protecting groups chosen (Bn, Bz, MOM), *S* monoesters of very low ee were formed by PLE-catalyzed hydrolysis of 3-protected diesters.

Experimental Section

PLE was purchased from Boehringer Mannheim (West Germany) and CHY was from Fluka (Switzerland). All enzymes were used without further purifications, and activities were assayed under standard conditions as indicated in the catalogs. Infrared spectra were recorded for solutions in chloroform; 60- and 200-MHz ^{1}H NMR spectra were taken on a Varian EM 360 L and XL 200, respectively, as chloroform-*d* solutions. The mass spectra were determined on a LKB 2091 mass spectrometer by direct inlet methods or by GC, using a 1% OV 17 column and helium as carrier. The progress of all reactions was monitored by TLC on silica gel (HF_{254}) plates or by GC analyses on a 2-m silanized column of 1% SE-30 on Gas Chrom Q, operating at 70–200 °C. Distillations were performed with a Buchi 500 glass oven. High-performance liquid chromatography (HPLC) was done with a Gilson Model 302 liquid chromatograph using a Merck Li Chrosorb Si 60 column (7 μm).

Methyl and Ethyl 3-Hydroxypentanedioates (1a and 1b). The ethyl ester was commercially available (Aldrich), while methyl ester **1a** was obtained by a modification of the literature procedure.[4] To a solution of dimethyl acetonedicarboxylate[4] (Fluka) (13 g, 74 mmol) in absolute ethanol (25 mL) at −30 °C was slowly added solid $NaBH_4$ (1.4 g, 37.8 mmol). The solution was stirred and cooled at −30 °C for 10 min, after which 2 N HCl was slowly added to pH 7. The solution was concentrated at reduced pressure and, after filtration of salts, evaporated to dryness. Water was added, and the products were extracted with ethyl acetate (4 × 15 mL). Evaporation of the solvent afforded 10.4 g of a mixture, which was purified by a silica gel chromatography (100 g) eluting with hexane/ethyl acetate (8:2). Distillation at 138–140 °C (8 mmHg)[4] afforded 10.8 g (83%) of ester **1a**: ^{1}H NMR δ 2.60 (d, 4 H), 3.50 (s, 1 H, exchangeable), 3.75 (s, 6 H), 4.27–4.77 (m, 1 H). Anal. Calcd for $C_7H_{12}O_5$: C, 47.7; H, 6.8. Found: C, 47.9; H, 7.0.

Methyl and Ethyl 3-Acetoxypentanedioates (1c and 1d). The title acetates were prepared by standard acetylation procedure. Thus to a solution of diester (2.5 mmol) in anhydrous pyridine (2 mL) at room temperature was added acetic anhydride (0.7 mL), and the solution was kept overnight at the same temperature. After the solution was poured into water (10 mL), the product was extracted with dichloromethane (3 × 5 mL) and the organic solution washed with water and dried (Na_2SO_4). Evaporation of the solvent at reduced pressure afforded the title compound as oils, which were purified by silica gel column chromatography (hexane–ethyl acetate, 8:2) and distilled under vacuum.

1c: 86% yield; bp 194 °C (16 mmHg) [lit.[14] bp 134–135 °C (8 mmHg)]; IR 1720, 1740 cm^{-1}; ^{1}H NMR δ 2.00 (s, 3 H), 2.75 (d, 4 H), 3.75 (s, 6 H), 5.30–5.80 (m, 1 H). Anal. Calcd for $C_9H_{14}O_6$: C, 49.55; H, 6.4. Found: C, 49.7; H, 6.5.

1d: 88% yield; bp 230 °C (16 mmHg) [lit.[14] bp 138–140 °C (8 mmHg)]; IR 1720, 1740 cm^{-1}; ^{1}H NMR δ 1.25 (t, 6 H), 2.00 (s, 3 H), 2.70 (d, 4 H), 4.20 (q, 4 H), 5.30–5.80 (m, 1 H). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.6; H, 7.3. Found: C, 53.8; H, 7.45.

