Pentacoordinate Allylsiliconates in Organic Synthesis: Synthesis of Triethylammonium Bis(catecholato)allylsiliconates and Selective Allylation of Aldehydes[1]

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Pentacoordinate triethylammonium bis(catecholato)allylsiliconates were synthesized by reaction of allyltrialkoxysilanes, catechol, and triethylamine. The allylsiliconates react with aldehydes without catalyst to give the corresponding homoallyl alcohols in high yields in a completely regiospecific and highly diastereoselective mode. The stereochemistry of the products can be reasonably interpreted by assuming a cyclic six-membered ring transition state. This allylation of aldehydes can also be effected by mixing them with an allyltrialkoxysilane, an alcohol, and an amine, generating the allylsiliconate in situ.

Much attention has recently been focused on the synthesis of tetracoordinate allylsilanes and their application in regio-, stereo-, and chemoselective organic synthesis.[2-6] Although stable penta- and hexacoordinate organosilicon compounds can be isolated, they have been little-used in organic synthesis.[7] Before our work was started, the synthesis and characterization of highly coordinate allylsiliconates had been unsuccessful, although some efforts were directed to isolating them,[8] and a pentacoordinate allylfluorosiliconate was considered as an intermediate in allylations with fluoro-substituted allylsilanes.[9] We report herein on the isolation of oxygen-substituted pentacoordinate allylsiliconates, on their use in the regio-, chemo-, and stereoselective allylation of aldehydes without catalyst, and on similar allylations with in situ generated allylsiliconates.[10-12]

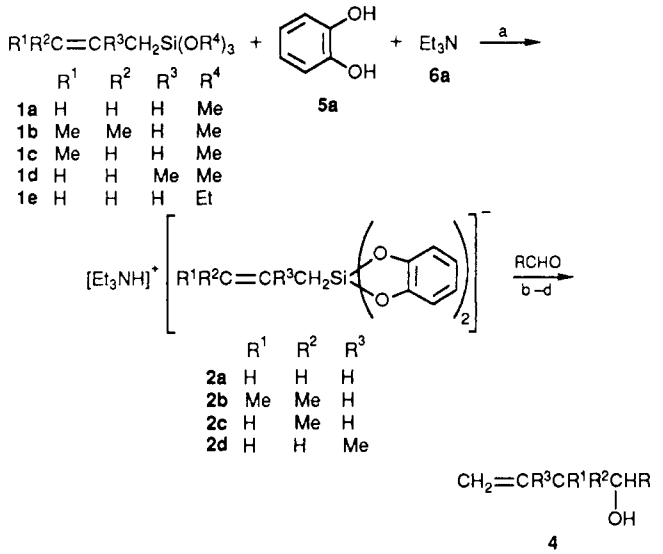
Results and Discussion

Synthesis and Isolation of Pentacoordinate Triethylammonium Bis(catecholato)allylsiliconates. Triethylammonium bis(catecholato)allylsiliconates **2** were prepared by reacting trialkoxy-substituted allylsilanes **1** with 2 equiv of catechol (**5a**) and a 4-fold excess of triethylamine (**6a**) either neat or in dichloromethane or chloroform at temperatures ranging from room temperature to 80 °C for 1–4 h (Scheme I).[10a-c] Thus triethylammonium bis(catecholato)allylsiliconate (**2a**) was obtained in quantitative yield by the reaction of allyltrimethoxysilane (**1a**) with **5a** in **6** for 5 h at 45 °C.

The ^{1}H NMR spectrum of **2a** showed a triplet at δ 1.25 and a quartet at δ 3.17, and a broad singlet at δ 7.69, assigned to the ethyl group and a proton of triethylammonium, respectively; and a doublet at δ 1.69 and two multiplets at δ 4.50–4.76 (2 H) and 5.52–5.91 (1 H) assigned to the allyl group. Aromatic protons appeared as a multiplet (8 H) at δ 6.67. The off-resonance and complete decoupling ^{13}C NMR spectral data were also in accord with the structure **2a**. The ^{29}Si NMR (79.3 MHz) spectrum showed only one high-field peak at δ −78.4 (ppm from tetramethylsilane in $CDCl_3$). The negative ion fast bombardment mass spectrum showed m/z 285 for the bis(catecholato)allylsiliconate anion.

Under similar conditions, **2b–d**, bearing substituents on the allylic group, were obtained from **1b–d** in quantitative yields. A slightly higher temperature (60–80 °C) was necessary to complete the reaction with **1e**. Attempts to

Scheme I. Synthesis and Allylation with Allylsiliconates (2)[a]



[a] Conditions: (a) 45 °C, 5 h; (b) reflux, CH_2Cl_2 or $CHCl_3$; (c) 1 M HCl, 1 h; (d) 1 M NaOH, 1 h.

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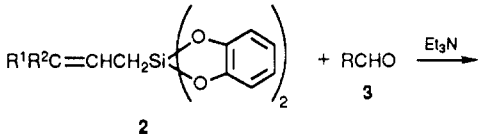
0022-3263/90/1955-2415$02.50/0

Table I. Reactions of 2a with 3[a]



2

$CH_2{=}CHCR^1R^2CHOHR$

4

2			4	
R^1	R^2	3, R		yield,[b] %
H	H	C_6H_5	**4a**	86[c] (84)[d]
CH_3	CH_3	p-$CH_3C_6H_4$	**4b**	84
H	H	p-ClC_6H_4	**4c**	97[d]
H	H	p-NCC_6H_4	**4d**	65[d]
H	H	p-$OHCC_6H_4$	**4e**[e]	62
H	H	p-$O_2NC_6H_4$	**4f**	93
H	H	$C_6H_4CH{=}CH$	**4g**	77
H	H	1-C_3H_7-n	**4h**	100[c,d]
H	H	1-C_7H_{15}-n	**4i**	67

[a] All reactions were carried out in $CHCl_3$ at reflux unless otherwise noted. [b] Yield after isolation by TLC. [c] Reaction carried out in CH_2Cl_2. [d] Yield determined by GLC. [e] R = p-$CH_2{=}CHCH_2CHOHC_6H_4$.

synthesize pentacorrdinate allylsiliconates by replacing **5a** and **6** with other combinations of aliphatic and aromatic diols (2,3-butanediol, pinacol, phenol, 2,2′-dihydroxybiphenyl) with amines (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, pyridine, aniline) or amino alcohols (2-amino-2-methyl-1-propanol, prolinol) were unsuccessful.

