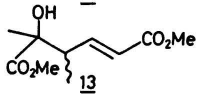
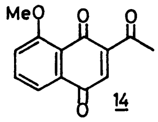
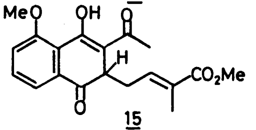
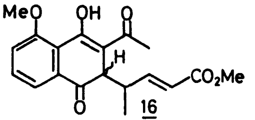
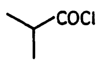
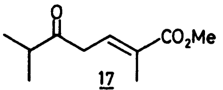
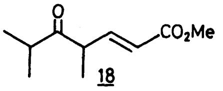
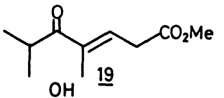
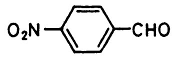
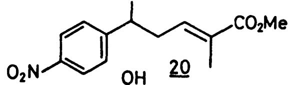
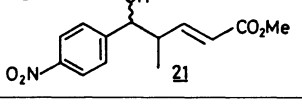
By treatment with CH_2N_2, α-carboxylated allylic silanes were converted to the corresponding methyl esters which proved to be useful for introduction of 3-(methoxycarbonyl)allyl groups.[11] We have demonstrated the utility of methyl 2-(dimethylphenylsilyl)-



(5)

5c $R^1=R^2=R^3=H$
5h $R^1=Me, R^2=R^3=H$
5i $R^1=R^3=H, R^2=Me$
5j $R^1=R^2=H, R^3=Me$

Table 2. Reaction of Allylic Silanes **5** with Electrophiles

Entry	Electrophile	Silane	Conditions	Product	Yield/%[a]
1	$MeOCH_2Cl$	**5h**	-78 °C, 1 h	 **6**	77[b]
2		**5j**	-78 °C, 1 h	 **7**	66
3		**5h**	-78 ~ -10 °C, 1 h	 **8**	73[b]
4		**5j**	-78 ~ -10 °C, 1 h	 **9**	66[c]
5		**5h**	-78 °C ~ r.t., 2 h	 **10**	48[b]
6		**5j**	-78 °C ~ r.t., 2 h	 **11**	70[c]
7	$MeCOCO_2Me$	**5h**	-78 °C ~ r.t., 3 h	 **12**	96[b]
8		**5j**	-78 °C ~ r.t., 2 h	 **13**	-[d]
9	 **14**	**5h**	-78 ~ -10 °C, 1 h[e]	 **15**	70[f]
10		**5j**	-78 ~ -10 °C, 1 h[e]	 **16**	72[f]
11		**5h**	-78 °C ~ r.t., 1 h	 **17**	54
12		**5j**	-78 °C ~ r.t., 1 h	 **18**  **19**	77[g]
13		**5h**	-78 °C ~ r.t., 1 h	 **20**	53
14		**5j**	-78 °C ~ r.t., 1 h	 **21**	69[h]

a) Isolated yield. b) Only E isomer. c) Diastereomeric mixture (ca. 1:1). d) Cyclic trimers of methyl pyruvate was obtained and **5j** was recovered in a 57% yield. e) Tin tetrachloride was employed instead of $TiCl_4$. f) Isolated yield of the corresponding hydroquinone diacetate after treatment with pyridine and acetic anhydride. g) During the purification by column chromatography the double bond of **18** migrated to give a mixture (**18**/**19**=1/5.8). h) The diastereomeric ratio was estimated to be 73:27 by the NMR analysis.

3-butenoate (**5c**) in the total syntheses of 1*H*-3,4-dihydronaphtho[2,3-*c*]pyran-5,10-dione antibiotics[18] and anthracyclinones.[19] α-Silyl β,γ-unsaturated esters (**5h** and **5j**) can be prepared only by our method[20] and are synthetically more valuable.

Lewis Acid-Mediated Reaction of Allylic Silanes 5 with Electrophiles. In the presence of $TiCl_4$, **5h** prepared from **3h** in quantitative yield reacted smoothly with electrophiles at γ position as expected[21] (Table 2). The reaction with chloromethoxymethane was carried out in the presence of $TiCl_4$ (1 equiv) at −78 °C to give a crude mixture which consisted of almost only (*E*)-**7**. After column chromatography, pure (*E*)-**7** was obtained in 77% yield. α-Chloroethyl phenyl sulfide, isobutyraldehyde, and methyl pyruvate were also reacted smoothly to give trans α,β-unsaturated esters (**8**; 73%, **10**; 48%, and **12**; 96%). The reaction of acetylquinone **14** occurred at the quinone nucleus to afford **15**, which was isolated as the corresponding hydroquinone diacetate **15a** after treatment with acetic anhydride and pyridine. In this reaction $SnCl_4$, as a milder Lewis acid than $TiCl_4$, was employed instead of $TiCl_4$ because the quinone **14** was a very good Michael acceptor. Isobutyryl chloride was also employed to give δ-oxo, α,β-unsaturated ester **17** which was isolated by column chromatography in a 54% yield without the double bond migration. Similarly, (*Z*)-**5j** also reacted with various electrophiles at γ position in the presence of a Lewis acid to give 3-substituted *trans*-pentenoates in good yields (Table 2). Pure (*Z*)-**5j** employed in this reaction was readily prepared from the corresponding (*Z*)-carboxylic acid **3j** which was purified by recrystallization. It is noteworthy that isobutyryl chloride reacted with **5j** to give only α,β-unsaturated ester **18**. During the isolation by column chromatography the double bond of **18** mostly migrated to give a mixture (**18**/**19** = 1/5.8). In Entry 8, **5j** was recoverd in a 57% yield instead of the expected compound **13**. Under the applied reaction conditions methyl pyruvate reacted with itself to give a cyclic trimer. The remarkable contrast between the reaction of **5h** and **5j** (Entries 7 and 8) could be attributed to the steric difference at their γ carbons. In any reactions of **5j**, diastereoselectivity could not be observed in spite of all our efforts. The lack of high selectivity might be considered as follows. The reaction of (2-butenyl)trimethylsilane probably proceeds via acyclic transition state to exibit the selectivity whereas in that of **5j**, cyclic transition state might participate since the reagent has a carbonyl group which could coordinate the Lewis acid.