CHY-Catalyzed Hydrolysis of 3-Acetoxyglutarate (1d). In a typical experiment 605 mg (2.46 mmol) of diester **1d** was suspended in a 0.1 M KH_2PO_4 solution (1 mL), and CHY (0.22 g, 60 U/mg) in distilled water (9 mL) was added. The suspension was stirred for 2 h while keeping the pH constant at 7.8 by addition of 1 M NaOH with a Radiometer automatic titrator. The extent of the reaction was estimated by the volume of base consumed during the reaction. The reaction was then acidified (HCl), the product was extracted with diethyl ether, and the organic phase was treated with diluted ammonia. Diethyl ether extraction of neutral products was done (3 × 5 mL), and acidification of ammonia solution (HCl) followed by extraction with ether afforded 450 mg (84%) of ester **2d**, which was essentially pure by TLC and ^{1}H NMR analyses. For analytical purposes, ester **2d** was purified by silica gel column chromatography (hexane/ethyl acetate, 6:4) and distilled at 141–143 °C at 0.2 mmHg: $[\alpha]_D$ +7.7° (*c* 1, $CHCl_3$); IR 3200, 1710 cm^{-1}; ^{1}H NMR δ 1.20 (t, 3 H), 2.00 (s, 3 H), 2.70–2.90 (dd, 4 H), 4.20 (q, 2 H), 5.20–5.80 (m, 1 H), 8.20 (s, 1 H, exchangeable). Anal. Calcd for $C_9H_{14}O_6$: C, 49.55; H, 6.4. Found: C, 49.7; H, 6.5.

PLE-Catalyzed Hydrolysis of Diester 1c. Diester **1c** (501 mg, 2.3 mmol) was suspended in a 0.1 M KH_2PO_4 solution (1 mL), and PLE (0.43 mL, 130 U/mg) was added. The suspension was stirred for 1.5 h, while the progress of the reaction was monitored by TLC (benzene/ethyl acetate, 1:1). When ca. 50% of starting diester reacted, the mixture was acidified (1 N HCl) and extracted with diethyl ether (4 × 10 mL). The solvent was removed, the residue was treated with dilute ammonia, and the neutral products were removed by extraction with diethyl ether. Acidification of ammonia solution (HCl) and extraction with ether afforded 0.169 g (36%) of monoester **2c**, which was essentially pure by TLC and ^{1}H NMR analyses. For analytical purposes, ester **2c** was purified by silica gel column chromatography (hexane/ethyl acetate, 6:4): bp 138–140 °C (0.2 mmHg) [lit.[10] bp 138–140 °C (0.2 mmHg)]; $[\alpha]_D$ +5.1° (*c* 1, $CHCl_3$); IR 3200, 1710 cm^{-1}; ^{1}H NMR δ 2.10 (s, 3 H), 2.70–2.90 (dd, 4 H), 3.70 (s, 3 H), 5.20–5.70 (m, 1 H), 8.20 (s, 1 H, exchangeable). Anal. Calcd for $C_8H_{12}O_6$: C, 47.05; H, 5.9. Found: C, 47.15; H, 6.1.

HPLC Analysis of Derivatives 2b from Monoester 2a. The procedure followed for preparation of the standard diastereomeric mixture and derivatives **2b** from enzymatic hydrolysis of diester **1a** was according to Rosen et al.[8] Products were analyzed by HPLC with the following parameters: solvent, 8:2 hexane/ethyl acetate; flow rate, 2.0 mL min^{-1}; pressure, 1500–2000 psi; detector, UV (254 nm); t_R 10.3 min (*R*)-(**2b**), t_R 16.2 min (*S*)-(**2b**).

Derivative 2e for 200-MHz ^{1}H NMR Analysis. To 3-acetoxy monoester **2d** (0.146 g, 0.67 mmol) from the enzymatic reaction dissolved in anhydrous benzene (5 mL) under nitrogen was added oxalyl chloride (0.08 mL, 0.94 mmol). The solution was stirred at room temperature (1.5 h). The solution was then cooled to 0 °C, and (*R*)-(+)-2-phenylethylamine (0.2 mL) was added. The solution was brought to ambient temperature and stirred (2 h). The product was isolated as described for silyl derivative **2b**.[8] A sample of **2e** was crystallized from diisopropyl ether: mp 81–82 °C; IR 3400, 1715 cm^{-1}, ^{1}H NMR δ 1.5 (d, 3 H), 2.00 (s, 3 H), 2.50–2.90 (m, 4 H), 3.65 (s, 3 H), 4.90–5.80 (m, 2 H), 6.65–7.10 (m, 1 H), 7.30–7.60 (m, 5 H). Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.55; H, 6.85; N, 4.6. Found: C, 62.7; H, 7.0; N, 4.75.