Pentacoordinate allylsiliconates are stable and can be stored under dry conditions; they are easily handled and were used as allylating reagents without further purification.

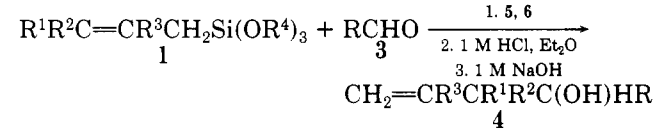
Regiospecific Allylation of Aldehydes 3 with 2. Pentacoordinate allylsiliconates reacted smoothly with aliphatic and aromatic aldehydes **3** without catalyst to furnish the corresponding homoallyl alcohols **4** (Scheme I, Table I). The allylation occurs even in the presence of nitro and cyano groups. The reaction of α,β-unsaturated aldehydes with **2a** proceeds exclusively by 1,2 addition.

Simple aliphatic, alicyclic, and aromatic ketones such as octan-2-one, cyclohexanone, and acetophenone did not give satisfactory results under our conditions.

The allylation of aldehydes was completely regiospecific, carbon–carbon bond formation occurring at the γ carbon of the allyl group of **2**. Thus the prenylsiliconate **2b** reacted with benzaldehyde and *p*-cyanobenzaldehyde regiospecifically to afford only 2,2-dimethyl-1-phenyl-3-buten-1-ol (**4j**, 72%) and 2,2-dimethyl-1-(*p*-cyanophenyl)-3-buten-1-ol (**4k**, 68%) (Table II). These results are in sharp contrast with those in the fluoride ion promoted allylation with allyltrimethylsilane, where no regiospecificity was observed.[6a]

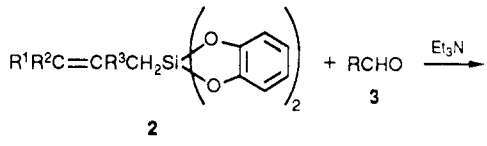
High regio- and diastereoselectivities were obtained in the reaction of the crotylsiliconate **2c** with benzaldehyde (Table II). Thus 2-methyl-1-phenyl-3-buten-1-ol (**4l**; erythro:threo = 10:90) was obtained regiospecifically in the reaction of **2c** (*E*:*Z* = 90:10) with **3a** in 88% yield. Similarly, *p*-cyanobenzaldehyde gave a diastereomeric mixture of 1-(*p*-cyanophenyl)-2-methyl-3-buten-1-ol (**4m**) (erythro:threo = 10:90) in 96% yield. These facts support a mechanism via a cyclic transition state.

Allylation of Aldehydes 3 Using Trialkoxy-Substituted Allylsilanes 1, a Hydroxy Compound 5, and an Amine 6. Aldehydes could also be allylated by reaction with **1**, **5a**, and **6a**, generating the allylsiliconates in situ, and giving the homoallyl alcohols **4**.



We explored several combinations of diols or alcohols **5** and bases **6** for this one-pot allylation of **3**. The allylation of **3a** with **1a** took place in the presence of **5a** and other amines to give the homoallyl alcohol **4a** (Table III). Not only amines but also amino alcohols, such as 2-amino-2-methyl-1-propanol (**6d**) and prolinol (**6e**), promoted the allylation to give **4a**. On the other hand, the reaction did not occur successfully with other diols or alcohols. With 2,2′-dihydroxybiphenyl (**5e**), **4a** was obtained in only 13% yield. In contrast, when salicylic acid (**5f**) or tartaric acid

Table II. Reactions of 2 with 3[a]



2

$CH_2{=}CR^3CR^1R^2CHOHR$

4

2				4		
	R^1	R^2	R^3	3, R		yield,[b] %	(erythro:threo)[c]
2b	CH_3	CH_3	H	C_6H_5	**4j**	72	–
2b	CH_3	CH_3	H	p-NCC_6H_4	**4k**	68	–
2c	H	CH_3	H	C_6H_5	**4l**	88	(10:90)
	(*E*:*Z* = 90:10)[d]						
2c	H	CH_3	H	p-NCC_6H_4	**4m**	96	(10:90)
	(*E*:*Z* = 90:10)[d]						
2d	H	H	CH_3	C_6H_5	**4n**	85	–

[a] All reactions were carried out with **2** (0.6 mmol) and **3** (0.5 mmol) at 80 °C for 12 h. [b] Isolated by TLC. [c] Determined by ^1H NMR. [d] Determined by GLC.