In both reactions of **5h** and **5j**, only (*E*)-olefins were obtained. This *E* selectivity could be easily interpreted if we assumed **5h** and **5j** would take the similar conformation as that of **5c** described in the preliminary report (Scheme 1).[11]

Experimental

All melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H NMR spectra were observed with Hitachi R-600 (60 MHz), JEOL-PS-100 (100 MHz), and/or JEOL-GX-400 (400 MHz) spectrometers with TMS as an internal standard. IR spectra were measured with a JASCO IRA-1 and/or Hitachi 270-30 spectrometers. Mass spectra were measured with Hitachi M-80B spectrometer. Column chromatography was performed using Wakogel C-200. Diethyl ether and THF were distilled from sodium benzophenone ketyl and stored over sodium wire. Dichloromethane was distilled from calcium hydride and stored over 4A molecular sieves. Other solvents were used after simple distillation otherwise noted. Allylic silanes; **1c** (bp 93 °C/2.27 kPa), **1d** (bp 85 °C/27 Pa), **1e** (bp 112 °C), **1f** (bp 80—84 °C/667 Pa), **1g** (bp, 147 °C), **1h**[22] (bp 106 °C/2.67 kPa), and **1i** (bp 110 °C/3.07 kPa), were prepared from chlorosilanes and the Grignard reagents. 2-Butenylsilane **1j** (bp 106 °C/2.67 kPa) and 3-methyl-2-butenylsilane **1k**[22] (bp 115—118 °C/2.00 kPa) were prepared from the silyllithium and allylic halides.

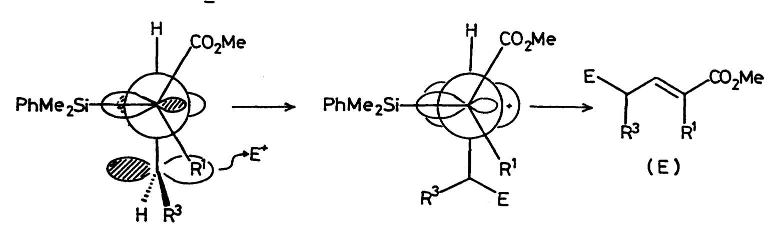
Lithiation of Allylic Silanes. Following methods A and B are applicable for almost cases except for **1e**, and give similar results. For the lithiation of **1e** method C was employed to privent from Michael addition to a vinyl group.

Method A: An allylic silane (1 equiv) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 1.5 equiv) were placed in a three-necked flask fitted with a stopcock, a rubber serum cap, and a thermometer. The vessel was filled with nitrogen. After addition of THF (3 ml/1 mmol) the mixture was cooled to −78 °C by Dry Ice acetone bath and then *t*-BuLi (pentane solution, 1.5 equiv) was added dropwise. After the addition the mixture was gradually warmed to −40 °C and stirred at −40—−30 °C for 1 h.

Method B: To a THF solution (3 ml/1 mmol) of an allylic silane (1 equiv) and TMEDA (1.5 equiv) was added *n*-BuLi (hexane solution, 1.5 equiv) under −70 °C. The mixture was gradually warmed up to −15 °C and allowed to stand for 2 d in a freezer (−15 °C).

Method C: To a THF solution (3 ml/1 mmol) of an allylic silane (1 equiv) and TMEDA (1.5 equiv) was added MeLi (ether solution, 1.5 equiv) at −20 °C. The mixture was allowed to stand for 3 d in a freezer (−15 °C).

Methylation of Allyldimethylphenylsilane 1c. To an orange yellow solution of lithiated **1c** prepared by method A (**1c**, 880 mg, 5 mmol) was added MeI (1.42 g, 10 mmol) at −78 °C. The resulted white suspension was allowed to warm to 0 °C and then aq NH_4Cl was added. The reaction mixture was extracted with ether. The ethereal phase was wash-



Scheme 1.

ed with brine and dried over Na_2SO_4. After the solvent was evaporated, the residue was simply purified by being passed through a short silica-gel column (hexane–ether). From the ^{1}H NMR spectrum (400 MHz), the mixture was proved to consist of the starting silane **1c** (32%), **1h** (53%), and **2c** (15%). Separation of the methylated compounds from **1c** was achieved by preparative GPC (Japan Analytical Industry, LC-08, JAI-1H (20 mmID × 60 cm) +JAI-2H (20 mmID× 60 cm)) using $CHCl_3$ as a carrier solvent to give 672 mg (65%) of **1h** (80%) and **2c** (20%). Isomer ratio of the purified products was almost unchanged from the crude one. **1h**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.30 (6H, s), 1.08 (3H, d, J= 17.3 Hz), 1.87 (1H, t-quintet, J=7.3, 1.6 Hz), 4.83 (1H, dt, J=17.1, 1.8 Hz), 4.89 (1H, dt, J=10.4, 1.5 Hz), 5.89 (1H, ddd, J=17.1, 10.4, 7.3 Hz), 7.39 (3H, m), and 7.54 (2H, m). **2c**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.35 (6H, s), 1.04 (3H, t, J=7.3 Hz), 2.19 (2H, m), 5.80 (1H, d, J=18.3 Hz), 6.21 (1H, dt, J=18.3, 5.6 Hz), 7.39 (3H, m), and 7.54 (2H, m).

Methylation of (1-Methyl-2-propenyl)dimethylphenylsilane (1h). The reaction of **1h** (380 mg, 2 mmol) was carried out in the similar manner as described above. By the NMR analysis of the reaction mixture, it was estimated to consist of **1h** (67%), **1l** (21%), and **2h** (12%). **1l**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.29 (6H, s), 1.02 (6H, s), 4.73 (1H, dd, J=17.4, 1.5 Hz), 4.91 (1H, dd, J=10.7, 1.5 Hz), 5.84 (1H, dd, J=17.4, 10.7 Hz), 7.38 (3H, m), and 7.53 (2H, m). **2h**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.35 (6H, s), 1.02 (3H, t, J=7 Hz), 1.68 (3H, m), 2.16 (2H, quintet, J=7 Hz), 5.40 (1H, m), 7.38 (3H, m), and 7.53 (2H, m).

