The reaction was stirred for 2 h at room temperature, and then excess PCl_5 was destroyed by stirring with acetic anhydride (14.7 mL, 0.156 mol) for 15 min. The solution was concentrated to dryness at 50 °C by using aspirator pressure at first and then higher vacuum. To remove residual acetic anhydride, the cubane-1,4-bis(carbonyl chloride) was dissolved in dry, ethanol-free $CHCl_3$, followed by concentrating to dryness at 50 °C at reduced pressure. This step was repeated two or three times, until no anhydride was present. Finally, the pale yellow crystals were dried under high vacuum for $\sim$2 h at 50 °C. The cubane-1,4-bis(acid chloride) was dissolved in 500 mL of dry $CHCl_3$ and transferred to a 1-L flask with mechanical stirrer, argon purge, 50-mL addition funnel, and cold water bath (5–10 °C). Triethylamine (31.6 g, 0.312 mol) was added slowly over 5 min and then *N*-*tert*-butyl-*N*-ethylamine (31.6 g, 0.312 mol) was added dropwise over 20 min while the cold water bath was maintained. After the addition, the reaction mixture was stirred for 2 h at room temperature and washed with 5% HCl (3 × 100 mL), 5% KOH (2 × 100 mL), and saturated NaCl (1 × 100 mL). The yellow $CHCl_3$ layer was treated with activated carbon, dried ($MgSO_4$), and filtered over Celite to give a less colored solution, which when concentrated to dryness left a pale yellow solid. This solid was slurried in 400 mL of dry ethyl acetate at 40–50 °C, cooled in ice, filtered, washed with cold ethyl acetate, and dried under high vacuum to yield 41.0 g (73%) of the title compound as pure white crystals: mp 185–188 °C; ^1H NMR (^1H, $CDCl_3$, TMS standard) δ 1.3 (t, 3 H, J = 7 Hz, CH_3), 1.4 (s, 9 H, *tert*-butyl), 3.8 (q, 2 H, J = 7 Hz, CH_2), 4.55 (s, 6 H); IR (KBr) 2970, 1610, 1390, 1205 cm^{-1}.

***N*,*N*′-Di-*tert*-butyl-*N*,*N*′-diethyl-2,7-dicarbamoylcubane-1,4-dicarboxylic Acid (2).** 2,2,6,6-Tetramethylpiperidine (107 g, 0.760 mol, 10 equiv) and tetramethylethylenediamine (12.6 mL, 1.1 equiv) were added to 600 mL of dry THF (distilled over CaH) in a 2-L flask equipped with an argon purge. The reaction mixture was cooled in dry ice/acetone, and 2.5 M *n*-butyllithium in hexane (304 mL, 0.760 mol, 10 equiv) was added dropwise with stirring over 2 h at −78 °C, and then the reaction was stirred at 0 °C for 1 h. The reaction mixture was cooled in a dry ice/acetone bath. $MgBr_2$ etherate (98.1 g, 0.380 mol, 5 equiv) and 1 (27.2 g, 0.076 mol, 1 equiv) were added all at once, and the mixture was then placed in the bath and stirred for 8 h. The reaction mixture was cooled in dry ice/acetone, and CO_2 was bubbled through the stirring reaction for 12 h at dry ice/acetone temperature to yield a light tan suspension, which was concentrated to dryness on the rotovap, first using aspirator pressure and then higher vacuum for about 2 h. The light tan solid was vigorously stirred with 1500 mL of H_2O for 1 h, and the resulting suspension was transferred to a 2-L flask and then cooled to 0 °C. Ice-cold 19% HCl was added slowly with stirring to bring the pH to 1 (about 250 mL; there was some foaming). The suspension was filtered to give a light brown paste, which was dissolved in 600 mL of boiling CH_2Cl_2, cooled in the freezer overnight, filtered, and washed with cold CH_2Cl_2 to give 20.0 g of diacid 2 as colorless plates which decompose exothermically without melting at 239.3 °C. The mother liquor was concentrated to one-third volume and cooled to give a second crop of 5.5 g for a total yield of 25.5 g (75%): ^1H NMR (CD_3OD) δ 1.25 (t, J = 6 Hz, 6 H), 1.5 (s, 9 H), 3.75 (q, J = 6 Hz, 4 H), 4.6 (s, 4 H), failed to observe carboxylic acid proton. Anal. Calcd C, 64.56; H, 7.67; N, 6.27. Found: C, 64.54; H, 7.55; N, 6.27.

