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Alkoxyallylsilanes: Functional Protecting Groups

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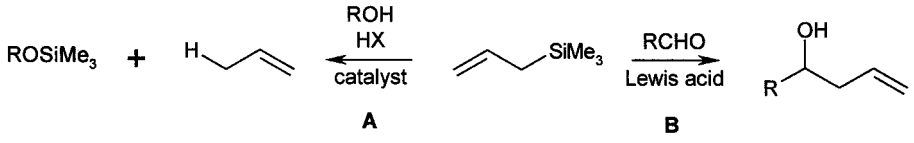
Abstract—Allyl-*t*-butylmethylsilyl groups were shown to function as alcohol protecting groups whose hydrolytic stability was greater than *t*-butyldimethylsilyl (TBS) and $Si(SiMe_3)_3$ (sisyl) groups. Pseudo-first-order rate constants for the acidic hydrolysis of primary, benzylic, and secondary allyl-*t*-butylmethylsilyl ethers in AcOD/THF-d_8/D_2O were determined to be 2.94×10^{-3}, 8.26×10^{-4}, and 8.26×10^{-4} s^{-1}, respectively. The regioselectivity of acidic hydrolysis of allylbenzyloxy-*t*-butylmethylsilane **1** was examined under strong acid (*p*-TsOH/CD_2Cl_2) and weak acid (AcOD/THF-d_8/D_2O) conditions. In both cases, benzyl alcohol was initially produced exclusively from silicon–oxygen bond cleavage: allylic cleavage was only subsequently observed over time. However, the allyl group of the silyl ether could be hydrosilylated. The resulting alkoxy-functionalized disiloxane had greater hydrolytic stability under acidic conditions than the starting alkoxyallyl-*t*-butylmethylsilane.

Introduction

The silyl ether has become the most commonly used alcohol protecting group in organic synthesis due to its ease of formation and the selectivity with which it can be removed.[1] The latter process is typically carried out either with a 'naked' fluoride source such as tetrabutylammonium fluoride, or via acidic hydrolysis.[2] The stability of silyl groups to hydrolysis and other nucleophilic conditions is generally proportional to the degree of steric hindrance at both the silicon atom and the alcohol carbon atom.[3] As a result, a large number of alkylsilanes possessing various degrees of steric bulk around the silicon atom have previously been prepared and utilized as alcohol protecting groups, particularly when the selective cleavage of one of two or more different silyl ether groups within the same molecule is required.

Silyl ethers can, in addition, serve quite a different purpose. The silylation of hydrophilic drugs is a method of imparting lipophilic character to them. For instance, the increased lipophilicity of trimethylsilylated α-hydroxyacids (e.g. $Me_3SiOCH_2COOSiMe_3$, an anti-oxidant for skin care)[4] or testosterone over the parent compounds led to improved delivery of the active agent and, in the latter case, to more potent androgenic activity.[5]

Usually, silyl ethers are prepared from chlorosilanes or silyl triflates and an alcohol in the presence of base. However, the protection of alcohols as silyl ethers has also been effected with allyltrimethylsilane, whereby the allyl moiety serves as the leaving group on silicon, giving a trimethylsilyl ether, and gaseous propene as the only by-product (Scheme 1A).[6]



Scheme 1.

This cleavage of the allylic silicon–carbon bond, which follows electrophilic addition to the double bond, has found significant synthetic application as a method of introducing the allyl group onto carbon electrophiles such as carbonyl compounds, acetals, ketals, and iminium ions (Scheme 1B).[7]

We were interested in determining if the utility of allylsilanes could be combined with that of silyl ethers. That is, to learn whether the reactivity of each of the functional groups remains unchanged when both are present within the same molecule. Towards this end, we have prepared several allyloxysilanes and examined their reactivity under acidic conditions to compare the lability of the allyl substituent

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versus the alkoxy substituent. The allyloxysilanes were also investigated as precursors for the preparation of lipophilic, silicone-modified ethers.