Derivative 2f. This compound was prepared exactly as the amide **2e** for the purpose of the 200-MHz ^{1}H NMR analysis: IR 3400, 1715 cm^{-1}; ^{1}H NMR δ 1.20 (t, 3 H), 1.5 (d, 3 H), 2.00 (s, 3 H), 2.50–2.90 (m, 4 H), 4.20 (q, 2 H), 5.00–5.80 (m, 2 H), 6.10–6.40 (m, 1 H), 7.30–7.60 (m, 5 H).

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Registry No. **1a**, 7250-55-7; **1b**, 32328-03-3; **1c**, 90613-44-8; **1d**, 91967-12-3; (*S*)-**2a**, 87118-64-7; (*R*)-**2a**, 87118-53-4; (*R*)-**2c**, 26432-16-6; (*R*)-**2d**, 113036-11-6; PLE, 9013-79-0; CHY, 9004-07-3; dimethyl acetonedicarboxylate, 1830-54-2.

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Synthesis of (α-Hydroxyalkyl)silanes from Formyltrimethylsilane. A New Route to Acetylenic Acylsilanes

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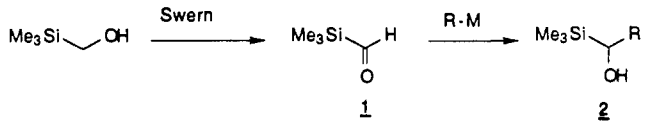
There has been considerable interest in the synthesis and chemistry of acylsilanes.[1] Many procedures have been

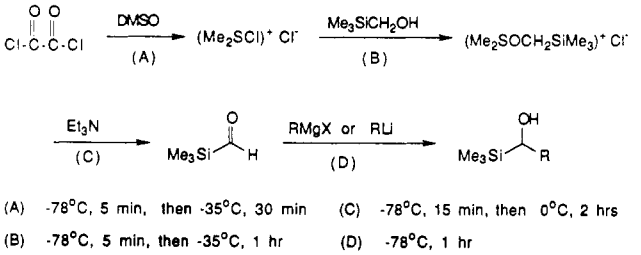
developed for the preparation of acylsilanes using acyl anion equivalents; however, these procedures are frequently tedious and are not amenable to the synthesis of many functionalized acylsilanes.[2] An attractive alternative approach would be the synthesis of (α-hydroxyalkyl)silanes and subsequent oxidation of the carbinol to the acylsilane. Methods for the direct preparation of (α-hydroxyalkyl)-silanes are limited. (Dimethylphenylsilyl)lithium has been added to an aldehyde,[3] but the corresponding reaction with (trimethylsilyl)lithium is not synthetically useful.[4] Trialkylsilyl ethers have undergone a reverse Brook rearrangement[5] to provide (α-hydroxyalkyl)silanes; however, this procedure is limited to allylic[6] or benzylic[7] systems which are acidic enough for deprotonation to generate the requisite silyloxy substituted carbanion. The direct addition of a nucleophile to formyltrimethylsilane (1) would seem to be an obvious solution to the problem, yet 1 has



1 2

been difficult to prepare. Sommer[8] initially attempted the synthesis of 1 by ozonolysis of vinyltrimethylsilane but was unsuccessful. Tilley[9] provided spectroscopic evidence for 1 generated from an acylzirconium species and found that 1 rapidly decomposed above −25 °C under the reaction conditions. Ireland[10] has achieved the synthesis of a vinylsilane by an in situ Wittig reaction with 1 generated by Swern oxidation[11] of (trimethylsilyl)methanol.[12] We now report the successful application of this approach as a general method for the preparation of (α-hydroxyalkyl)silanes. The utility of the procedure is demonstrated by the synthesis of synthetically useful acetylenic acylsilanes.[13]