Cubane-1,2,4,7-tetracarboxylic Acid (3). Compound 2 (5.82 g, 0.013 mol) was added to 125 mL of 70% HNO_3. The mixture was heated and at 58 °C the reaction instantly turned dark red, evolving NO_2, and the temperature went rapidly to 75 °C. Mild reflux was continued for 4 h, at which time the reaction was pale yellow. The reaction was cooled in the freezer overnight, filtered, washed with cold 70% HNO_3 and then, after changing the filter flask, with 100% ethanol, and dried to give 3.44 g of the product (95%) as a pure white powder which decomposes quite exothermically at 267 °C. Dilute HCl at reflux can be substituted for nitric acid; however, the isolation of the product is more difficult. Identification was based on comparison with the known material.[5] ^1H NMR (CD_3OD) δ 4.3 (s). Anal. Calcd: C, 51.44; H, 2.88. Found: C, 51.21; H, 2.88.

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A New Method for the Synthesis of Acylsilanes via One-Carbon Homologation of Aldehydes

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Recently acylsilanes have received increasing research interest from the physical organic[1] and synthetic organic[2] view points. For example, highly diastereoselective addition of nucleophiles[3] and stereoselective Wittig reactions[4] utilizing the bulky silyl groups demonstrate the synthetic utility of acylsilanes. Recently we have developed an electrochemical oxidation of acylsilanes in which the carbon–silicon bond is cleaved and oxygen and nitrogen nucleophiles are introduced at the carbonyl carbon.[5] Easy migration of the silyl group from carbon to oxygen immediately after a nucleophile attacks the carbonyl carbon is also an important property of acylsilanes.[6]

Although several methods for the synthesis of acylsilanes have been reported,[7] recent developments in the synthetic applications of acylsilanes increase the demand for new versatile methods. In this paper we present a new method for the synthesis of acylsilanes from aldehydes by one-carbon homologation. This reaction provides general and convenient access to saturated, α,β-unsaturated, and (α-haloacyl)silanes.

Methoxybis(trimethylsilyl)methane was deprotonated with *n*-butyllithium in tetrahydrofuran (THF), and the resulting anion was allowed to react with aldehydes. The crude 1-methoxy-1-(trimethylsilyl)-1-alkenes (1) thus obtained were readily hydrolyzed[8] with dilute hydrochloric

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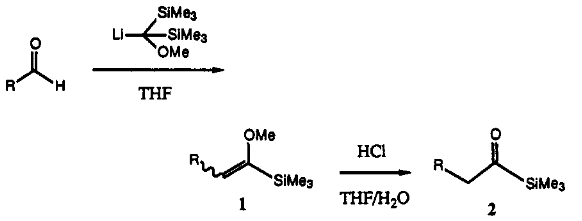
Table I. Synthesis of Acylsilanes from Aldehydes

aldehyde	acylsilane	% yield[a]
$CH_3(CH_2)_8CHO$	$CH_3(CH_2)_9COSi(CH_3)_3$	75
$PhCH_2CHO$	$PhCH_2CH_2COSi(CH_3)_3$	51
PhCHO	$PhCH_2COSi(CH_3)_3$	67
c-$C_6H_{11}CHO$	c-$C_6H_{11}CH_2COSi(CH_3)_3$	92
$C_{10}H_{21}CH{=}CH(CH_2)_2CHO$	$C_{10}H_{21}CH{=}CH(CH_2)_3COSi(CH_3)_3$	87

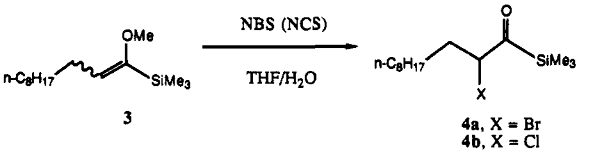
[a] Isolated yields.

acid in H_2O/THF to give the corresponding acylsilanes (eq 1). This method is experimentally quite simple to perform, and the yields range from 51 to 92% (Table I).