Results and Discussion

Allyl-*t*-butylchloromethylsilane was prepared by the reaction of *t*-butylmagnesium chloride with allyldichloromethylsilane. This route was more efficacious in our hands than the complementary approach involving substitution at *t*-butyltrichlorosilane by allylmagnesium bromide, followed by methylmagnesium chloride. The presence of catalytic quantities of CuCN affords high yields of organosilanes under very mild conditions from the reaction of organomagnesium reagents and chlorosilanes.[8] The *t*-butyl and methyl substituents were chosen in order to create a steric environment at silicon which is comparable to that found in the *t*-butyldimethylsilyl group—the most frequently utilized member of the repertoire of alcohol protecting groups, whose reactivity is well defined. The allyl-*t*-butylmethylsilyl ethers of representative primary, benzylic and secondary alcohols, 2-phenylethanol, benzyl alcohol and cyclopentanol, respectively, were then prepared from allyl-*t*-butylchloromethylsilane using the standard conditions for silylation of alcohols.[9]

Initially, an examination of the relative reactivity of the two functional groups on the allylsilyl ethers was attempted: it was important to distinguish between acidic hydrolysis at the Si–O group and cleavage of the allyl group via the β-effect under acidic conditions.[10] Thus, the hydrolytic stability of these silyl ethers was compared with that of the corresponding *t*-butyldimethylsilyl ethers (TBS), and with the corresponding tris(trimethylsilyl)silyl (sisyl) ethers, the latter being susceptible to both hydrolytic and photolytic cleavage.[11] This was accomplished by measuring the rates of acid-catalyzed hydrolysis in AcOD/THF-d_8/D_2O under pseudo-first-order conditions using a modification of the procedure established by Corey et al.[9] The observed rate constants are given in Table 1.

For each of the three silyl groups, an increased rate of hydrolysis of the silyl ether derived from the primary alcohol, when compared with the secondary alcohol, was observed, which is consistent with the well-documented correlation of increased hydrolytic stability with increased steric hindrance at the alcohol carbon (Fig. 1).[1–3] The decreased lability in protic media on going from sisyl to TBS to allyl-*t*-butylmethylsilyl ethers reflects an increase in steric bulk at silicon.

Table 1. Rate constants (s^{-1}) for acidic hydrolysis of silyl ethers $ROSiR'_3$

SiR'_3	R		
	CH_2CH_2Ph	CH_2Ph	C_5H_9
$Si(Si(CH_3)_3)_3$[a]	3.74×10^{-2}	1.94×10^{-2}	1.30×10^{-2}
$Si(CH_3)(CH_2CH{=}CH_2)t$-Bu	2.94×10^{-3}	8.26×10^{-4} **1**	8.26×10^{-4}
$Si(CH_3)_2t$-Bu[a]	6.04×10^{-3}	3.53×10^{-3}	3.49×10^{-3}

[a] Rate constants previously reported, see Ref. 11.

Two possible reaction pathways for acidic hydrolysis of allylsilyl ethers are illustrated in Scheme 2. Path A involves nucleophilic substitution at silicon with cleavage of the silicon–oxygen bond, for which considerable evidence has been put forth to support a mechanism involving extracoordination at silicon.[12] Path B involves cleavage of the allylic silicon–carbon bond via electrodesilylation of the allyl group.[7,10] Since the versatility of the allyl-*t*-butylmethylsilyl ether as a protecting group would be altered in the case of electrophilic substitution or electrophilic addition at the allyl group, the ability for this to occur was examined.

An analysis of the reaction products from the hydrolysis of allylbenzyloxy-*t*-butylmethylsilane **1** with both a weak acid (AcOD/THF-d_8/D_2O) and a strong acid (*p*-toluenesulfonic acid/CD_2Cl_2), revealed that in both cases benzyl alcohol was initially produced exclusively (Scheme 2A). No loss of the allyl group was observed under weakly acidic conditions, although the silyl by-product **2** subsequently reacted further to give the disiloxane **3** (Scheme 2). Under strongly acidic conditions, **4** subsequently underwent protiodesilylation: there was no evidence for Path B (Scheme 2). Strong acids rather than moderate nucleophiles are clearly required for the hydrodesilylation of these allylsilanes.

From the preceding experiments it is clear that protonation preferentially occurs at oxygen rather than the allyl group of **1**. It seemed possible that this bias could be overcome by the use of a bulky electrophile which, for steric reasons, would be prone to attack electrophilically at the allyl group rather than at the alkoxy group. Although allylsilanes typically react with aldehydes and ketones in the presence of Lewis acids to form homoallylic alcohols (Scheme 1), **1** did not react with benzaldehyde in the presence of boron trifluoride etherate. In a competition reaction between 1 equiv. of each of **1**, allyltrimethylsilane, and benzaldehyde, only allyltrimethylsilane gave allylic transposition onto benzaldehyde.

However, when **1** was allowed to react with the sterically hindered and strongly electrophilic triphenylcarbenium hexafluorophosphate, a small quantity of 4,4,4-triphenyl-1-butene **5**, the product of allylic cleavage, was observed. The major product was triphenylmethyl benzyl ether. This suggests that a bias towards allyl cleavage might only be established with alkoxy groups that are bulkier than benzyloxy, and perhaps, with even bulkier electrophiles than Ph_3C^+. This is clearly a significant synthetic limitation to the use of these bifunctional silanes as both allylsilanes and alkoxysilanes.