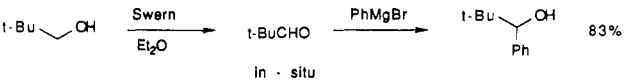
Several attempts at nucleophilic addition of excess butyllithium to 1 generated by Swern oxidation in methylene chloride[10] met with no success. Only traces of the adduct 2 could be identified by GC analysis of the crude reaction mixture. When the solvent was changed to ether, a small amount of 2 was observed along with a considerable amount of unoxidized (trimethylsilyl)methanol. Each step of the procedure was then optimized, as illustrated in the reaction sequence depicted, by monitoring the ratio of



(A) −78°C, 5 min, then −35°C, 30 min (C) −78°C, 15 min, then 0°C, 2 hrs
(B) −78°C, 5 min, then −35°C, 1 hr (D) −78°C, 1 hr

(trimethylsilyl)methanol to the addition product 2. Ether was found to be superior to methylene chloride, tetrahydrofuran, or hexane. Interestingly, we noted that the temperature at which oxalyl chloride and dimethyl sulfoxide were combined (A) had an effect on the extent of oxidation. A more pronounced effect was noted at step B, the temperature at which the (trimethylsilyl)methanol was added to the active oxidant. The final step of the oxidation (C), the addition of triethylamine, was initially carried out at −78 °C with little success. Longer reaction times or the use of a variety of bases, such as LDA, provided no improvement. When the oxidation mixture was allowed to warm to 0 °C for 2 h, a dramatic improvement was observed. This result is surprising, considering the previous reports on the thermal stability of 1.[9,10] Even under the optimized conditions, 15–20% of (trimethylsilyl)methanol remained unoxidized, and the condensation product 2 when *n*-BuLi was used was only obtained in 16% isolated yield (based on (trimethylsilyl)methanol) uncorrected for recovered starting material). The yield increased and the reaction mixture was noticeably cleaner (GC analysis) when *n*-BuMgBr was used; compare entries 1 and 2 in Table I. Other primary alkyl Grignard reagents as well as PhMgBr gave comparable yields, while cyclohexyl Grignard did not afford good yields of the adduct (entries 3–5). Vinyl Grignard species produced the known allylic alcohols 7 and 8[10] in somewhat improved yields relative to the aliphatic or aryl Grignards. The best yields were obtained with acetylenic lithio anions; see entries 8–12, Table I. The (α-hydroxyalkyl)silanes prepared by this direct condensation route were then oxidized to the corresponding acylsilanes, 14–21, by using the Swern oxidation procedure, in reasonable yields; see Table II. Only one other method for the preparation of acetylenic acylsilanes from seleno substituted allenol ethers has been reported.[12] The new procedure reported herein provides ready access to functionalized acetylenic acylsilanes from (trimethylsilyl)methanol in only two steps. An additional advantage is that the unreacted acetylene can be recovered (>95% material balance) from the initial condensation reaction and recycled. Compounds 9 and 10 have been prepared in gram quantities by using this procedure, indicating the feasibility of preparative-scale synthesis.

In an attempt to determine if the yield of 1 was low due to steric hindrance in the oxidation step by the trimethylsilyl group, pivaldehyde was generated from neopentyl alcohol under the same reaction conditions and reacted in situ with excess PhMgBr. The *tert*-butyl-



phenylcarbinol was obtained in 83% yield. The lower yield for the silicon analogue 4 (46%, see Table I) can be attributed to the inherent instability of 1 as well as incomplete oxidation of (trimethylsilyl)methanol.

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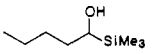
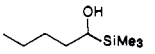
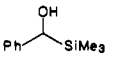
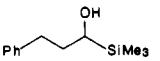
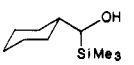
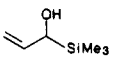
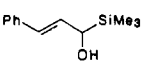
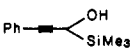
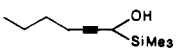
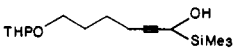
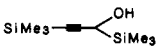
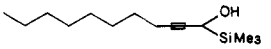
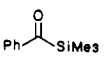
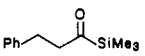
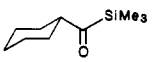
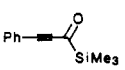
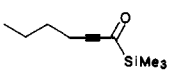
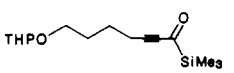
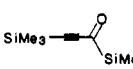
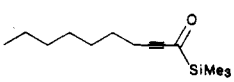
Table I. Direct Synthesis of (α-Hydroxyalkyl)silanes