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Table III. In Situ Allylations of Aldehydes 3 with Allyltrimethoxysilane 1a in the Presence of a Hydroxy Compound 5 and an Amine 6[a]

entry	aldehyde (3)	hydroxy compound (5)	amine (6)	product 4 (% yield[b])
1	C_6H_5CHO (**3a**)	catechol (**5a**)	Et_3N (**6a**)	**4a** (95)
2	**3a**	**5a**	$Me_2N(CH_2)_2NMe_2$ (**6b**)	**4a** (69)
3	**3a**	**5a**	pyridine (**6c**)	**4a** (65)
4	**3a**	**5a**	$Me_2C(NH_2)CH_2OH$ (**6d**)	**4a** (64)
5	**3a**	**5a**	prolinol (**6e**)	**4a** (39)[c]
6	**3a**	**5a**	**6e**	**4a** (73)
7	n-$C_7H_{15}CHO$ (**3i**)	**5a**	**6b**	**4k** (58)
8	**3a**	2,3-butanediol (**5b**)	**6a**	–[d]
9	**3a**	pinacol (**5c**)	**6a**	–[d]
10	**3a**	phenol (**5d**)	**6a**	**4a** (3)
11	**3a**	2,2′-dihydroxybiphenyl (**5e**)	**6a**	**4a** (13)
12	**3a**	salicylic acid (**5f**)	**6a**	**4a** (57)[e]
13	**3i**	**5f**	**6a**	**4k** (37)[e]
14	**3a**	tartaric acid (**5g**)	**6a**	**4a** (31)[f]
15	**3a**	o-aminophenol (**5h**)	**6a**	–[d]
16	**3a**	o-phenylenediamine (**5i**)	**6a**	–[d]

[a] All reactions were carried out with **1a** (0.6 mmol), **3a** (0.5 mmol), **5** (1.2 mmol), and **6** (0.6 mmol) at 50 °C for 12 h, unless otherwise noted. [b] Yield determined by ^1H NMR. [c] The reaction was carried out for 5 h. [d] **4a** was not detected by GLC. [e] The reaction was carried out for 48 h. [f] At 100 °C for 48 h.

Table IV. Reactions of 1 with 3 in the Presence of 5a and 6a[a]

$$\underset{1}{R^1R^2C{=}CR^3CH_2Si(OCH_3)_3} + \underset{3}{RCHO} \xrightarrow[\text{catechol}]{Et_3N} \underset{4}{CH_2{=}CR^3CR^1R^2CHOHR}$$

1					4	
	R^1	R^2	R^3	3, R		yield,[b] %
1a	H	H	H	C_6H_5	**4a**	95
1b	CH_3	CH_3	H	C_6H_5	**4j**	75
1a	H	H	H	p-$CH_3C_6H_4$	**4b**	98
1a	H	H	H	p-ClC_6H_4	**4c**	87
1a	H	H	H	p-NCC_6H_4	**4d**	97
1a	H	H	H	o-$O_2NC_6H_4$	**4s**	85
1a	H	H	H	m-$O_2NC_6H_4$	**4t**	94
1a	H	H	H	p-$O_2NC_6H_4$	**4f**	86
1a	H	H	H	$C_6H_5CH{=}CH$	**4g**	62
1a	H	H	H	1-C_3H_7-n	**4h**	68
1a	H	H	H	1-C_7H_{15}-n	**4i**	95
1a	H	H	H	1-naphthyl	**4u**	59

[a] All reactions were carried out in $CHCl_3$ at reflux. [b] Yield after isolation by TLC.

(**5g**) was used, **4a** was obtained in 57% and 31% yields, respectively, under similar conditions. It appears that a combination of **5a** and **6a** is the most expedient and effective in promoting allylation of **3**. Aliphatic diols like pinacol are probably not sufficiently acidic to generate allylsiliconates by the alkoxy exchange reaction, and pentacoordinate siliconate species generated from phenol and **5e** are probably unstable.

The reactions of a variety of aldehydes with **1a** in the presence of **5a** and **6a** proceeded smoothly at 50 °C for 12 h without solvent to afford **4a** in high yields (Table IV). The solvent effect, regioselectivity, and addition mode to **3g** are similar to the results with isolated **2**.

The catalytic activity of **5a** in this allylation was examined, since it had been shown earlier that a catalytic amount of the base will promote reduction of carbonyl compounds to alcohols with trialkoxy-substituted silanes.[7p] However, it was found that a catalytic amount of **5** or **6** was insufficient to promote the present allylation. For example, the reaction of **3a** (0.5 mmol), **1a** (0.6 mmol), **6a** (0.6 mmol), and a catalytic amount of **5a** (0.06 mmol) gave the corresponding homoallyl alcohol **4a** in only 12% yield.

All of these results, which are almost parallel to the allylation using isolated **2**, indicate that the reaction proceeds via in situ generated pentacoordinate allylsiliconates.

Soai et al.[13] have reported the asymmetric synthesis of homoallyl alcohols by the diastereoselective addition of allyltrimethylsilane to chiral γ-keto amides[13a,b] and imides.[13c] In an extension of the asymmetric reduction of prochiral ketones with trialkoxy-substituted silanes catalyzed by a chiral base,[7q] we investigated the enantioselective one-pot allylation of **3** using a combination of **1a** with a chiral **5** or a chiral **6** instead of **5a** and **6a** (Table V).

Although (*S*)-prolinol and (*R,R*)-tartaric acid were used as chiral sources of **5** and **6**, the enantiomeric excess of **4**, whose absolute configuration was *S*, was not improved. For example, **4a**, obtained from the reaction of **2a**, **5a**, and (*S*)-prolinol, showed $[\alpha]^{22}_D$ −7.95°, which corresponds to at most 17% ee.[14b] Trombini et al. have reported the enantioselective allylation (16–65% ee) of aldehydes using chiral tin(IV) complexes containing diethyl tartrate as an auxiliary ligand at 0 °C.[14a] Our lack of success might be due to the higher reaction temperature or the lower reactivity of the reagents. The reaction of **3a** and **1a** using (*S*)-proline instead of **5a** and **6a** gave no allylation product.