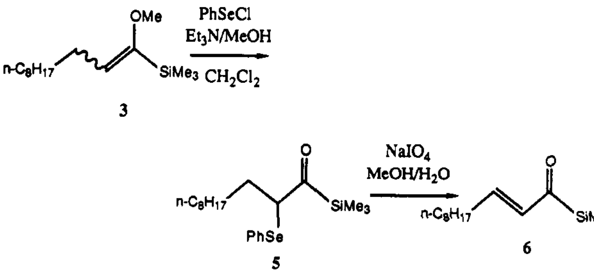
(eq. 1)

Although the enol ether intermediates are sensitive to acid, they can be isolated by silica gel flash chromatography using eluate containing a small amount of triethylamine and can be allowed to react with various electrophiles.[9] For example, the treatment of **3** with *N*-bromosuccinimide in the presence of a small amount of water in THF afforded the (α-bromoacyl)silane (**4a**) in 71% yield (eq 2).[10] The (α-chloroacyl)silane (**4b**) was also obtained using *N*-chlorosuccinimide under similar conditions. The reaction with *N*-iodosuccinimide, however, did not afford the desired (α-iodoacyl)silane under similar conditions.



(eq. 2)

Phenylselenenyl chloride also serves as an electrophile. The reaction of **3** with phenylselenenyl chloride in the presence of triethylamine and methanol in dichloromethane gave (α-(phenylseleno)acyl)silane (**5**) (72% yield). Oxidation with sodium periodate in methanol afforded the α,β-unsaturated acylsilane (**6**) in quantitative yield (eq 3). Various reactions of α,β-unsaturated acylsilanes have been reported in the literature,[11] and the present procedure provides convenient access to these useful compounds.



(eq. 3)

Experimental Section

General Comments. Glass-support precoated (Merk Silica gel 60 F252, 0.25 mm) plates were employed for analytical TLC. Vapor phase chromatography (VPC) was performed on a 2 m × 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. ^1H NMR spectra were determined at 90 MHz. Mass spectra were obtained at an ionization potential of 70 eV.

Methoxybis(trimethylsilyl)methane.[12] Methoxy(trimethylsilyl)methane (Aldrich) was deprotonated according to Magnus's procedure.[13] To a solution of methoxy(trimethylsilyl)methane (6.00 g, 49.7 mmol) in 50 mL of THF was added *sec*-butyllithium/cyclohexane (1.3 M, 65 mL, 84.5 mmol) at −78 °C. The mixture was warmed to −25 °C and stirred at this temperature for 40 min. The mixture was recooled to −78 °C, and chlorotrimethylsilane (9.84 g, 90.6 mmol) was added. The mixture was warmed to room temperature and stirred at this temperature for 1 h. Brine was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via distillation (65–70 °C/15 mmHg) to obtain the title compound (9.13 g, 96%): VPC t_R 1.75 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.06 (s, 18 H), 2.46 (s, 1 H), 3.32 (s, 3 H); IR (neat) 2950 (s), 2800 (m), 1443 (m), 1245 (s), 1085 (s), 1025 (m), 860 (s), 840 (s), 752 (m), 690 (m) cm^{-1}; MS *m/e* (%) 190 (11), 175 (26), 147 (100), 133 (14), 102 (9), 89 (19), 73 (30), 59 (10). Anal. Calcd for $C_5H_{14}OSi$: C, 50.46; H, 11.64. Found: C, 50.68; H, 11.73.