entry	nucleophile	(α-hydroxyalkyl)silane structure	compd no.	isolated yield,[a] %
1	*n*-BuLi		3	16
2	*n*-BuMgBr		3	38
3	PhMgBr		4	46
4	$PhCH_2CH_2MgBr$		5	40
5	c-$C_6H_{11}MgCl$		6	19
6	$CH_2CHMgBr$		7	59
7	*trans*-PhCHCHMgBr		8	56
8	PhC≡CLi		9	76
9	*n*-BuC≡CLi		10	60
10	$THPO(CH_2)_4C{\equiv}CLi$		11	33
11	$Me_3SiC{\equiv}CLi$		12	73
12	$C_8H_{17}C{\equiv}CLi$		13	75

[a] The isolated yields reported are based on (trimethylsilyl)methanol and have not been corrected for incomplete oxidation. In each case, 15–20% of the starting material was recovered.

Table II. Synthesis of Acylsilanes

entry	acylsilane	compd no.	isolated yield, %
1		14	68
2		15	73
3		16	55
4		17	69
5		18	71
6		19	73
7		20	60
8		21	55

In conclusion, formyltrimethylsilane can be generated easily from (trimethylsilyl)methanol and provides direct access to (α-hydroxyalkyl)silanes. The carbinols obtained in this fashion allow for the synthesis of functionalized acylsilanes which are not readily available by other routes.

Experimental Section

Infrared spectra were obtained on either a Beckman Acculab I spectrophotometer or a Perkin-Elmer 1430 ratio recording spectrophotometer. ^1H NMR spectra were obtained on a Varian EM360A or EM390 spectrometer using tetramethylsilane as an internal standard. Capillary gas chromatographic analyses were accomplished by using a Hewlett-Packard 5890 gas chromatograph equipped with a FID detector. All analyses were carried out on a SE-30, 25-m fused silica column. Ether was freshly distilled from lithium aluminum hydride or sodium/benzophenone. All reactions were carried out in flame-dried glassware under an argon atmosphere. Grignard reagents were prepared from freshly distilled alkyl or aryl halide precursors. Alkynyllithium reagents were generated from the alkyne and butyllithium at −20 °C in ether. Alkyne reagents were purchased from Aldrich or Farchan and distilled prior to use. (Trimethylsilyl)methanol was purchased from Aldrich or prepared by the method of Peterson.[13] Flash chromatography was performed on silica gel 60, 230–400 mesh ASTM, obtained from American Scientific Products. All chromatography solvents were distilled prior to use. Elemental analyses were carried out by Atlantic Microlab, Inc., Atlanta, GA. Exact-mass mass spectroscopic analysis was carried out on a JEOL HMX-110 mass spectrometer.

General Procedure for the Preparation of (α-Hydroxyalkyl)silanes. To a round-bottom flask containing 10 mL of anhydrous ether at −78 °C under an Ar atmosphere was added 0.84 mmol (1.05 equiv) of oxalyl chloride (freshly distilled). Dimethyl sulfoxide, 0.88 mmol (1.10 equiv), was then added dropwise. The mixture was warmed to −35 °C (bath temperature, CO_2/acetone) and maintained at that temperature for 30 min. The cloudy mixture was then recooled to −78 °C, and 0.80 mmol (1.00 equiv) of (trimethylsilyl)methanol was added dropwise. The mixture was allowed to warm to −35 °C and maintained at −35 °C to −40 °C for 1 h. After recooling to −78 °C, triethylamine (freshly distilled from CaH_2), 4.0 mmol (5.0 equiv), was added dropwise. The mixture was stirred for 1 h at −78 °C and then warmed to 0 °C for 2 h. The mixture was then recooled to −78 °C, and 4.0 mmol (5.0 equiv) of the Grignard or organolithium reagent was added. After the mixture was stirred for 1 h at −78 °C, 20 mL of water and 90 mL of ether were added and the mixture was allowed to warm to room temperature before extractive workup. The (α-hydroxyalkyl)silanes were purified by flash chromatography on silica gel using 10% ether/hexane eluent. The allylic and propargylic α-hydroxysilanes are somewhat unstable and decompose under acidic conditions.