Methylation of Allylmethyldiphenylsilane (1d). The reaction of **1d** (476 mg, 2 mmol) was carried out in the similar manner. By the NMR analysis of the reaction mixture, it was proved to consist of **1d** (65%), **1m** (18%), and **2d** (7%). **1m**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.58 (3H, s), 1.19 (3H, d, J=7.3 Hz), 2.34 (1H, m), 4.95 (2H, m), 5.98 (1H, ddd, J=17.1, 10.4, 7.0 Hz), 7.40 (6H, m), and 7.57 (4H, m). **2d**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.65 (3H, s), 1.08 (3H, t, J=7.5 Hz), 2.25 (2H, m), 6.00 (1H, d, J=18.6 Hz), 6.28 (1H, dt, J=18.6, 5.6 Hz), 7.40 (6H, m), and 7.57 (4H, m).

Carboxylation of Lithiated Allylic Silanes. General Procedure: Dry CO_2 gas (through a $CaCl_2$ column) was bubbled into THF (5 ml/1 mmol) at −78 °C under argon. A solution of the lithiated allylic silane was slowly introduced into the THF solution absorbing CO_2 at −78 °C by a stainless steel transfer tube. The color of the lithiated allylic silane (yellow or orange yellow) rapidly faded to give a clear colorless solution. The reaction was quenched by adding an aqueous NH_4Cl solution and acidified by 5% HCl. The reaction mixture was extracted with ether. The ethereal phase was washed with brine and dried over Na_2SO_4. After the solvent was evaporated in vacuo at room temperature, the residue was chromatographed on silica gel (hexane/CH_2Cl_2/ether=1/1/0—1/1/0.1).

Carboxylation of Allylic Aluminates. General Procedure: A hexane solution of triethylaluminum (ca. 1.4 M[†]) was slowly added to the solution of the lithiated allylic silane at −78° C untill the color of the solution became almost colorless. The mixture was stirred for additional 10 min and then dry CO_2 gas was slowly introduced to the solution at −78° C. After a large excess amount of CO_2 was absorbed, the solution was gradually warmed to 0° C and stirred for 15 min. After being recooled to −30° C, the reaction mixture was poured into a cold aq NH_4Cl solution (ca. −10° C) and then ether was added. The mixture was acidified by cold 5% aq HCl until both phases became clear. The organic phase was separated and the aqeous phase was extracted twice with ether. The combined organic phase was washed twice with cold 5% aq HCl and brine and dried over Na_2SO_4. After the solvent was evaporated in vacuo at ambient temperature, the residue was chromatographed on silica gel (hexane/CH_2Cl_2/ether=1/1/0—1/1/0.1).

2-(Trimethylsilyl)-3-butenoic Acid (3a): Colorless crystals (ether/hexane); mp 72—73° C; ^{1}H NMR ($CDCl_3$) δ= 0.13 (9H, s), 2.95 (1H, d, J=10 Hz), 4.76—5.08 (2H, m), 6.00 (1H, dt, J=16, 10 Hz), and 9.02 (1H, broad s). Found: C, 53.31; H, 8.97%. Calcd for $C_7H_{14}O_2Si$: C, 53.12; H, 8.92%.

4-(Trimethylsilyl)-3-butenoic Acid (4a): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.08 (9H, s), 3.13 (2H, d, J=6 Hz), 5.76 (1H, d, J=19 Hz), 6.09 (1H, dt, J=19, 6 Hz), and 10.90 (1H, broad s); IR (neat) 2960 (broad s), 1714 (vs), 1616 (m), 1418 (m), 1250 (s), 862 (s), and 840 cm^{-1} (s).

2-(Triphenylsilyl)-3-butenoic Acid (3b):[8b)] Colorless prisms (benzene/hexane); mp 179—180° C; ^{1}H NMR ($CDCl_3$) δ=3.75 (1H, d, J=10 Hz), 4.80—5.10 (2H, m), 6.02 (1H, dt, J=16, 10 Hz), 7.20—7.80 (15H, m), and 10.0 (1H, broad s); IR (KBr) 300 (broad s), 1675 (vs), 1425 (vs), 1200 (s), and 1115 cm^{-1} (vs).

4-(Triphenylsilyl)-3-butenoic Acid (4b):[8b)] Colorless crystals (benzene/hexane); mp 157—158° C; ^{1}H NMR ($CDCl_3$) δ=3.31 (2H, d, J=5 Hz), 6.10 (1H, dt, J=16, 5 Hz), 6.36 (1H, d, J=16 Hz), 7.2—7.7 (15H, m), and 10.30 (1H, broad s).

2-(Dimethylphenylsilyl)-3-butenoic Acid (3c): Colorless crystals (ether/hexane); mp 48—49.5° C; ^{1}H NMR ($CDCl_3$) δ=0.42 (6H, s), 3.04 (1H, d, J=10 Hz), 4.56—4.96 (2H, m), 5.87 (1H, dt, J=17, 10 Hz), 7.16—7.50 (5H, m), and 10.58 (1H, broad s); IR (neat) 3200 (broad m), 1690 (vs), 1430 (s), 1255 (s), and 1120 cm^{-1} (s). Found: C, 65.47; H, 7.44%. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.31%.

4-(Dimethylphenylsilyl)-3-butenoic Acid (4c): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.35 (6H, s), 3.14 (2H, d, J=5 Hz), 5.83 (1H, d, J=19 Hz), 6.10 (1H, dt, J=19, 5 Hz), 7.20 (5H, m), and 11.35 (1H, broad s); IR (neat) 3000 (broad s), 1700 (vs), 1420 (s), 1245 (s), and 1100 cm^{-1} (s).

2-(Methyldiphenylsilyl)-3-butenoic Acid (3d): Colorless crystals (ether/hexane); mp 65—68 °C; ^{1}H NMR (CCl_4) δ=0.65 (3H, s), 3.35 (1H, d, J=10 Hz), 4.45—4.85 (2H, m), 5.75 (1H, dt, J=16, 10 Hz), 6.9—7.5 (10H, m), and 10.53 (1H, s); IR (KBr) 3000 (broad s), 1680 (vs), 1430 (s), 1315 (s), 1200 (s), and 1100 cm^{-1} (s). Found: C, 71.97; H, 6.43%. Calcd for $C_{17}H_{18}O_2Si$: C, 72.30; H, 6.42%.