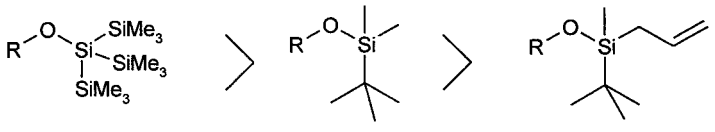
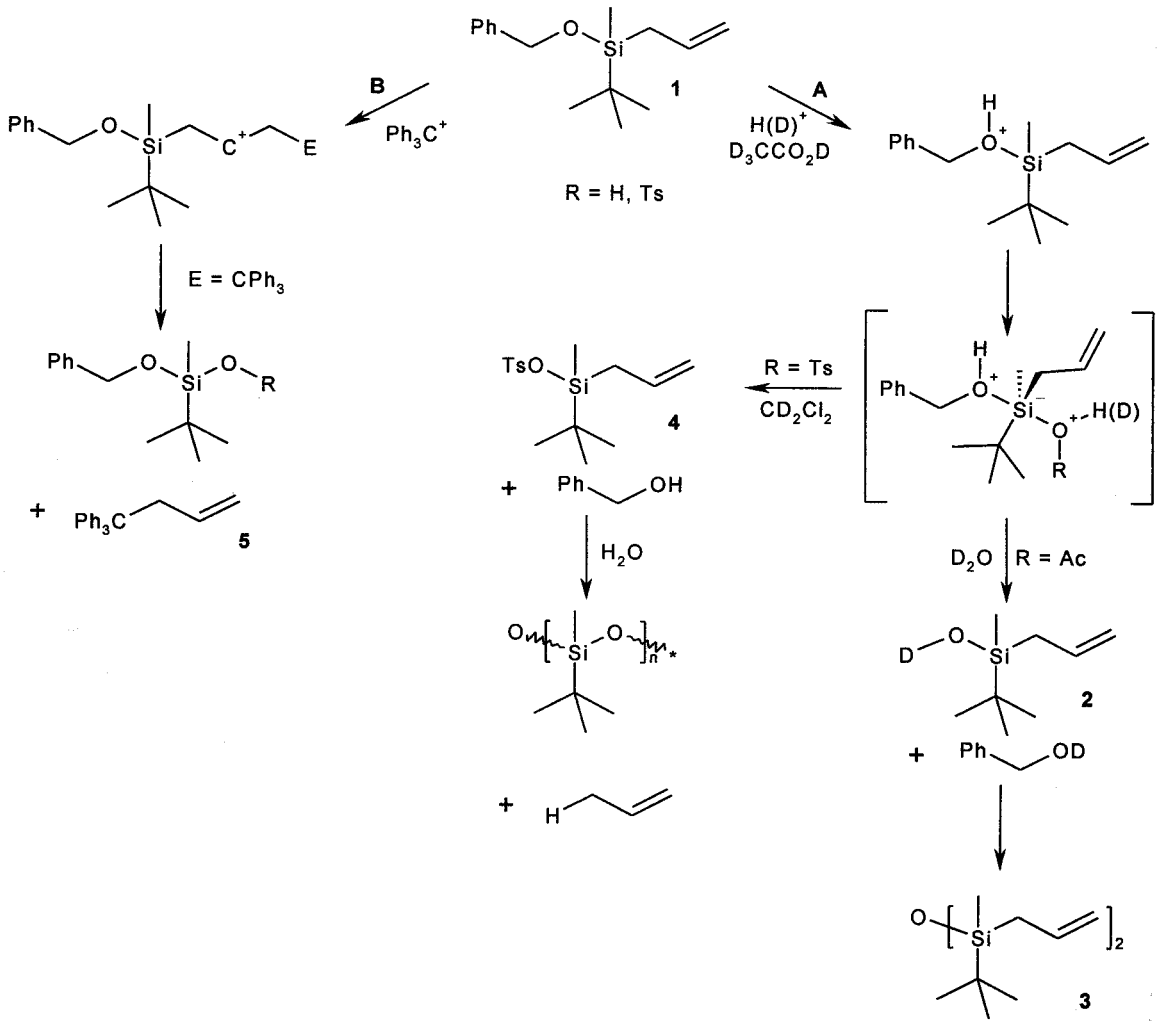


Figure 1. Relative rates of hydrolytic cleavage of silyl ethers in AcOD/THF-d_8/D_2O.