General Procedure for the Synthesis of Acylsilanes from Aldehydes. To a solution of methoxybis(trimethylsilyl)methane (5 mmol) in 10 mL of THF was added *n*-butyllithium/hexane (5 mmol) at −78 °C. The mixture was warmed up to 0 °C and stirred at this temperature for 30 min. The resulting yellow solution was recooled to −78 °C, and the aldehyde (5 mmol) was added. The mixture was stirred at this temperature for 1 h and warmed up to room temperature over 0.5–2 h. Brine was added, and the organic materials were extracted with ether and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was dissolved in 8 mL of THF. Hydrochloric acid (1%, 1 mL) was added, and the mixture was stirred at room temperature overnight. The mixture was partitioned between saturated aqueous Na_2CO_3 and ether. The organic layer was separated and dried ($MgSO_4$). After evaporation of the solvent the crude product was purified via flash chromatography on silica gel.

Undecanoyltrimethylsilane: 1.13 g (75%); TLC R_f 0.67 (hexane/ethyl acetate, 9:1); VPC t_R 5.9 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.70–1.00 (m, 3 H), 1.00–1.60 (m, 7 H), 2.53 (t, J = 7.5 Hz, 2 H); IR (neat) 2940 (s), 2860 (s), 1645 (s), 1465 (m), 1255 (s), 845 (s) cm^{-1}; MS *m/e* (%) 242 (2.3), 237 (3.2), 199 (1.9), 185 (1.7), 171 (2.2), 151 (2.1), 129 (26), 101 (13), 73 (100); HRMS calcd for $C_{14}H_{30}OSi$ 242.2065, found 242.2052.

(3-Phenylpropanoyl)trimethylsilane: 0.123 g (51%); TLC R_f 0.38 (hexane/ethyl acetate, 19:1); VPC t_R 5.9 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 2.65–2.85 (m, 4 H), 6.93–7.25 (m, 5 H); IR (neat) 2950 (m), 1640 (s), 1600 (w), 1500 (m), 1450 (w), 1250 (s), 840 (s) cm^{-1}; MS *m/e* (%) 205 (10), 191 (4.2), 163 (2.0), 135 (4.4), 117 (2.9), 101 (2.7), 91 (2.5), 75 (31), 73 (100); HRMS $C_{12}H_{18}OSi$ 206.1127, found 206.1115.

(Phenylacetyl)trimethylsilane: 0.154 g (67%); TLC R_f 0.42 (hexane/ethyl acetate, 19:1); VPC t_R 4.6 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 3.83 (s, 2 H), 6.95–7.30 (m, 5 H); IR (neat) 2975 (s), 1700 (w), 1640 (s), 1600 (w), 1500 (m), 1450 (w), 1250 (s), 840 (s), 750 (m), 700 (s) cm^{-1}; MS *m/e* (%) 192 (0.1), 177 (0.3), 164 (93), 149 (56), 121 (47), 101 (100), 91 (11), 73 (100), 63 (8), 53 (23); HRMS calcd for $C_{11}H_{16}OSi$ 192.0970, found 192.0960.

(Cyclohexylacetyl)trimethylsilane: 0.437 g (92%); TLC R_f 0.80 (hexane/ethyl acetate, 19:1); VPC t_R 4.7 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.60–2.00 (m, 11 H), 2.46 (d, J = 6.2 Hz, 1 H); IR (neat) 2900 (s), 2850 (s), 1640 (s), 1450 (m), 1250 (s), 850 (s), 750 (w) cm^{-1}; MS *m/e* (%) 198 (17), 183 (19), 155 (38), 116 (29), 108, (48), 101 (68), 93 (16), 79

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[13] Magnus, P.; Roy, G. *Organometallics* **1982**, *1*, 553–559.

(22), 75 (100), 73 (100), 55 (18); HRMS calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1458.