4-(Methyldiphenylsilyl)-3-butenoic Acid (4d): Colorless crystals (ether/hexane); mp 93—96° C; ^{1}H NMR ($CDCl_3$) δ=0.62 (3H, s), 3.21 (2H, m), 6.09 (2H, m), 7.1—7.6 (10H, m), and 10.56 (1H, broad s); IR (KBr) 2900 (broad m), 1700 (vs), 1420 (vs), 1245 (vs), 1220 (vs), and 1110 cm^{-1} (s). Found: C, 72.42; H, 6.56%. Calcd for $C_{17}H_{18}O_2Si$: C, 72.30; H, 6.42%.

2-(Dimethylvinylsilyl)-3-butenoic Acid (3e): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=(6H, s), 2.92 (1H, d, J=10 Hz), 4.9 (2H, m), 5.9 (4H, m), and 9.0 (1H, broad s); IR (neat) 2950 (broad s), 1685 (vs), 1405 (s), 1250 (s), 905 (s), and 840 cm^{-1} (vs).

4-(Dimethylvinylsilyl)-3-butenoic Acid (4e): ^{1}H NMR ($CDCl_3$) δ=0.20 (6H, s), 3.18 (2H, d, J=5 Hz), 5.3—6.4 (5H, m), and 9.4 (1H, broad s); IR (neat) 2950 (broad s), 1700 (vs), 1610

[†] 1 M=1 mol dm^{-3}.

(s), 1405 (s), 1250 (vs), and 840 cm^{-1} (vs).

2-(Dimethyl-*p*-tolylsilyl)-3-butenoic Acid (3f): Colorless crystals (ether/hexane); mp 50—51 °C; ^{1}H NMR ($CDCl_3$) δ=0.39 (6H, s), 2.32 (3H, s), 3.06 (1H, d, J=10 Hz), 4.6—5.0 (2H, m), 5.85 (1H, dt, J=16, 10 Hz), 7.10 (2H, d, J=8 Hz), 7.34 (2H, d, J=8 Hz), and 9.46 (1H, broad s); IR (CCl_4) 2960 (broad s), 1690 (vs), 1250 (s), and 1110 cm^{-1} (vs). Found: C, 66.44; H, 7.77%. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74%.

2-(*t*-Butyldimethylsilyl)-3-butenoic Acid (3g): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.08 (6H, s), 0.95 (9H, s), 2.93 (1H, d, J=10 Hz), 4.70—4.92 (2H, m), 5.84 (1H, dt, J=16, 10 Hz), and 10.98 (1H, broad s); IR (neat) 3080 (broad s), 1690 (vs), 1630 (m), 1405 (m), 1250 (m), 1200 (m), 1075 (m), 835 (m), and 815 cm^{-1} (m).

2-Methyl-2-(dimethylphenylsilyl)-3-butenoic Acid (3h): Colorless crystals (ether/hexane); mp 103—105° C; ^{1}H NMR ($CDCl_3$) δ=0.39 (6H, s), 1.20 (3H, s), 4.59 (1H, d, J=17 Hz), 4.84 (1H, d, J=10 Hz), 6.20 (1H, dd, J=17, 10 Hz), 7.0—7.3 (5H, m), and 11.65 (1H, broad s); IR (KBr) 2960 (broad m), 1680 (vs), 1628 (m), 1430 (m), 1410 (m), 1280 (vs), 1260 (s), 1112 (s), 914 (s), 832 (m), 812 (vs), 738 (m), and 700 cm^{-1} (s). Found: C, 66.40; H, 7.93%. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74%.

4-(Dimethylphenylsilyl)-3-pentenoic Acid (4h): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.40 (6H, s), 1.67 (3H, m), 3.15 (2H, d, J=7 Hz), 5.92 (1H, m), 7.1—7.5 (5H, m), and 10.08 (1H, broad s); IR 2960 (broad s), 1712 (vs), 1620 (m), 1430 (s), 1250 (s), 1216 (m), 1114 (s), 910 (m), 834 (s), 816 (s), 776 (s), 732 (s), and 702 cm^{-1} (s).

3-Methyl-2-(dimethylphenylsilyl)-3-butenoic Acid (3i): Colorless crystals (ether/hexane); mp 65—67° C; ^{1}H NMR ($CDCl_3$) δ=0.48 (6H, s), 1.62 (3H, s), 3.04 (1H, s), 4.74 (1H, m), 4.84 (1H, m), 7.20—7.35 (3H, m), 7.35—7.55 (2H, m), and 10.5 (1H, broad s); IR (KBr) 2900 (broad s), 1680 (vs), 1425 (s), 1250 (vs), 1115 (vs), 810 (vs), and 700 cm^{-1} (vs). Found: C, 66.33; H, 7.86%. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74%.

3-Methyl-4-(dimethylphenylsilyl)-3-butenoic Acid (4i): ^{1}H NMR ($CDCl_3$) δ=0.39 (6H, s), 1.80 (3H, s), 3.12 (2H, s), 5.51 (1H, s), 7.1—7.6 (5H, m), and 8.27 (1H, broad s); IR (neat) 2960 (broad s) 1710 (vs), 1622 (m), 1430 (m), 1252 (s), 1114 (m), 836 (s), 730 (s), and 702 cm^{-1} (s).

***cis*-2-(Dimethylphenylsilyl)-3-pentenoic Acid (3j):** Colorless crystals (ether/hexane); mp 84—88° C; ^{1}H NMR ($CDCl_3$) δ=0.43 (6H, s), 1.27 (3H, d, J=6 Hz), 3.37 (1H, d, J=10 Hz), 5.40 (1H, dq, J=10, 6 Hz), 5.59 (1H, t, J=7 Hz), 7.2—7.6 (5H, m), and 8.40 (1H, broad s); IR (KBr) 2900 (broad m), 1675 (vs), 1430 (s), 1310 (vs), 1250 (s), 1195 (s), 1120 (s), 820 (s), and 725 cm^{-1} (vs). Found: C, 66.38; H, 7.87%. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74%.

2-Methyl-4-(dimethylphenylsilyl)-3-butenoic Acid (4j): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.36 (6H, s), 1.29 (3H, d, J=7 Hz), 3.20 (1H, m), 5.88 (1H, d, J=19 Hz), 6.10 (1H, dd, J=19, 6 Hz), 7.3 (5H, m), and 10.5 (1H, broad s); IR (neat) 2960 (broad s), 1710 (vs), 1614 (m), 1430 (s), 1250 (s), 116 (s), 824 (s), 732 (s), and 700 cm^{-1} (s).