Scheme 2.

Although the allyl group does not undergo selective acidic cleavage, it remains reactive under other non-acidic conditions. In particular, as is widely practiced in the silicone industry, it readily undergoes hydrosilylation with hydrosilanes. It was anticipated that the resulting product would be approximately as stable towards hydrolysis as the parent allylsilane. To establish whether allylalkoxysilanes could provide a general route to lipophilic, silicone-modified alcohols, **1** was subjected to hydrosilylation with the model silicone pentamethyldisiloxane and Karstedt's catalyst ($Pt_n((H_2C{=}CHSiMe_2)_2O)_m$ typically $n{=}2$, $m{=}3$[13]) to give **6** (Scheme 3).

As **6** was insoluble in the aqueous solvent system used for the measurement of rate constants (Table 1), a relative reactivity order of hydrolysis of the benzyloxysilyl ethers was determined in $CDCl_3$ using *p*-toluenesulfonic acid monohydrate.[11] The hydrolysis rates under identical reaction conditions for benzyloxy-*t*-butyldimethylsilane, benzyloxy-(tris(trimethylsilyl)silyl), **1**, and **6** were determined to be 2.5, 0.9, 0.8, and 0.7 ($\times 10^{-4}$ mol L^{-1} min^{-1}), respectively (Fig. 2). The reversal of reactivity observed between TBS and sisyl ethers when the solvent was changed from protic to aprotic has previously been reported to be attributed to a changeover in mechanism due to the protic solvent's ability to facilitate extracoordination at silicon.[11]

These results are consistent with our expectation that the steric bulk associated with the distal silicon atom (Si^*, Fig. 2), which is separated by a propyl unit from the silicon

Scheme 3.

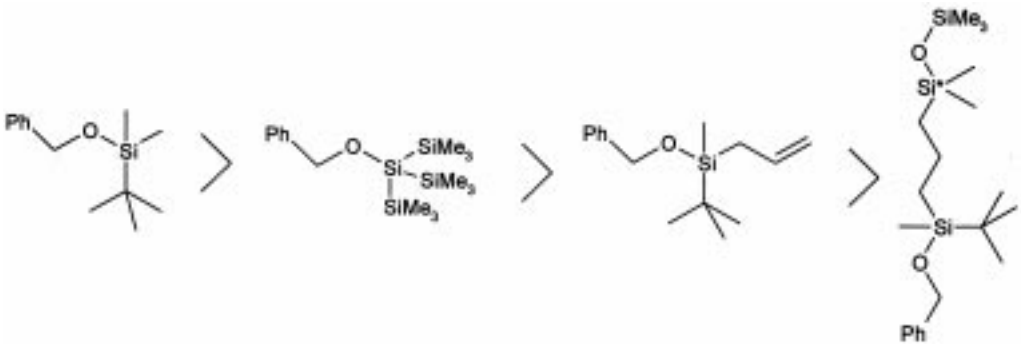


Figure 2. Reactivity order of silyl ethers with *p*-TsOH in $CDCl_3$.

at which hydrolysis takes place, does not affect the rate of alkoxysilane hydrolysis. It further suggests that hydrosilylation of allylalkoxysilanes could serve as a useful, practical, and predictable method of improving the lipophilicity of hydroxy-containing drugs, and as a strategy for the introduction of organic functional groups onto silicones. These are research directions that are currently being investigated in our laboratory, and will be reported in due course.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer with $CDCl_3$ as an internal standard. ^{29}Si NMR spectra were recorded on a Bruker AC-300 spectrometer (at 59.6 Hz). Infrared spectra were acquired on samples prepared as KBr pellets or as liquid films on NaCl discs, on a Perkin–Elmer 283 spectrometer. Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of 200°C on a VG analytical ZAB-R mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectral (HRMS) data were obtained using the EI method.

The starting alcohols, DMAP, and imidazole were obtained from Aldrich and used without further purification. Allyldichloromethylsilane, pentamethyldisiloxane and platinum–divinyltetramethyldisiloxane complex (Karstedt's catalyst) were obtained from Gelest and used without further purification. CH_2Cl_2 was distilled from P_2O_5 prior to use. Tris(trimethylsilyl)silyl chloride (sisyl chloride) was prepared using the procedure reported by Bürger et al.[14]