Mechanism. Reactions of **2** with **3** are highly sensitive to the solvent employed. The allylation of **3a** (0.5 mmol) with **2a** (0.6 mmol) was examined neat and in nine solvents at room temperature for 12 h. The neat reaction gave the best yield of **4a** (63%). Both CH_2Cl_2 and $CHCl_3$, as well as EtOH, a protic solvent, gave satisfactory results. In contrast, the reaction proceeded very slowly in the aprotic dipolar solvent hexamethylphosphoric triamide. Thus the choice of the solvent is critical, and it appears that nonpolar and noncomplexing solvents work well, whereas those with high dielectric constants (associated with the ability to complex with silicon) do not give satisfactory results. The yields in various solvents are listed in decreasing order in Table VI.

The high threo selectivity in the reaction of the (*E*)-crotyl siliconate **2c** with **3a** suggests that the reaction proceeds via the cyclic transition state **7** (Scheme II). This transition state is similar to those with allylic boron and aluminum reagents[15] and is in contrast with the results for

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Table V. Allylations of Benzaldehyde (3a) Using a Chiral Hydroxy Compound (5) or a Chiral Amine (6)[a]

entry	5	6	temp, °C	time, h	% yield[b] of 4a	% ee[c]
1	catechol (**5a**)	(*S*)-prolinol (**6e**)	80	5	39	17
2	**5a**	(*S*)-valinol (**6f**)	60	12	66	8
3	(*R*,*R*)-tartaric acid (**5g**)	Et_3N (**6a**)	100	72	42	10
4	**5g**	$Me_2N(CH_2)_2NMe_2$ (**6b**)	100	72	29	2
5	**5g**	pyridine (**6c**)	100	72	39	3

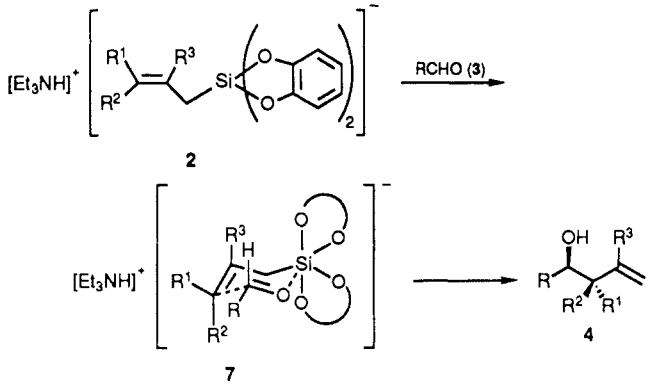
[a] All reactions were carried out with **1a** (1.0 mmol), **3a** (1.2 mmol), **5** (2.0 mmol), and **6** (2.0 mmol). [b] Isolated by TLC. [c] Determined by optical rotation measurements. The product has the *S* configuration.

Table VI. Solvent Effect in Allylation of 3a with 2a[a]

solvent	yield,[b] %	solvent	yield,[b] %
–	63	dioxane	29
$CHCl_3$	48	DMSO	26
CH_2Cl_2	44	THF	23
EtOH	44	DMF	19
CH_3CN	32	HMPA	1

[a] All reactions were carried out with **3a** (0.5 mmol) and **2a** (0.6 mmol) in 4 mL of solvent at rt for 12 h. [b] Yields determined by GLC.

Scheme II. Mechanism of Allylation with Pentacoordinate Allylsiliconates (2)



the tetracoordinate allylsilane, which proceeds by an acyclic $S_{E'}$ reaction.

The Hammett plot (log k_X/k_H vs σ[16]) for the allylation of substituted benzaldehydes with **2a** displays a ρ value of 1.18 with a good correlation factor (r = 0.992) (Figure 1). The positive ρ value indicates that **2** exhibits a weak, somewhat nucleophilic character in the rate-determining step. Therefore the slightly polar but nonionic six-membered cyclic transition state shown in scheme II is compatible with our observations. This mechanism for the allylation with **2** is supported by the stereochemical results in the asymmetric allylation with optically active pentacoordinate allylsiliconates.[17]

The observed solvent effect can be explained by considering the Lewis acidity of the silicon atom of **2**. When a dipolar aprotic solvent is used, the solvent occupies a coordination site on the silicon atom prior to the carbonyl oxygen at the initial stage (Scheme II). As a result, the reaction via a six-membered cyclic transition state should become slower.

In summary, pentacoordinate allylsiliconates can be viewed as a new type of organosilicon reagent that has both an allyl group with high nucleophilicity and a silicon atom with oxophilicity (Lewis acidity) in the same molecule. Thus they resemble organoaluminum reagents, which possess ambiphilic character.[18] The reagents **2** can be

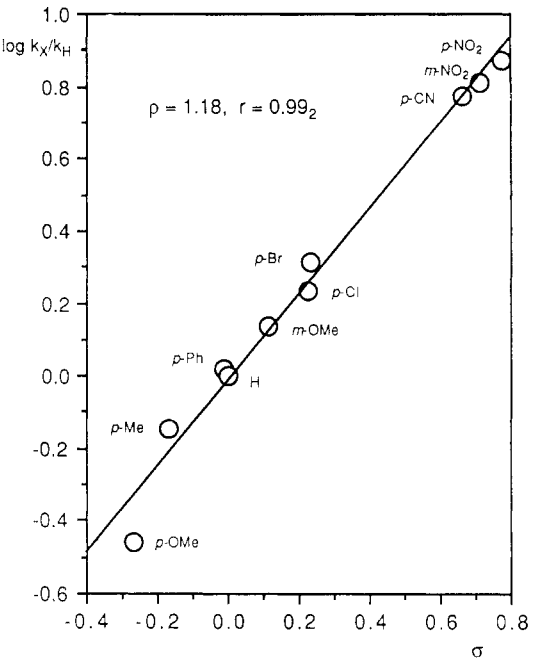


Figure 1. Hammett plot for the allylation of substituted benzaldehydes with triethylammonium bis(catecholato)allylsiliconate (**2a**) in CH_2Cl_2 at reflux.

coordinated by a Lewis basic part of an electrophile such as a carbonyl oxygen, and as a result, the electrophile itself is activated. Then a nucleophilic allyl ligand on the silicon atom attacks the activated electrophile because of the coordination. Therefore **2** reacts with carbon electrophiles without an activator such as a Lewis acid or fluoride ion, which is always required for the reactions of tetracoordinate silicon reagents.