2,2-Dimethyl-4-(dimethylphenylsilyl)-3-butenoic Acid (4k): Colorless crystals (ether/hexane); mp 62—64 °C; ^{1}H NMR ($CDCl_3$) δ=0.40 (6H, s), 1.35 (6H, s), 5.84 (1H, d, J=19 Hz), 6.20 (1H, d, J=19 Hz), 7.25 (m, 5H), and 11.1 (1H, broad s); IR (KBr) 2900 (broad s), 1685 (vs), 1295 (s), 1250 (s), 1110 (s), 995 (s), 840 (vs), 730 (vs), and 700 cm^{-1} (vs). Found: C, 68.01; H, 8.47%. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12%.

Methyl 2-(Dimethylphenylsilyl)-3-butenoate (5c). To a solution (ether) of **3c** (3.749 g, 17 mmol) was added an ethereal solution of CH_2N_2 under 0° C until the solution became slightly yellow. After ether was evaporated in vacuo, the residue was chromatographed on silica gel (CH_2Cl_2/hexane) to give 2.952 g (74%) of **5c** as a colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.38 (6H, s), 3.10 (1H, d, J=10 Hz), 3.48 (3H, s), 4.64—5.00 (2H, m), 5.93 (1H, dt, J=17, 10 Hz), and 7.25—7.5 (5H, m); IR (neat) 2950 (m), 1630 (m), 1430 (s), 1315 (s), 1250 (s), 1165 (vs), 1135 (s), 1115 (vs), 835 (vs), 810 (s), and 695 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 234 (M^+, 15), 203 (4), 151 (19), 135 (81), and 68 (100).

Methyl 2-Methyl-2-(dimethylphenylsilyl)-3-butenoate (5h): A colorless oil; ^{1}H NMR (CCl_4) δ=0.31 (6H, s), 1.19 (3H, s), 3.41 (3H, s), 4.60 (1H, dd, J=17, ≈1 Hz), 4.81 (1H, dd, J=11, ≈1 Hz), 6.16 (1H, dd, J=17, 11 Hz), and 7.13 (5H, m); IR (neat) 2960 (m), 1720 (vs), 1635 (m), 1440 (s), 1245 (vs), 1120 (vs), 905 (s), 840 (s), 820 (s), 790 (s), 745 (s), and 710 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 248 (M^+, 21), 233 (6), 217 (7), 151 (13), 135 (69), and 82 (100).

Methyl 3-Methyl-2-(dimethylphenylsilyl)-3-butenoate (5i): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.43 (6H, s), 1.66 (3H, s), 3.08 (1H, s), 3.54 (3H, s), 4.88 (2H, m), and 7.40 (5H, m); IR (neat) 2956 (m), 1724 (vs), 1638 (m), 1434 (s), 1250 (s), 1152 (vs), 1118 (s), 838 (s), 816 (s), 734 (m), and 702 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 248 (M^+, 8), 233 (5), 217 (4), 151 (9), 135 (69), and 82 (100).

Methyl *cis*-2-(Dimethylphenylsilyl)-3-pentenoate (5j): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=0.39 (6H, s), 1.32 (3H, d, J=7 Hz), 3.39 (1H, d, J=11 Hz), 3.52 (3H, s), 5.40 (1H, dq, J=11, 7 Hz), 5.65 (1H, t, J=11 Hz), 7.36 (3H, m), and 7.49 (2H, m); IR (neat) 2950 (m), 1720 (vs), 1430 (s), 1305 (vs), 1250 (vs), 1150 (vs), 1115 (s), 835 (s), 810 (s), 725 (s), and 695 cm^{-1} (vs); MS (20 eV) m/z (rel intensity) 248 (M^+, 12), 217 (3), 151 (6), 135 (55), and 82 (100).

Methyl *trans*-2-(Dimethylphenylsilyl)-3-butenoate: Typical ^{1}H NMR signals: δ=5.21 (1H, dq, J=15, 6 Hz) and 5.59 (1H, ddq, J=15, 9, 2 Hz).

Reaction of 5. General Procedure: To a CH_2Cl_2 solution (20 ml/1 mmol) of **5** (1 equiv) and an electrophile (1.2 equiv) was added a CH_2Cl_2 solution of $TiCl_4$ (1 M solution, 2.4 equiv) at −78° C with stirring. The reaction was continued under the conditions listed in Table 2. The reaction mixture was quenched with water and extracted with ether or CH_2Cl_2. The organic phase was washed with brine, and dried over Na_2SO_4. After the solvent was removed, the residue was chromatographed on silica gel (hexane/ether or hexane/CH_2Cl_2).

Methyl 5-Methoxy-2-methyl-2-pentenoate (6): A colorless oil; ^{1}H NMR (CCl_4) δ=1.76 (3H, s), 2.32 (2H, q, J=7 Hz), 3.20 (3H, s), 3.30 (2H, t, J=7 Hz), 3.59 (3H, s), and 6.50 (1H, t, J=7 Hz); IR (neat) 2952 (m), 1720 (vs), 1652 (m), 1438 (m), 1228 (s), 1152 (s), and 1118 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 158 (M^+, 1), 127 (37), 126 (93), 113 (17), 111 (15), 95 (18), and 82 (100).

Methyl 5-Methoxy-4-methyl-2-pentenoate (7): A colorless oil; ^{1}H NMR (CCl_4) δ=0.74 (3H, d, J=7 Hz), 2.19 (1H, m), 2.85 (2H, d, J=7 Hz), 2.89 (3H, s), 3.26 (3H, s), 5.30 (1H, d, J=16 Hz), and 6.35 (1H, dd, J=16, 7 Hz); IR (neat) 1726 (vs), 1660 (m), 1438 (m), 1276 (s), 1198 (s), 1178 (s), and 1150 cm^{-1} (s); MS (70 eV) m/z (rel intensity) 158 (M^+, 1), 137 (8), 127 (13), 113 (7), and 82 (100).

Methyl 2-Methyl-5-phenylthio-2-hexenoate (8): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, d, J=7 Hz), 2.13 (3H, d, J=1 Hz), 2.35 (2H, m), 3.35 (1H, m), 3.67 (3H, s), 5.70 (1H, m), and 7.35 (5H, m); IR (neat) 1720 (vs), 1650 (s), 1440 (s), 1226 (vs), 1150 (vs), 748 (s), and 694 cm^{-1} (s); MS (70 eV) m/z (rel intensity) 250 (M$^+$, 10), 219 (2), 141 (38), and 137 (100).