Allyl-*t*-butylchloromethylsilane. A solution of *t*-butylmagnesium chloride in THF (1.0 M, 100 mL, 100 mmol) was added dropwise to a flask containing allyldichloromethylsilane (13 mL, 90.1 mmol) and copper (I) cyanide (0.45 g, 5.0 mmol) in THF (90 mL) at 0°C, over a period of 2 h. After stirring at 0°C for 2 h, the solution was warmed to 25°C and stirring was continued for an additional 24 h. After filtration of the precipitate under N_2, distillation under reduced pressure yielded 7.1 g, 40% of a colorless oil (bp 55°C/25 mmHg). ^1H NMR($CDCl_3$): δ 5.78 (m, 1H), 4.99 (m, 2H), 1.82 (m, 2H), 0.97 (s, 9H), 0.32 (s, 3H); ^{13}C NMR ($CDCl_3$): 132.7, 115.1, 25.6, 22.3, 19.6, −3.7; ^{29}Si NMR ($CDCl_3$): δ 32.14; IR (neat, NaCl): ν 2959, 2934, 2862, 1633, 1471, 1256, 901, 826, 776 cm^{-1}; MS (EI, *m*/*z*): 176 (10), 135 (20), 119 (20); MS (CI, NH_3, *m*/*z*): 194 (50), 176 (30), 152 (50); HRMS (*m*/*z*) calcd for $C_8H_{17}Si_1Cl_1$ (M^+): 176.0788, found: 176.0778.

General procedure for protection of the alcohol

To a stirring solution of the alcohol (1 mmol) and 4-dimethylaminopyridine (or imidazole) (1.20 mmol) in CH_2Cl_2 (or DMF) was added a solution of the silyl chloride (1 mmol) in CH_2Cl_2 (or DMF) (1 M). The solution was stirred overnight at room temperature under N_2. Water was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed under reduced pressure. Separation by flash chromatography gave the products in 80–90% yields.

Allylbenzyloxy-*t*-butylmethylsilane 1. Benzyl alcohol (0.75 mL, 7.2 mmol), imidazole (1.0 g, 14.7 mmol), DMF (1.5 mL), allyl-*t*-butylchloromethylsilane (0.90 g, 5.1 mmol). Purification by chromatography with eluent pentane/diethyl ether=19:1 yielded 0.93 g, 74% of a colorless oil. ^1H NMR ($CDCl_3$): δ 7.27 (m, 5H), 5.84 (m, 1H), 4.86 (m, 2H), 4.75 (s, 2H), 1.66 (m, 2H), 0.92 (s, 9H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 141.2, 134.5, 128.1, 126.8, 125.9, 113.7, 65.2, 26.2, 20.7, 18.9, −7.45; ^{29}Si NMR ($CDCl_3$): δ 15.12; IR (neat, NaCl): ν 2956, 2930, 2858, 1631, 1470, 1255, 1096, 1070, 833, 770, 728 cm^{-1}; MS (EI, *m*/*z*): 248 (3), 207 (55), 191 (15), 91 (85); MS (CI, NH_3, *m*/*z*): 266 (5), 224 (100); HRMS (*m*/*z*): calcd for $C_{15}H_{24}O_1Si_1$ (M^+): 248.1596, found: 248.1600.

Allyl-*t*-butylmethyl-(2-phenyl)ethanoxysilane. 2-Phenylethanol (0.65 mL, 5.4 mmol), DMAP (0.86 g, 7.0 mmol), CH_2Cl_2 (5 mL), allyl-*t*-butylchloromethylsilane (0.77 g, 4.3 mmol). Purification by chromatography with eluent pentane/diethyl ether=9:1 yielded 0.87 g, 78% of a colorless oil. ^1H NMR (CD_2Cl_2): δ 7.23 (m, 5H), 5.82 (m, 1H), 4.85 (m, 2H), 3.83 (t, J=6.9 Hz, 2H), 2.79 (t, J=6.9 Hz, 2H), 1.60 (m, 2H), 0.88 (s, 9H), 0.01 (s, 3H); ^{13}C NMR (CD_2Cl_2): δ 139.7, 135.2, 129.5, 128.5, 126.3, 113.5, 65.1, 39.8, 26.3, 20.9, 19.1, −7.4; ^{29}Si NMR ($CDCl_3$): δ 14.36; IR (neat, NaCl): ν 3076, 3022, 2953, 2928, 2887, 2859, 1733, 1633, 1473, 1254, 1105, 896, 832, 768, 693, 610 cm^{-1}; MS (EI, *m*/*z*): 221 (40), 179 (75), 163 (50), 105 (75), 75 (60), 41 (100); MS (CI, NH_3, *m*/*z*): 238 (20), 221 (100), 179 (40), 105 (40).