Experimental Section

General. Diethyl ether and tetrahydrofuran were freshly distilled over benzophenone ketyl under nitrogen or distilled and stored over molecular sieves (3A). Acetonitrile, dichloromethane, chloroform, hexamethylphosphoric triamide, and dimethyl sulfoxide were distilled over calcium chloride after standing overnight and stored over molecular sieves (3A). Dioxane was distilled over sodium under nitrogen and stored over molecular sieves (3A). Absolute methanol and ethanol were distilled over magnesium alkoxide after standing overnight and stored over molecular sieves (3A). Carbonyl compounds, alcohols, diols, amines, and carboxylic acids were commercially available and used without purification. Allyltrimethoxysilane and allyltriethoxysilane were also purchased. Catechol was used after recrystallization from hexane–benzene.

Melting points were determined on a Gallenkamp apparatus and are uncorrected. Bulb-to-bulb distillation was conducted with a Sibata glass tube oven GTO-250RS apparatus. IR spectra were recorded on sodium chloride plates on a SHIMADZU IR-460 spectrometer. ^1H NMR spectra were determined on JEOL PMX-60 (60 MHz), FX-90Q (90 MHz), and JNM-GX400 (400 MHz) spectrometers with tetramethylsilane as an internal

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standard in carbon tetrachloride or deuteriochloroform. ^{13}C NMR spectra were recorded on a JEOL FX-90Q (90 MHz) or a JEOL JNM-GX400 (400 MHz) spectrometer in deuteriochloroform as solvent and internal standard. ^{29}Si NMR spectra were determined on a JEOL JNM-GX400 (400 MHz) spectrometer in deuteriochloroform with TMS as an internal standard. Mass spectra (MS) were recorded on a JEOL JMS-DX303 spectrometer and a JEOL JMA-DA-5000 data processor by the electron impact (EI) or fast atom bombardment (FAB) ionization method. Preparative TLC was performed on Merck silica gel GF 254 (type 60). For GLC analysis and preparative purification, SHIMADZU GC-8A and GC-6A gas chromatographs, equipped with a 2-m column packed with 30% SE-30 or DC-550 on Celite, were used. GC peak integrals were recorded with a SHIMADZU Chromatopac C-R3A or C-R1B integrator. Optical rotations were determined with a JASCO DIP-181 digital polarimeter.

(3-Methyl-2-butenyl)trimethoxysilane (1b).[19] Isoprenyl chloride[20] (4.85 g, 0.046 mol) was added to dried magnesium (5.5 g, 0.23 mol) in dry Et_2O (30 mL) in a 300-mL three-necked flask equipped with a dropping funnel, a mechanical stirrer, and a condenser connected with a nitrogen inlet tube. After the reaction started, a solution of tetramethoxysilane in dry Et_2O (50 mL) and a solution of isoprenyl chloride (12.7 g, total 17.5 g, 0.167 mol) in dry ether (50 mL) were added dropwise. After completion of the addition, the reaction mixture was gently refluxed for 2 h and stirred overnight. After the addition of dry Et_2O, the mixture was filtered as soon as possible. The filtrate was distilled to remove the solvent. The residue was distilled under reduced pressure to afford 5.94 g (0.031 mol, 19%) of a colorless oil: bp 70–76 °C (24 mmHg); ^1H NMR (CCl_4) δ 1.28 (1 H, d, J = 7 Hz), 1.43 (3 H, s), 1.53 (3 H, s), 3.33 (9 H, s), 4.92 (1 H, t, J = 7 Hz); HRMS calcd for $C_8H_{18}O_3Si$ (M) 190.306, found m/e 190.1048.

2-Butenyltrimethoxysilane (1c).[19] Compound **1c** (5.73 g, 0.032 mol, 57%) was prepared as a colorless oil from 2-butenyltrichlorosilane (10.60 g, 0.056 mol), triethylamine (18.68 g, 0.184 mol), and absolute MeOH (5.92 g, 0.184 mol): bp 63–68 °C (21 mmHg); ^1H NMR (CCl_4) δ 1.52 (2 H, bs), 1.76 (3 H, bs), 3.48 (9 H, s), 4.55 (2 H, bs). Anal. Calcd for $C_7H_{16}O_3Si$: C, 47.69; H, 9.15. Found: C, 47.40; H, 8.83.

(2-Methyl-2-propenyl)trimethoxysilane (1d). Under a nitrogen atmosphere, to an ice-cold solution of (2-methyl-2-propenyl)trichlorosilane (4.45 g, 0.024 mol) and triethylamine (8.55 g, 0.085 mol) in dry Et_2O (150 mL) was added dropwise a solution of absolute MeOH (2.48 g, 0.078 mol) in dry ether (30 mL) with vigorous stirring. The resulting white suspension was stirred at room temperature for 2 h, and then dry ether (100 mL) was added. The mixture was filtered to remove the salt. The solvent was removed by distillation, and the residue was distilled in vacuo to give 2.16 g (0.012 mol, 50%) of a colorless oil: bp 56–66 °C (35 mmHg); ^1H NMR (CCl_4) δ 1.40 (2 H, m), 1.60 (3 H, m), 3.43 (9 H, s), 5.22 (2 H, m). Anal. Calcd for $C_7H_{16}O_3Si$: C, 47.69; H, 9.15. Found: C, 47.68; H, 8.95.