Methyl 4-Methyl-5-phenylthio-2-hexenoate (9): A diastereomeric mixture; a colorless oil; ^{1}H NMR (CCl$_4$) δ= 1.12 (3H, m), 1.16 (3H, m), 2.25 (1H, m), 3.23 (1H, m), 3.62 (3H, s), 5.70 (1H, d, J=16 Hz), 6.82 (1H, m), and 7.18 (5H, m); IR (neat) 2972 (m), 1724 (vs), 1656 (s), 1440 (s), 1276 (s), 1196 (s), 1178 (s), 748 (m), and 694 cm^{-1} (m); MS (70 eV) m/z (rel intensity) 250 (M$^+$, 7), 219 (2), 141 (3), and 137 (100).

Methyl 5-Hydroxy-2,6-dimethyl-2-heptenoate (10): A colorless oil; ^{1}H NMR (CDCl$_3$) δ=0.95 (6H, m), 1.80 (1H, m), 1.95 (1H, broad), 2.20 (3H, m), 2.30 (2H, m), 3.60 (1H, m), 3.69 (3H, s), and 5.80 (1H, m); IR (neat) 3468 (broad m), 2964 (s), 1720 (vs), 1648 (m), 1440 (m), 1230 (s), 1154 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 154 (M$^+$−MeOH, 3), 126 (5), 111 (100), and 82 (31).

Methyl 5-Hydroxy-4,6-dimethyl-2-heptenoate (11): A diastereomeric mixture; a colorless oil; ^{1}H NMR (CDCl$_3$) δ=0.90 (6H, d, J=6 Hz), 1.08 (3H, d, J=7 Hz), 1.65 (1H, m), 2.45 (1H, broad s), 2.48 (1H, m), 3.16 (1H, m), 3.62 (3H, s), 5.72 (1H, d, J=16 Hz), and 6.80 (1H, m); IR (neat) 3476 (broad s), 2964 (s), 1724 (vs), 1658 (m), 1440 (m), 1282 (s), 1198 (m), 1178 (m), 1156 (m), and 994 cm^{-1} (m); MS (70 eV) m/z (rel intensity) 186 (M$^+$, 0.2), 155 (1), 114 (100), and 82 (41).

Dimethyl 5-Hydroxy-2,5-dimethyl-2-hexenedioate (12): A colorless oil; ^{1}H NMR (CDCl$_3$) δ=1.36 (3H, s), 1.76 (3H, s), 2.46 (2H, d, J=7 Hz), 3.30 (1H, broad), 3.61 (3H, s), 3.68 (3H, s), and 6.47 (1H, t, J=7 Hz); IR (neat) 3500 (broad m), 2956 (m), 1722 (vs), 1648 (s), 1440 (s), 1224 (vs), 1154 (vs), and 1120 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 216 (M$^+$, 0.2), 185 (7), 184 (3), 157 (5), 125 (42), and 114 (100).

Methyl 4-(3-Acetyl-4-hydroxy-5-methoxy-1-oxo-1,2-dihydro-2-naphthyl)-2-methyl-2-butenoate (15): ^{1}H NMR (CDCl$_3$) δ=2.20 (3H, broad s), 2.23 (3H, s), 2.50 (2H, m), 3.55 (1H, m), 3.65 (3H, s), 3.98 (3H, s), 6.90 (1H, m), 7.4 (3H, m), and 17.05 (1H, s).

Methyl 4-(1,4-Acetoxy-3-acetyl-5-methoxy-2-naphthyl)-2-methyl-2-butenoate (15a): Colorless crystals (CH$_2$Cl$_2$/ether); mp 149—151°C; ^{1}H NMR (CDCl$_3$) δ=2.15 (3H, broad s), 2.31 (3H, s), 2.39 (3H, s), 2.47 (3H, s), 3.49 (2H, m), 3.62 (3H, s), 3.87 (3H, s), 5.50 (1H, m), 6.85 (1H, m), and 7.35 (2H, m); IR (KBr) 1764 (vs), 1714 (vs), 1652 (m), 1574 (s), 1440 (s), 1366 (s), 1270 (s), 1212 (vs), 1186 (vs), 1144 (s), and 1070 cm^{-1} (m); MS (70 eV) m/z (rel intensity) 429 (M$^+$+1, 2), 428 (M$^+$, 8), 344 (52), 326 (20), and 270 (100). Found: C, 64.21; H, 5.70%. Calcd for C$_{23}$H$_{24}$O$_8$: C, 64.48; H, 5.64%.

Methyl 4-(3-Acetyl-4-hydroxy-5-methoxy-1-oxo-1,2-dihydro-2-naphthyl)-2-pentenoate (16): A diastereomeric mixture; ^{1}H NMR (CDCl$_3$) δ=0.75 (3H of one diastereomer, d, J= 7 Hz), 1.15 (3H of another, d, J=7 Hz), 2.2 (3H, m), 2.5 (1H, m), 3.1 (4H, m), 3.98 (3H, m), 5.5 (1H, d, J=16 Hz), 6.5 (1H, m), 7.4 (3H, m), 17.15 (1H of one diastereomer, s), and 17.24 (1H of another, s).

Methyl 4-(1,4-Diacetoxy-3-acetyl-5-methoxy-2-naphthyl)-2-pentenoate (16a): Colorless crystals (CH$_2$Cl$_2$/ether); mp 146—148°C; ^{1}H NMR (CDCl$_3$) δ=1.45 (3H, d, J=7 Hz), 2.25 (3H, s), 2.33 (3H, s), 2.49 (3H, s), 3.63 (1H, m), 3.66 (3H, s), 3.80 (3H, s), 5.88 (1H, d, J=16 Hz), 6.80 (1H, m), and 7.2 (3H, m); IR (KBr) 1764 (vs), 1722 (vs), 1704 (vs), 1650 (m), 1574 (s), 1368 (vs), 1270 (vs), 1198 (vs), and 1064 cm^{-1} (s); MS (70 eV) m/z (rel intensity) 429 (M$^+$+1, 9), 428 (M$^+$, 32), 386 (80), 344 (97), 326 (78), 312 (52), 270 (100), and 267 (99). Found: C, 64.34; H, 5.75%. Calcd for C$_{23}$H$_{24}$O$_8$: C, 64.48; H, 5.64%.