1-(Trimethylsilyl)pentan-1-ol (3) (38%): ^1H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.8–1.8 (m, 9 H), 3.3 (br t, 1 H, J = 7 Hz); IR (neat) (cm^{-1}) 3400 (br), 1250. Anal. Calcd for $C_8H_{20}OSi$: C, 59.93; H,

12.57. Found: C, 60.00; H, 12,53.

1-Phenyl-1-(trimethylsilyl)methanol (4) (46%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 4.6 (s, 1 H), 7.3 (s, 5 H); IR (neat) (cm^{-1}) 3400 (br), 1590, 1250. Anal. Calcd for $C_{10}H_{16}OSi$: C, 66.61; H, 8.94. Found: C, 66.38; H, 8.99.

3-Phenyl-1-(trimethylsilyl)propan-1-ol (5) (40%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 1.90 (q, 2 H, J = 7 Hz), 2.85 (t, 2 H, J = 7 Hz), 3.40 (t, 1 H, J = 7.0 Hz), 7.25 (s, 5 H); IR (neat) (cm^{-1}) 3400 (br), 1590, 1250. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.02; H, 9.74.

1-Cyclohexyl-1-(trimethylsilyl)methanol (6) (19%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.8-1.9 (m, 11 H), 3.2 (d, 1 H, J = 7 Hz); IR (neat) (cm^{-1}) 3400 (br), 1450, 1250. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.44; H, 11.90. Found: C, 64.52; H, 11.89.

3-Phenyl-1-(trimethylsilyl)-2-propyn-1-ol (9) (76%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 4.3 (s, 1 H), 7.3 (br s, 5 H); IR (neat) (cm^{-1}) 3350 (br), 2200, 1590, 1480, 1250. Anal. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.75; H, 7.42.

1-(Trimethylsilyl)-2-heptyn-1-ol (10) (60%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.9 (br t, 3 H, J = 6 Hz), 1.2-1.7 (m, 4 H), 2.1-2.3 (m, 2 H), 4.05 (t, 1 H, J = 2 Hz); IR (neat) (cm^{-1}) 3400 (br), 1250. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 65.29; H, 10.96.

6-(Tetrahydropyranyloxy)-1-(trimethylsilyl)-2-heptyn-1-ol (11) (33%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 1.4-1.8 (m, 10 H), 2.1-2.3 (m, 2 H), 3.2-4.0 (m, 5 H), 4.55 (br s, 1 H); IR (neat) (cm^{-1}) 3400 (br), 1250; MS, m/z 284 (M^+).

1,3-Bis(trimethylsilyl)-2-propyn-1-ol (12) (73%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 18 H), 4.5 (s, 1 H); IR (neat) (cm^{-1}) 3350 (br), 1250; exact mass calcd for $C_9H_{20}OSi$ 200.1053, found 200.1054.

1-(Trimethylsilyl)-2-undecyn-1-ol (13) (75%): ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9 H), 0.8-1.0 (br t, 3 H, J = 6 Hz), 1.2-1.5 (m, 12 H), 2.1-2.3 (m, 2 H), 4.05 (m, 1 H); IR (neat) (cm^{-1}) 3400 (br), 1255. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.05; H, 11.76.

General Procedure for the Synthesis of Acylsilanes. The acylsilanes were obtained by oxidation of the (α-hydroxyalkyl)-silanes using the Swern oxidation procedure described earlier, omitting the nucleophilic addition step, and allowing the oxidation reaction mixture to warm to room temperature before aqueous quench. The known compounds **14**,[2a] **15**,[13b] and **16**[14] were obtained in 68%, 73%, and 55% yields, respectively.

3-Phenyl-1-(trimethylsilyl)-2-propyn-1-one (17) (69%): ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9 H), 7.2-7.5 (m, 5 H); IR (neat) (cm^{-1}) 2170, 1655, 1590, 1245; exact mass calcd for $C_{12}H_{14}OSi$ (M + H) 203.0891, found 203.0892.

1-(Trimethylsilyl)-2-heptyn-1-one (18) (71%): ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H), 0.9 (t, 3 H, J = 6 Hz), 1.3-1.6 (m, 4 H), 2.3-2.5 (m, 2 H); IR (neat) (cm^{-1}) 2150, 1580, 1240; exact mass calcd for $C_{10}H_{18}OSi$ 182.1127, found 182.1140.