Pentacoordinate Allylsiliconates (2). Typical Procedure. Triethylammonium Bis(catecholato)allylsiliconate (2a). Under a nitrogen atmosphere, a mixture of allyltrimethoxysilane (82.1 mg, 0.506 mmol), catechol (114.4 mg, 1.04 mmol), and triethylamine (217 mg, 2.15 mmol) was stirred at room temperature to 40 °C for 4 h. The resulting precipitate was dried at room temperature in vacuo to give **2a** quantitatively: mp 120 °C dec; ^1H NMR ($CDCl_3$) δ 1.25 (9 H, t, J = 7 Hz), 1.69 (2 H, d, J = 8 Hz), 3.17 (6 H, q, J = 7 Hz), 4.50–4.76 (2 H, m), 5.52–5.91 (1 H, m), 6.67 (8 H, m, Ar), 7.69 (1 H, bs); ^{13}C NMR ($CDCl_3$) δ 8.72 (q), 24.60 (t), 46.43 (t), 110.69 (d), 111.56 (t), 118.77 (d), 136.91 (d), 149.48 (s); ^{29}Si NMR ($CDCl_3$) δ −78.4; FAB-MS (negative ion) m/e 286. Anal. Calcd for $C_{21}H_{29}NO_4Si$: C, 65.08; H, 7.54; N, 3.61. Found: C, 65.10; H, 7.41; N, 3.60.

Triethylammonium bis(catecholato)(3-methyl-2-butenyl)siliconate (2b): mp 94 °C dec; ^1H NMR ($CDCl_3$) δ 1.14–1.81 (17 H, m), 3.15 (6 H, q, J = 7 Hz), 5.09 (1 H, m), 6.65 (8 H, m), 8.13 (1 H, bs); ^{13}C NMR ($CDCl_3$) δ 8.56 (q), 17.15 (q), 8.39 (q), 25.57 (t), 46.38 (t), 110.58 (d), 116.76 (s), 118.55 (d), 127.36 (d), 149.57 (s); ^{29}Si NMR ($CDCl_3$) δ −76.68; FAB-MS (negative ion) m/e 314. Anal. Calcd for $C_{23}H_{33}NO_4Si$: C, 66.47; H, 8.00; N, 3.37. Found: C, 66.23; H, 7.93; N, 3.39.

Triethylammonium bis(catecholato)-2-butenylsiliconate (2c): mp 124 °C dec; ^1H NMR ($CDCl_3$) δ 1.18–1.63 (14 H, m), 3.20 (6 H, q, J = 7 Hz), 5.23 (2 H, m), 6.66 (8 H, m), 6.89 (1 H, bs); ^{29}Si NMR ($CDCl_3$) δ −77.45; FAB-MS (negative ion) m/e 299. Anal. Calcd for $C_{22}H_{31}NO_4Si$: C, 65.80; H, 7.78; N, 3.49. Found: C, 65.63; H, 7.73; N, 3.44.

Triethylammonium bis(catecholato)(2-methyl-2-propenyl)siliconate (2d): ^1H NMR ($CDCl_3$) δ 1.21 (3 H, s), 1.21 (9 H, t, J = 7 Hz), 3.14 (6 H, q, J = 7 Hz), 4.35 (1 H, m), 4.65 (1 H, m), 6.43–6.78 (8 H, m), 7.08 (1 H, bs); FAB-MS (negative ion) m/e 299. Anal. Calcd for $C_{22}H_{31}NO_4Si$: C, 65.80; H, 7.78; N, 3.49. Found: C, 65.53; H, 7.70; N, 3.41.

Reaction of Triethylammonium Bis(catecholato)allylsiliconates (2) with Aldehydes (3). Typical Procedure. An allylsiliconate (**2**) (0.6 mL) and an aldehyde (**3**) (0.5 mmol) were stirred in CH_2Cl_2 (2 mL) at room to reflux temperature for 10 h. Et_2O (20 mL) and hydrochloric acid (1 M, 5 mL) were then added, and the mixture was stirred for 1 h. The resulting mixture was separated, and the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layer was washed with water (10 mL), aqueous sodium hydroxide (1 M, 10 mL), water (3 × 10 mL), and brine (10 mL). After drying over anhydrous Na_2SO_4, the solvent was removed to give an oily residue. The crude product was purified by preparative TLC on silica gel to give a pure homoallyl alcohol **4**.

1-Phenyl-3-buten-1-ol (4a):[21] ^1H NMR (CCl_4) δ 2.13 (1 H, bs), 2.43 (2 H, t, J = 7 Hz), 4.64 (1 H, t, J = 6 Hz), 4.86–5.33 (3 H, m), 7.23 (5 H, s); IR (neat) 3400, 3070, 1640, 1495, 1460 cm^{-1}.

1-(*p*-Methylphenyl)-3-buten-1-ol (4b):[21] ^1H NMR (CCl_4) δ 2.23 (6 H, m), 4.40 (1 H, t, J = 7 Hz), 4.70–6.00 (3 H, m), 6.95 (4 H, s); IR (neat) 3400, 2900, 1640, 1515 cm^{-1}.

1-(*p*-Chlorophenyl)-3-buten-1-ol (4c):[21] ^1H NMR (CCl_4) δ 2.30 (2 H, t, J = 7 Hz), 2.95 (1 H, bs), 4.50 (1 H, t, J = 7 Hz), 4.75–6.00 (3 H, m), 7.10 (4 H, s); IR (neat) 3400, 3080, 2900, 1640, 1600, 1495 cm^{-1}.