Methyl 2,6-Dimethyl-5-oxo-2-heptenoate (17): A colorless oil; ^{1}H NMR (CDCl$_3$) δ=1.12 (6H, d, J=7 Hz), 1.86 (3H, s), 2.65 (1H, m), 3.44 (2H, d, J=7 Hz), 3.73 (3H, s), and 6.97 (1H, t, J=7 Hz); IR (neat) 2968 (m), 1712 (vs), 1652 (m), 1440 (s), 1256 (vs), 1122 (s), 1092 (vs), and 1038 cm^{-1} (s); MS (20 eV) m/z (rel intensity) 184 (M$^+$, 3), 153 (10), 152 (5), 141 (35), 114 (41), 113 (52), 109 (24), 82 (44), and 71 (100).

Methyl 4,6-Dimethyl-5-oxo-2-heptenoate (18): ^{1}H NMR (CDCl$_3$) δ=1.2 (9H, m), 2.70 (1H, m), 3.55 (1H, m), 3.75 (3H, s), 5.95 (1H, d, J=15 Hz), and 6.95 (1H, dd, J=15, 8 Hz).

Methyl 4,6-Dimethyl-5-oxo-3-heptenoate (19): (**19**/**18**=5.8/1); ^{1}H NMR (CDCl$_3$) δ=1.10 (6H, d, J=7 Hz), 1.70 (3H, s), 3.30 (2H, d, J=7 Hz), 3.4 (1H, m), 3.75 (3H, s), and 6.80 (1H, t, J=7 Hz); IR (neat) 2972 (m), 1742 (vs), 1672 (vs), 1440 (m), 1236 (m), 1200 (s), 1172 (s), and 1046 cm^{-1} (m); MS (20 eV) m/z (rel intensity) 184 (M$^+$, 1.4), 153 (3), 152 (3), 141 (100), and 113 (42).

Methyl 5-Hydroxy-2-methyl-5-(4-nitrophenyl)-2-pentenoate (20): A pale yellow oil; ^{1}H NMR (CDCl$_3$) δ=1.80 (3H, s), 2.65 (3H, m), 3.74 (3H, s), 5.00 (1H, t, J=6 Hz), 6.80 (1H, t, J=7 Hz), 7.57 (2H, d, J=9 Hz), and 8.23 (2H, d, J=9 Hz); IR (neat) 3464 (broad m), 2950 (m), 1710 (vs), 1650 (m), 1604 (m), 1522 (vs), 1440 (s), 1348 (vs), 1282 (vs), 1064 (s), 856 (s), 734 (s), and 702 cm^{-1} (m); MS (20 eV) m/z (rel intensity) 234 (M$^+$-MeO, 22), 217 (45), 158 (51), 152 (88), 122 (85), 115 (81), and 114 (100).

Methyl 5-Hydroxy-4-methyl-5-(4-nitrophenyl)-2-pentenoate (21): A diastereomeric mixture (73/27); a pale yellow oil; ^{1}H NMR (CDCl$_3$) δ=1.01 (3H of major isomer, d, J=6.6 Hz), 1.04 (3H of minor isomer, d, J=7.0 Hz), 2.66 (1H, m), 2.75 (1H, m), 3.70 (3H of minor isomer, s), 3.71 (3H of major isomer, s), 4.70 (1H of major isomer, d, J=6.6 Hz), 4.85 (1H of minor isomer, d, J=5.1 Hz), 5.79 (1H of minor isomer, dd, J=15.7, 1.1 Hz), 5.81 (1H of major isomer, dd, J=15.7, 1.1 Hz), 6.96 (1H, dd, J=15.7, 8.0 Hz), 7.49 (2H, d, J=9 Hz), and 8.18 (2H, d, J=9 Hz); IR (neat) 3460 (broad m), 2976 (m), 1722 (vs), 1658 (m), 1606 (m), 1522 (vs), 1440 (m), 1348 (vs), 1282 (s), 1200 (m), 1178 (m), 1034 (m), and 862 cm^{-1} (m); MS (20 eV) m/z (rel intensity) 234 (M$^+$−MeO, 11) 217 (14), 188 (17), 158 (26), 152 (100).

The author wishes to thank Prof. Kazuhiro Maruyama, Prof. Yoshinori Yamamoto, Dr. Yoshinori Naruta, and Prof. Hitomi Suzuki for their guidance and valuable discussions. The author also wishes to thank Dr. Hiroyuki Furuta for the measurement of 400 MHz NMR. Gifts of chlorosilanes from Shin-etsu Chemical Co. are greatly appreciated.

References

1) For recent reviews, see: a) J. C. Stowell, *Chem. Rev.*, **84**, 409 (1984); b) S. F. Martin, *Synthesis*, **1979**, 633; c) G. Courtois and L. Maginiac, *J. Organomet. Chem.*, **69**, 1 (1974); d) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).

2) a) K. H. Geiss, B. Seuring, R. Piefer, and D. Seebach, *Angew. Chem. Int. Ed. Engl.*, **13**, 479 (1974); b) D. Seebach, K. H. Geiss, and M. Pohmakotor, *ibid.*, **15**, 437 (1976); c) K. H. Geiss, D. Seebach, and B. Seuring, *Chem. Ber.*, **110**, 1833 (1977); d) M. Pohmakotor, K. H. Geiss, and D. Seebach, *ibid.*,

112, 1420 (1979); e) S. F. Martin, and M. T. DuPrest, *Tetrahedron Lett.*, **1977**, 3925; f) H. Ahlbrecht and J. Eicher, *Synthesis*, **1974**, 672; g) M. Julia, A. Schouteeten, and M. M. Baillarge, *Tetrahedron Lett.*, **1974**, 3433.