6-(Tetrahydropyranyloxy)-1-(trimethylsilyl)-2-heptyn-1-one (19) (73%): ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9 H), 1.4-1.8 (m, 10 H), 2.3-2.5 (br t, 2 H, J = 6 Hz), 3.3-3.95 (m, 4 H), 4.4-4.5 (m, 1 H); IR (neat) (cm^{-1}) 2185, 1590, 1250; exact mass calcd for $C_{15}H_{26}O_3Si$ (M + H) 283.1736, found 283.1729.

1,3-Bis(trimethylsilyl)-2-propyn-1-one (20) (60%): ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 18 H); IR (neat) (cm^{-1}) 1590, 1250.

1-(Trimethylsilyl)-2-undecyn-1-one (21) (55%): ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9 H), 0.9 (t, 3 H, J = 6 Hz), 1.2-1.6 (m, 12 H), 2.2-2.4 (m, 12 H), 2.2-2.4 (m, 2 H); IR (neat) (cm^{-1}) 2190, 1590, 1250.

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Registry No. 1, 106881-61-2; **3**, 112947-61-2; **4**, 17876-95-8; **5**, 112947-62-3; **6**, 66235-32-3; **7**, 95061-68-0; **8**, 95606-82-9; **9**, 112947-63-4; **10**, 112947-64-5; **11**, 112947-65-6; **12**, 112947-66-7; **13**, 112947-67-8; **14**, 5908-41-8; **15**, 61157-31-1; **16**, 112947-68-9; **17**, 112947-69-0; **18**, 112947-70-3; **19**, 112947-71-4; **20**, 86934-46-5; **21**, 112947-72-5; ClCOCOCl, 79-37-8; Me_3SiCH_2OH, 3219-63-4; *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-03-8; PhMgBr, 100-58-3; $PhCH_2CH_2MgBr$, 3277-89-2; c-$C_6H_{11}MgCl$, 931-51-1; CH_2CH-MgBr, 1826-67-1; *trans*-PhCHCHMgBr, 35672-47-0; PhC≡CLi, 4440-01-1; *n*-BuC≡CLi, 17689-03-1; $THPO(CH_2)_4C{\equiv}CLi$, 112947-73-6; $Me_3SiC{\equiv}CLi$, 54655-07-1; $C_8H_{17}C{\equiv}CLi$, 21433-46-5.

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Cyclizations of 2-(Allyldimethylsilyl)ethyl Radicals

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The cyclizations of 5-hexenyl radicals have attracted considerable interest, since the radicals strongly favor exo cyclization over endo cyclization, forming a thermodynamically unfavorable five-membered ring (Baldwin-Bechwith rules)[1] (Scheme I). It was explained in terms of the instability of the transition complex of endo mode. The introduction of a N atom[4] or an O atom[5] to 5-hexenyl radicals at the C-3 position enhances the rate of the exo mode, resulting in a greater preference for the five-membered ring. The cyclizations of 5-hexenyl radical analogues containing silicon have been studied. (Alloxydimethylsilyl)methyl radicals favor kinetically controlled exo cyclization,[6] while the direction of ring closure of 5-pentenylsilyl radicals is dependent on the substituents to a Si atom.[7] The cyclization of (3-butenyldimethylsilyl)methyl radical slightly favor endo mode.[8] We wish to report here the cyclizations of 5-hexenyl radical anologues substituted at the C-3 position by dimethylsilylene such as 2-(allyldimethylsilyl)ethyl radical (**1**) and 2-(allyldimethylsilyl)-propyl radical (**2**) (Scheme II).

The two halides **6** and **8** were prepared as precursors[9] of the radicals. The straightforward preparations of **6** and **8** via **3**, **4**, **5**, and **7** are described in the Experimental Section.

Cyclizations were conducted under variety conditions[13] using Bu_3SnH and azobis(isobutyronitrile) (AIBN) as an initiator, although only one set of conditions will be reported here. No characteristic effect of condition change (e.g., solvent and reaction temperature) was observed. A solution of **6** (1 mmol), Bu_3SnH (1.2 mmol), and AIBN

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(13) The reaction temperature, the reaction time, and the mole ratio (halide compounds/Bu_3SnH) were changed in a range of 1-8 h, 60-80 °C, and 0.5-1.5, respectively. As solvents, benzene, and MEK were employed.

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