1-(*p*-Cyanophenyl)-3-buten-1-ol (4d):[22] ^1H NMR (CCl_4) δ 2.37 (2 H, t, J = 7 Hz), 3.05 (1 H, bs, OH), 4.63 (1 H, t, J = 7 Hz), 4.60–6.00 (3 H, m), 7.40 (4 H, s); IR (neat) 3450, 3070, 2900, 2250, 1640, 1610, 1550 cm^{-1}.

1-(*p*-1′-Hydroxy-3′-butenylphenyl)-3-buten-1-ol (4e): mp 108–109 °C; ^1H NMR (CCl_4) δ 2.00 (2 H, bs), 2.43 (4 H, t, J = 7 Hz), 4.65 (2 H, t, J = 7 Hz), 4.84–6.10 (6 H, m), 7.20 (4 H, s). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.78; H, 8.29.

1-(*p*-Nitrophenyl)-3-buten-1-ol (4f):[23] ^1H NMR (CCl_4) δ 2.40 (2 H, t, J = 7 Hz), 2.77 (1 H, bs), 4.70 (1 H, t, J = 7 Hz), 4.70–6.00 (3 H, m), 7.33 (2 H, d, J = 9 Hz), 7.95 (2 H, d, J = 9 Hz); IR (neat) 3450, 3070, 2900, 1640, 1605, 1520, 1345 cm^{-1}.

1-Phenyl-1,5-hexadien-3-ol (4g):[24] ^1H NMR (CCl_4) δ 2.15 (1 H, bs), 2.23 (2 H, t, J = 7 Hz), 4.13 (1 H, q, J = 7 Hz), 4.75–6.65 (5 H, m), 7.10 (5 H, s); IR (neat) 3400, 3080, 3030, 1640, 1495, 1455 cm^{-1}.

1-Hepten-3-ol (4h):[24] ^1H NMR (CCl_4) δ 0.65–2.40 (7 H, m), 2.10 (2 H, t, J = 7 Hz), 3.50 (1 H, m), 4.75–6.15 (3 H, m); IR (neat) 3400, 2950, 1640 cm^{-1}.

1-Undecen-3-ol (4i):[25] ^1H NMR (CCl_4) δ 0.60–1.80 (15 H, m), 2.00 (1 H, bs), 2.10 (2 H, t, J = 7 Hz), 3.50 (1 H, m), 4.75–6.15 (3 H, m); IR (neat) 3400, 2950, 1640 cm^{-1}.

2,2-Dimethyl-1-phenyl-3-buten-1-ol (4j):[21] ^1H NMR (CCl_4) δ 0.90 (6 H, s), 2.00 (1 H, bs), 4.20 (1 H, s), 4.60–6.15 (3 H, m), 7.10 (5 H, s); IR (neat) 3450, 2970, 1635, 1460 cm^{-1}.

1-(*p*-Cyanophenyl)-2,2-dimethyl-3-buten-1-ol (4k):[26] ^1H NMR (CCl_4) δ 0.95 (6 H, s), 2.50 (1 H, bs), 4.33 (1 H, s), 4.65–6.10 (3 H, m), 7.13–7.50 (4 H, m); IR (neat) 3500, 2975, 2250, 1635, 1610, 1505, 1420, 1060 cm^{-1}.

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2-Methyl-1-phenyl-3-buten-1-ol (4l, Erythro:Threo = 10:90):[27] ^{1}H NMR (CCl_4) δ 0.87 (3 H, d, J = 7 Hz, threo), 1.00 (d, J = 7 Hz, erythro), 2.48 (1 H, q, J = 7 Hz), 4.36 (1 H, d, J = 8 Hz), 5.07–6.00 (3 H, m), 7.32 (5 H, s); IR (neat) 3550, 2975, 1635, 1490, 1460, 1020, 920 cm^{-1}.

1-(*p*-Cyanophenyl)-2-methyl-3-buten-1-ol (4m: Erythro:Threo = 90:10):[28] ^{1}H NMR (CCl_4) δ 0.91 (3 H, d, J = 7 Hz, threo), 0.96 (3 H, d, J = 7 Hz, erythro), 2.44 (1 H, q, J = 7 Hz), 4.45 (1 H, dd, J = 7 and 3 Hz), 5.00–5.90 (3 H, m), 7.42 (2 H, d, J = 8 Hz), 7.62 (2 H, d, J = 8 Hz); IR (neat) 3500, 2975, 2250, 1635, 1610, 1500, 1429 cm^{-1}.

3-Methyl-1-phenyl-3-buten-1-ol (4n):[22] ^{1}H NMR (CCl_4) δ 1.80 (3 H, s), 2.16 (1 H, bs), 2.42 (2 H, d, J = 7 Hz), 4.72–4.91 (3 H, m), 7.33 (5 H, s); IR (neat) 3400, 3075, 2950, 1645, 1495, 1460 cm^{-1}.

Allylation of Aldehydes with Allyltrimethoxysilane in the Presence of Catechol and Triethylamine. Typical Procedure. An allyltrialkoxysilane (0.75 mmol) was added to a mixture of an aldehyde (0.5 mmol), **5a** (1.5 mmol), and **6a** (1.0 mmol), and the resulting mixture was stirred for 12 h at 60 °C. Et_2O (20 mL) and hydrochloric acid (1 M, 5 mL) were then added, and the mixture was stirred for 1 h. The ethereal layer was separated, and the aqueous layer was extracted with Et_2O (2 × 15 mL). The organic layers were combined and washed with water (10 mL) and then with aqueous sodium hydroxide (1 M, 10 mL), water (3 × 10 mL), and brine (10 mL). After being dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and separation by preparative TLC on silica gel to give the pure homoallyl alcohol **3**.