Allyl-*t*-butylcyclopentanoxymethylsilane. Cyclopentanol (0.50 mL, 5.5 mmol), DMAP (0.90 g, 7.4 mmol), CH_2Cl_2 (5 mL), allyl-*t*-butylchloromethylsilane (0.77 g, 4.3 mmol). Purification by chromatography with eluent pentane/diethyl ether=9:1 yielded 0.80 g, 80% of a colorless oil. ^{1}H NMR (CD_2Cl_2): δ 5.84 (m, 1H), 4.85 (m, 2H), 4.27 (m, 1H), 1.65 (m, 2H), 1.52 (m, 2H), 0.89 (s, 9H), 0.06 (s, 3H); ^{13}C NMR (CD_2Cl_2): δ 135.5, 113.3, 75.1, 36.1, 26.3, 23.5, 21.5, 19.0, 6.9; ^{29}Si NMR ($CDCl_3$): δ 11.63; IR (neat, NaCl): ν 3075, 2955, 2929, 2895, 2858, 1633, 1474, 1362, 1248, 1054, 895, 824, 767, 610 cm^{-1}; MS (EI, *m*/*z*): 185 (25), 143 (30), 101 (20), 75 (100), 41 (70); MS (CI, NH_3, *m*/*z*): 227 (10), 202 (100), 185 (25), 134 (40), 92 (40), 75 (40); HRMS (*m*/*z*): calcd for $C_{13}H_{26}OSi$ (M^+): 226.1752, found: 226.1752.

1-[Tris(trimethylsilyl)silyl]cyclopentanol. Cyclopentanol (0.12 mL, 1.3 mmol), DMAP (0.18 g, 1.6 mmol), CH_2Cl_2 (2.0 mL), sisyl chloride (0.38 g, 1.3 mmol). Purification by chromatography with eluent pentane yielded 0.33 g, 90% of a colorless oil. ^{1}H NMR ($CDCl_3$) δ 3.90 (m, 1H), 1.64 (m, 2H), 1.58 (m, 2H), 1.08 (m, 4H), 0.16 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 78.9, 35.8, 36.0, 23.4, 23.3; ^{29}Si NMR ($CDCl_3$): δ −2.72, 11.30; IR (neat, NaCl): ν 2952, 2895, 1439, 1246, 1060, 836 cm^{-1}; MS (EI, *m*/*z*): 263 (20), 191 (20), 175 (30), 131 (35), 73 (100); MS (CI, NH_3, *m*/*z*): 264 ($Si(TMS)_3^+ + NH_3$, 8).

1-[Tris(trimethylsilyl)silyl]-2-phenylethanol. 2-Phenylethanol (0.24 mL, 2.1 mmol), DMAP (0.29 g, 2.5 mmol), CH_2Cl_2 (3.0 mL), sisyl chloride (0.61 g, 2.1 mmol). Purification by chromatography with eluent pentane/diethyl ether=9:1 yielded 0.50 g, 80% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 5H), 3.74 (t, *J*=6.9 Hz, 2H), 2.85 (t, *J*=6.9 Hz, 2H), 0.24 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 139.0, 129.0, 128.0, 126.0, 69.0, 39.8, 0.3; ^{29}Si NMR ($CDCl_3$): δ 1.47, −16.55; IR (neat, NaCl): ν 3029, 2950, 2893, 1396, 1376, 1245, 1088, 1078, 836.9 cm^{-1}; MS (EI, *m*/*z*): 263 (15), 175 (10), 131 (15), 105 (100), 73 (60); MS (CI, NH_3, *m*/*z*): 369 (100), 263 (50), 138 (50), 122 (60), 105 (70), 90 (50).

1-[Tris(trimethylsilyl)silyl]benzyl alcohol. Benzyl alcohol (0.085 mL, 8.1 mmol), DMAP (1.33 g, 10.9 mmol), CH_2Cl_2 (8.0 mL), sisyl chloride (2.29 g, 8.1 mmol). Purification by chromatography with eluent petroleum ether/diethyl ether=39:1 yielded 2.33 g, 82% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 5H), 4.59 (s, 2H),18 (s, 27H); ^{13}C NMR ($CDCl_3$,): δ 141.7, 128.1, 126.8, 125.6, 69.3, −0.1; ^{29}Si NMR ($CDCl_3$,): δ 3.47, −15.61; IR (neat, NaCl): ν 2952, 2893, 2857, 1245, 1085, 1063, 836, 690 cm^{-1}; MS (EI, *m*/*z*): 339 (10), 263 (90), 248 (15), 189 (30), 175 (40), 131 (25), 117 (25), 91 (100), 73 (75); MS (CI, NH_3, *m*/*z*): 372 (15), 355 (100), 264 (70), 108 (20), 90 (25); HRMS (*m*/*z*): calcd for $C_{15}H_{31}O_1Si_1$ (M^+-CH_3): 339.1451, found: 339.0750.