(*E*)-(5-Hexadecenoyl)trimethylsilane: 1.05 g (87%); TLC R_f 0.88 (hexane/ethyl acetate, 19:1); VPC t_R 13.5 min (100–230 °C, 20 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.7–1.0 (m, 3 H), 1.10–2.25 (m, 22 H), 2.57 (t, *J* = 7.0 Hz, 2 H), 5.3 (m, 2 H); IR (neat) 2900 (s), 2850 (m), 1640 (m), 1460 (w), 1250 (m), 840 (s) cm^{-1}; MS *m/e* (%) 310 (4.2), 183 (38), 169 (100), 101 (14), 73 (72); HRMS calcd for $C_{19}H_{38}OSi$ 310.2692, found 310.2719.

1-Methoxy-1-(trimethylsilyl)-1-undecene (3). To a solution of methoxybis(trimethylsilyl)methane (1.762 g, 9.25 mmol) in 20 mL of THF was added *n*-butyllithium/hexane (6.3 mL, 10.1 mmol) at −78 °C. The mixture was warmed up to 0 °C and stirred at this temperature for 0.5 h. After being recooled to −78 °C, decanal (1.569 g, 10.04 mmol) was added dropwise. The mixture was stirred at −78 °C for 0.5 h and warmed to room temperature. Aqueous saturated $NaHCO_3$ was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent flash chromatography (hexane/ethyl acetate, 19:1, containing 1% triethylamine) of the residue yielded the title compound (1.569 g, 84% yield). ^{1}H NMR spectral analysis indicated that essentially one isomer was obtained with respect to the geometry of the carbon–carbon double bond, although it was difficult to determine whether it is *E* or *Z*: TLC R_f 0.68 (hexane/ethyl acetate, 19:1); VPC t_R 7.9 min (100–230 °C, 20 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.5 (m, 14 H), 1.85–2.2 (m, 2 H), 3.45 (s, 3 H), 5.15 (t, *J* = 7.9 Hz, 1 H); IR (neat) 2930 (s), 2850 (m), 1610 (m), 1460 (m), 1250 (s), 1190 (m), 1110 (s), 840 (s), 760 (m) cm^{-1}; MS *m/e* (%) 257 (1.2), 256 (5), 241 (45), 183 (22), 143 (29), 129 (16), 109 (12), 95 (45), 89 (100); HRMS calcd for $C_{15}H_{32}OSi$ 256.2222, found 256.2194.

(2-Bromoundecanoyl)trimethylsilane (4a). To a solution of *N*-bromosuccinimide (0.098 g, 0.55 mmol) in THF (1 mL) was added water (0.020 mL, 1.1 mmol). Then enol ether **3** (0.149 g, 0.57 mmol) was added at −78 °C. The mixture was stirred at this temperature for 10 min and at 0 °C for 20 min. To the resulting yellow solution was added brine. The organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane/ethyl acetate, 39:1) to obtain the title compound (0.126 g, 71%): TLC R_f 0.33 (hexane/ethyl acetate, 39:1); VPC t_R 7.9 min (100–230 °C, 20 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–2.1 (m, 16 H), 4.44 (dd, *J* = 6.4 and 7.7 Hz, 1 H); IR (neat) 2950 (s), 2900 (s), 2850 (s), 1640 (m), 1460 (m), 1250 (m), 850 (s), 760 (m) cm^{-1}; MS *m/e* (%) 305 (5), 271 (2), 241 (41), 225 (5), 207 (8), 193 (19), 183 (11), 167 (30), 139 (7), 129 (2), 101 (27), 73 (100); HRMS calcd for $C_{13}H_{26}BrOSi$ 305.0937, found 305.0955; calcd for $C_{13}H_{26}{}^{*}BrOSi$ 307.0916, found 307.0929.