3) a) K. Narasaka, H. Hayashi, and T. Mukaiyama, *Chem. Lett.*, **1972**, 259; b) T. Mukaiyama and M. Yamaguchi, *ibid.*, **1979**, 657; c) J. Hartmann, M. Stahle, and M. Schlosser, *Synthesis*, **1974**, 888; d) J. Hartmann, R. Muthukrishnan, and M. Schlosser, *Helv. Chim. Acta*, **57**, 77 (1977); e) K. Hirai and Y. Kishida, *Org. Synth.*, **56**, 77 (1977); f) D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, **96**, 5560 (1974); g) W. C. Still and T. L. MacDonald, *ibid.*, **96**, 5561 (1974); h) T. Hassel and D. Seebach, *Angew. Chem. Int. Ed. Engl.*, **18**, 399 (1979); i) R. Kow and M. Rathke, *J. Am. Chem. Soc.*, **95**, 2715 (1973); j) E. Dziadulewicz and T. Gallagher, *Tetrahedron Lett.*, **26**, 4547 (1985).

4) a) K. Ohshima, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **48**, 1567 (1975); b) F. E. Ziegler and C. C. Tam, *J. Org. Chem.*, **44**, 3428 (1979); c) D. A. Evans, D. J. Baillargeon, and J. V. Nelson, *J. Am. Chem. Soc.*, **100**, 2242 (1978); d) P. Brownbrige and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1131; e) A. P. Kozikowski and K. Isobe, *Tetrahedron Lett.*, **20**, 833 (1979); and also see Ref. 2e, 3f, and 3h.

5) a) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, **45**, 195 (1980); b) Y. Yamamoto, H. Yatagai, and K. Maruyama, *Chem. Lett.*, **1979**, 385; c) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1979**, 157.

6) a) S. Torii, H. Tanaka, and Y. Tomotaki, *Chem. Lett.*, **1974**, 1541; For a discussion of hard-soft behavior, see: b) T.-L. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press, Inc., New York (1977); c) I. Fleming "Frontier Orbitals and Organic Chemical Reactions," John Wiley & Sons, London.

7) See Ref. 2—6.

8) a) R. J. P. Corriu and J. Masse, *J. Organomet. Chem.*, **57**, C5 (1973); b) R. J. P. Corriu, J. Masse, and D. Samate, *ibid.*, **93**, 71 (1975); c) R. J. P. Corriu, G. F. Lanneau, J. P. Masse, and D. Samate, *ibid.*, **127**, 281 (1977); d) R. J. P. Corriu, G. F. Lanneau, D. Leclercq, and D. Sammate, *ibid.*, **144**, 155 (1978); e) R. J. P. Corriu, C. Guerin, and J. M'Boula, *Tetrahedron Lett.*, **22**, 2985 (1981); f) P. W. K. Lau and T. H. Chan, *ibid.*, **19**, 2383, (1978); g) K. Koumaglo and T. H. Chan, *ibid.*, **25**, 717 (1984); h) E. Ehlinger and P. Magnus, *J. Chem. Soc., Chem. Commun.*, **1979**, 421; i) E. Ehlinger and P. Magnus, *J. Am. Chem. Soc.*, **102**, 5004 (1980); j) K. S. Kyler and D. S. Watt, *J. Org. Chem.*, **46**, 5182 (1981); k) P. E. Bauer, K. S. Kyler, and D. S. Watt, *J. Org. Chem.*, **48**, 34 (1983); l) K. S. Kyler, M. A. Netzel, S. Arsenigadis, and D. S. Watt, *ibid.*, **48**, 383 (1983); m) J. M. Muchowski, R. Naef, and M. L. Maddox, *Tetrahedron Lett.*, **26**, 5375 (1985); n) N. Ryu, H. Yamamoto, S. Murai, and N. Sonoda, 50th Japan Chem. Soc. Meeting, Koen Yokoshu II, **1985**, 2V34, p. 1483.

9) D. J. S. Tsai and D. S. Matteson, *Tetrahedron Lett.*, **22**, 2751 (1981).

10) F. Sato, Y. Suzuki, and M. Sato, *Tetrahedron Lett.*, **23**, 4589 (1982).

11) Y. Naruta, H. Uno, and K. Maruyama, *Chem. Lett.*, **1982**, 961.

12) D. Kempf; personal communication to Prof. Y. Yamamoto about his presentation at the university of Illinois Seminar Series in Organic Chemistry (December 3, 1979). Results of MINDO/3 caluculation about hetero-substituted allylic carbanions were included in the abstract accompanying his presentation. According to them, charge densities of α and γ positions for a carbanion of allylsilane were -0.4167 and -0.4416, and HOMO coefficients of α and γ positions were -0.69729 and $+0.66642$, respectively.

13) E. Colvin, "Silicon in Organic Synthesis," Butterworth, London (1981), Chap. 2.

14) For a qualitative discussion in terms of PMO theory, see ref. 7c.

15) Carboxylation of (1,2-dimethyl-2-propenyl)dimethylphenylsilane and (2-methyl-2-butenyl)dimethylphenylsilane did not occur sufficiently, though generation of γ-carboxylated compounds could only be detected. In the case of (1-methyl-2-butenyl)dimethylphenylsilane, any carboxylated compounds were not obtained in detectable amounts.

16) L. Pauling, "The nature of the Chemical Bond," 3rd ed., Cornell University Press. Ithaca, New York (1960).

17) V. Rautenstrauch, *Helv. Chim. Acta*, **57**, 496 (1974).

18) a) Y. Naruta, H. Uno, and K. Maruyama, *Chem. Lett.*, **1982**, 609; b) H. Uno, *J. Org. Chem.*, **51**, 350 (1986).

19) a) K. Maruyama, H. Uno, and Y. Naruta, *Chem. Lett.*, **1983**, 1767; b) H. Uno, Y. Naruta, and K. Maruyama, *Tetrahedron*, **40**, 4725 (1984).

20) Katzenellenbogen reported the synthesis of 3-methyl-2-trimethylsilyl-3-butenoate, but this method does not have wide applicability for the preparation of α-silyl β,γ-unsaturated esters, such as **5h** and **5j**: see P. Albaugh-Robertson and J. A. Katzenellenborgen, *Tetrahedron Lett.*, **1982**, 723; P. Albaugh-Robertson and J. A. Katzenellenbogen, *J. Org. Chem.*, **48**, 5288 (1983); and also see Y. Morizawa, S. Kanemoto, K. Ohshima, and H. Nozaki, *Tetrahedron Lett.*, **23**, 2953 (1982).

21) H. Sakurai, K. Sasaki, and A. Hosomi, *Tetrahedron Lett.*, **22**, 745 (1981), and references cited therein.

22) a) J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95**, 8678 (1973); b) I. Fleming and D. Waterson, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1809.