1-(*t*-Butyldimethylsilyl)-2-phenylethanol. 2-Phenylethanol (1.5 mL, 12.5 mmol), DMAP (1.84 g, 15.0 mmol), CH_2Cl_2 (13.0 mL), *t*-butylchlorodimethylsilane (1.88 g, 12.5 mmol). Purification by chromatography with eluent pentane/diethyl ether=19:1 yielded 2.6 g, 88% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 5H), 3.78 (t, *J*=7.1 Hz, 2H), 2.80 (t, *J*=7.1 Hz, 2H), 0.85 (s, 9H), −0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ(139.2, 129.2, 128.20, 126.1, 64.6, 39.7, 25.9, 18.3, −5.4; ^{29}Si NMR ($CDCl_3$): δ 18.80; IR (neat, NaCl): ν 3023, 2953, 2930, 2854, 1474, 1254, 1102, 827, 781, 692 cm^{-1}; MS (EI, *m*/*z*): 221 (10), 179 (100), 161 (25), 105 (50), 75 (25); MS (CI, NH_3, *m*/*z*): 254 (35), 237 (100), 196 (35), 179 (15), 122 (15), 105 (15); HRMS (*m*/*z*): calcd for $C_{13}H_{21}O_1Si_1$ (M^+-CH_3): 221.1361, found: 221.1361.

1-(*t*-Butyldimethylsilyl)benzyl alcohol. Benzyl alcohol (2 ml, 19.3 mmol), imidazole (1.57 g, 23.1 mmol), DMF (20.0 mL), *t*-butylchlorodimethylsilane (2.9 g, 19.3 mmol). Purification by chromatography with eluent petroleum ether/diethyl ether=39:1 yielded 3.69 g, 86% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 29 (m, 5H), 4.73 (s, 2H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$); δ 141.4, 128.2, 126.8, 126.0, 64.9, 25.9, 18.4, −5.3; ^{29}Si NMR ($CDCl_3$): δ 19.44; IR (neat, NaCl): ν 2955, 2930, 2857, 1470, 1254, 1096, 1070, 838, 776, 728 cm^{-1}; MS (EI, *m*/*z*): 165 (100), 135 (40), 91 (45); MS (CI, NH_3, *m*/*z*): 240 (75), 223 (15), 182 (15), 108 (100), 91 (20); HRMS (*m*/*z*): calcd for $C_{13}H_{22}Si_1O_1$ (M^+): 222.1439, found: 222.1429.

1-(*t*-Butyldimethylsilyl)cyclopentanol. Cyclopentanol (1.6 mL, 17.6 mmol), DMAP (2.58 g, 21.1 mmol), CH_2Cl_2 (18.0 mL), *t*-butylchlorodimethylsilane (2.65 g, 17.6 mmol). Purification by chromatography with eluent pentane yielded 2.61 g, 75% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.20 (m, 1H), 1.66 (m, 4H), 1.47 (m, 4H), 0.85 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 74.4, 35.7, 25.9, 23.1, 18.2, −4.7; ^{29}Si NMR ($CDCl_3$): δ 15.82; IR (neat, NaCl): ν 2951, 2930, 2855, 1468, 1252, 1060, 832, 775 cm^{-1}; MS (EI, *m*/*z*): 185 (5), 143 (50), 75 (100), 59 (10), 43 (15); MS (CI, NH_3, *m*/*z*): 201 (100), 162 (20), 133 (35), 92 (55), 74 (15); HRMS (*m*/*z*): calcd for $C_{10}H_{21}O_1Si_1$ (M^+-CH_3): 185.1361, found: 185.1361.