1-(*o*-Nitrophenyl)-3-buten-1-ol (4s): bp (bulb-to-bulb) 100 °C (0.6 mmHg); ^{1}H NMR (CCl_4) δ 2.50 (2 H, t, J = 7 Hz), 2.60 (1 H, bs), 4.90–6.30 (4 H, m), 7.17–8.20 (4 H, m); IR (neat) 3450, 3070, 1710, 1640, 1610, 1510, 1355 cm^{-1}. Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.11; H, 5.74; N, 7.25. Found: C, 62.09; H, 5.74; N, 7.29.

1-(*m*-Nitrophenyl)-3-buten-1-ol (4t):[21] ^{1}H NMR (CCl_4) δ 2.37 (2 H, t, J = 7 Hz), 3.17 (1 H, bs), 4.70 (1 H, t, J = 7 Hz), 4.70–6.10 (3 H, m), 7.15–8.20 (4 H, m); IR (neat) 3450, 3070, 2900, 1640, 1530, 1350 cm^{-1}.

1-(1-Naphthyl)-3-buten-1-ol (4u):[29] ^{1}H NMR (CCl_4) δ 2.63 (2 H, t, J = 7 Hz), 2.65 (1 H, bs), 4.90–6.70 (4 H, m), 7.25–8.14 (7 H, m); IR 3400, 3060, 2900, 1640, 1595, 1510 cm^{-1}.

Allylation of Benzaldehyde Using Allyltrimethoxysilane, (*R*)-(+)-Tartaric Acid (5g), and an Amine (6). Typical Procedure. A mixture of **3a** (1.2 mmol), **1a** (1.0 mmol), **5g** (2.0 mmol), and **6** (2.0 mmol) was stirred. The reaction mixture was treated with Et_2O (20 mL) and 1 M hydrochloric acid (10 mL), and the resulting mixture was stirred at room temperature for 30 min. The ethereal layer was separated, and the aqueous layer was extracted into Et_2O (2 × 15 mL). The combined organic layer was washed with water (2 × 20 mL), 1 M sodium hydroxide (20 mL), water (3 × 20 mL), and brine (10 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by preparative TLC to give pure 1-phenyl-3-buten-1-ol (**4a**). Its absolute configuration and enantiomeric excess were determined by its optical rotation: $[\alpha]^{22}_D$ −7.95° (*c* 1.3, benzene), corresponding to the *S* isomer in 17% ee (lit.[14b] $[\alpha]^{23}_D$ −44.92° (*c* 7.4, benzene) for a sample of the *S* isomer reported to be 96% ee).

Determination of Relative Reactivities in the Allylation of Substituted Benzaldehydes with 2a. A mixture of allylsiliconate (**2a**) (97 mg, 0.25 mmol), **3a** (265 mg, 2.5 mmol), and a substituted benzaldehyde (2.5 mmol) in CH_2Cl_2 (5 mL) was stirred at reflux for 3 h. The relative yields of the corresponding homoallyl alcohols were determined by GLC using a 1.5-m column of Silicone SE 30 on Celite 545.

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Registry No. **1a**, 2551-83-9; **1b**, 72142-16-6; **1c**, 13436-83-4; **1d**, 125715-25-5; **2a**, 114612-18-9; **2b**, 114571-77-6; (*E*)-**2c**, 125715-28-8; (*Z*)-**2c**, 125715-32-4; **2d**, 125715-30-2; **3** (R = C_6H_5), 100-52-7; **3** (R = *p*-$CH_3C_6H_4$), 104-87-0; **3** (R = *p*-ClC_6H_4), 104-88-1; **3** (R = *p*-NCC_6H_4), 105-07-7; **3** (R = *p*-$OHCC_6H_4$), 623-27-8; **3** (R = *p*-$O_2NC_6H_4$), 555-16-8; **3** (R = C_6H_5CH=CH), 104-55-2; **3** (R = 1-C_3H_7-*n*), 123-72-8; **3** (R = 1-C_7H_5-*n*), 124-13-0; **3** (R = *o*-$O_2NC_6H_4$), 552-89-6; **3** (R = M-$O_2NC_6H_4$), 99-61-6; **3** (R = 1-naphthyl), 66-77-3; **4a**, 936-58-3; **4b**, 24165-63-7; **4c**, 14506-33-3; **4d**, 71787-53-6; **4e**, 114659-04-0; **4f**, 14506-32-2; **4g**, 13891-95-7; **4h**, 3521-91-3; **4i**, 13891-96-8; **4k**, 113365-35-8; *erythro*-**4l**, 52922-10-8; *threo*-**4l**, 52922-19-7; *erythro*-**4m**, 83173-80-2; *thre*-**4m**, 125715-26-6; **4n**, 23092-23-1; **4s**, 125715-24-4; **4t**, 71787-52-5; **4u**, 72551-06-5; **5a**, 120-80-9; **5b**, 513-85-9; **5c**, 76-09-5; **5d**, 108-95-2; **5e**, 1806-29-7; **5f**, 69-72-7; **5g**, 87-69-4; **5h**, 95-55-6; **5i**, 95-54-5; **6a**, 121-44-8; **6b**, 110-18-9; **6c**, 110-86-1; **6d**, 124-68-5; **6e**, 23356-96-9; **6f**, 2026-48-4; DMSO, 67-68-5; THF, 109-99-9; DMF, 68-12-2; HMPA, 680-31-9; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; EtOH, 64-17-5; CH_3CN, 75-05-8; dioxane, 123-91-1; isoprenyl chloride, 503-60-6; 2-butenyltrichlorosilane, 18147-55-2; (2-methyl-2-propenyl)trichlorosilane, 18147-56-3.

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