1-(Benzyloxy-*t*-butylmethylsilyl)-3-(pentamethyldisiloxane)-propane 6. To a flask containing pentamethyldisiloxane (0.28 g, 2 mmol) and allylbenzyloxy-*t*-butylmethylsilane (0.5 g, 2 mmol) in hexanes (5 mL), was added platinum–divinyltetramethyldisiloxane complex (one drop) at 25°C. After stirring overnight, purification by chromatography with eluent pentane/ether (19:1) yielded 0.75 g, 96% of a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.46 (m, 5H), 4.92 (s, 2H), 1.65 (m, 2H), 1.12 (s, 9H), 1.05 (m, 2H), 0.79 (m, 2H), 0.27 (s, 3H), 0.23 (s, 9H), 0.20 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 141.5, 128.1, 126.8, 126.0, 65.3, 26.4, 23.2, 18.8, 17.8, 17.1, 2.0, 0.5, −7.0; ^{29}Si NMR ($CDCl_3$): δ 18.43, 9.07, 6.55; IR (neat, NaCl): ν 2957, 2930, 2859, 1254, 1064, 842 cm^{-1}; MS (EI, *m*/*z*): 181 (12), 91 (100); MS (CI, NH_3, *m*/*z*): 207 (26), 91 (100), 72 (22), 43 (16); HRMS (*m*/*z*): calcd for $C_{20}H_{39}O_2Si_3$ (M^+-H): 395.2257, found: 395.2215.

General procedure for acidic hydrolysis

(A) Relative rates in aqueous media. To an NMR tube containing the silyl ether (0.076 mmol) under N_2 at 25°C was added THF-d_8 (0.26 mL), D_2O (0.12 mL), and CD_3CO_2D (0.38 mL), to make a 0.1 M solution of the silyl ether. The ^{1}H NMR spectra were acquired initially

within 2 min of addition of CD_3CO_2D, and subsequently every 10 min. The presence of benzyl alcohol was confirmed by injecting an authentic sample into the NMR tube containing the reaction mixture. The presence of allyl-*t*-butylmethyldisiloxane was confirmed by comparison with an authentic sample that was prepared by hydrolyzing allyl-*t*-butylchloromethylsilane.

(B) Organic media. To an NMR tube containing allylbenzyloxy-*t*-butylmethylsilane (0.022 g, 0.091 mmol) in CD_2Cl_2 (0.5 mL) under N_2 at 25°C was added *p*-toluenesulfonic acid, which had been dried by azeotropic distillation (0.091 mmol in 0.5 mL CD_2Cl_2). The ^1H NMR spectra were acquired initially within 5 min, and subsequently every 15 min. This was then repeated using 0.4, 0.8, and 1.5 molar equivalents of *p*-toluenesulfonic acid. The absence of benzyl *p*-toluenesulfonate was confirmed by comparison with an authentic sample that had been prepared by the method of Tipson.[15]

(C) Relative rates in organic media. To the silyl ether in a flask (0.07 mmol) with $CDCl_3$ (3 mL), was added *p*-toluenesulfonic acid monohydrate (0.28 mmol). The reaction was monitored by ^1H NMR every 10 min.

Reactions with electrophiles

(A) Carbenium ion. To an NMR tube containing allylbenzyloxy-*t*-butylmethylsilane (0.02 g, 0.08 mmol) in CD_2Cl_2 (0.8 mL) under N_2 at 25°C was added triphenylcarbenium hexafluorophosphate (0.031 g, 0.08 mmol). The ^1H NMR spectra were acquired initially within 5 min, and subsequently every 15 min. The presence of 4,4,4-triphenyl-1-butene and triphenylmethyl benzyl ether was confirmed by comparison with authentic samples that were prepared according to the procedures of Bachmann et al.[16] and Chaudhary et al.,[17] respectively.

(B) Aldehyde. To a flask containing benzaldehyde (0.1 mL, 0.98 mmol) and $BF_3{\cdot}OEt_2$ (0.12 mL, 0.98 mmol) in CD_2Cl_2 (10 mL) was added allylbenzyloxy-*t*-butylmethylsilane (0.24 g, 0.96 mmol) at 0°C. After stirring at 25°C for 24 h, only the starting material was detected by TLC.

(C) Competition reaction with allyltrimethylsilane. To a flask containing benzaldehyde (0.1 mL, 0.98 mmol) and $BF_3{\cdot}OEt_2$ (0.12 mL, 0.98 mmol) in CD_2Cl_2 (5 mL) was added a solution of allylbenzyloxy-*t*-butylmethylsilane (0.23 g, 0.93 mmol) and allyltrimethylsilane (0.15 mL, 0.93 mmol) in CD_2Cl_2 (5 mL) at 0°C. When benzaldehyde could no longer be detected using TLC, a saturated aqueous solution of $NaHCO_3$ was added at 0°C, followed by extraction using CH_2Cl_2, drying over $MgSO_4$, and removal of solvent under reduced pressure. The presence of 1-phenyl-3-butene-1-ol was confirmed by comparison with an authentic sample. This had been prepared by the reaction of benzaldehyde with allytrimethylsilane in the presence of $BF_3{\cdot}OEt_2$, and compared with previously reported characterization.[18]

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