(2-Chloroundecanoyl)trimethylsilane (4b). To a solution of *N*-chlorosuccinimide (0.141 g, 1.06 mmol) in 5 mL of THF was added water (0.030 ml, 1.66 mmol). Then **3** (0.270 g, 1.04 mmol) was added at 0 °C, and the mixture was stirred at this temperature for 0.5 h and at room temperatue for 5 h. Brine was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane/ethyl acetate, 39:1) to obtain the title compound (0.16 g, 56%): TLC R_f 0.44 (hexane/ethyl acetate, 19:1); VPC t_R 7.1 min (100–230 °C, 20 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–2.0 (m, 16 H), 4.23 (dd, *J* = 5.5 and 7.8 Hz, 1 H); IR (neat) 2925 (s), 2850 (s), 1645 (s), 1470 (m), 1250 (s), 850 (s), 760 (m) cm^{-1}; MS *m/e* (%) 276 (0.5), 261 (1.0), 241 (1.6), 149 (7), 140 (43), 101 (100), 93 (76), 74 (100), 73 (100); HRMS calcd for $C_{14}H_{29}OSi{}^{*}Cl$ 278.1647, found 278.1658; calcd for $C_{14}H_{29}OSiCl$: 276.1676, found 276.1660.

(2-(Phenylseleno)undecanoyl)trimethylsilane (5). To a solution of enol ether **3** (0.506 g, 1.9 mmol) in 6 mL of CH_2Cl_2 were added methanol (0.089 mL, 2.2 mmol) and triethylamine (0.31 mL, 2.2 mmol). The mixture was cooled to −78 °C, and a solution of phenylselenenyl chloride (0.408 g, 2.1 mmol) in 4 mL of CH_2Cl_2 was added dropwise. The mixture was warmed to room temperature and stirred at this temperature overnight. Water was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane to hexane/ethyl acetate, 9:1) to obtain the title compound (0.545 g, 72%): TLC R_f 0.48 (hexane/ethyl acetate, 19:1); VPC t_R 15.8 min (100–240 °C, 10 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.7 (m, 16 H), 3.90 (t, *J* = 6.8 Hz, 1 H), 7.23 (m, 5 H); IR (neat) 2920 (s), 2850 (s), 1735 (w), 1635 (s), 1580 (w), 1460 (m), 1440 (m), 1250 (s), 850 (s), 740 (s), 690 (m) cm^{-1}; MS *m/e* (%) 398 (4.2), 383 (1.6), 321 (1.4), 310 (3.2), 285 (14), 241 (97), 230 (8), 129 (100), 103 (24), 95 (66); HRMS calcd for $C_{20}H_{34}OSiSe$ 398.1544, found 398.1550.

(*E*)-(2-Undecenoyl)trimethylsilane (6). To a solution of acylsilane **5** (0.335 g, 0.84 mmol) in 5 mL of methanol was added $NaIO_4$ (0.201 g, 0.94 mmol) at room temperature, and the mixture was stirred at this temperature for 2 h. Aqueous saturated NH_4Cl was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane to hexane/ethyl acetate, 9:1) to obtain the title compound (0.205 g, quantitative): TLC R_f 0.40 (hexane/ethyl acetate, 19:1); VPC t_R 6.7 min (100–230 °C, 20 °C/min); ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.65 (m, 12 H), 2.05–2.4 (m, 2 H), 6.20 (dt, *J* = 16.3 and 1.3 Hz, 1 H), 6.59–6.93 (m, 1 H); IR (neat) 2920 (s), 2850 (m), 1580 (m), 1250 (m), 1195 (m), 980 (w), 845 (s) cm^{-1}; MS *m/e* (%) 240 (2), 225 (4), 197 (4), 169 (5), 155 (26), 142 (16), 127 (15), 73 (100); HRMS calcd for $C_{14}H_{28}OSi$ 240.1910, found 240.1919.

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Supplementary Material Available: ^{1}H NMR spectra of methoxybis(trimethylsilyl)methane, 1-methoxy-1-(trimethylsilyl)-1-undecene, and the acylsilanes synthesized in this study (11 pages). Ordering information is given on any current masthead page.

3-Hydroxy-4-methylthiazole-2(3*H*)-thione Carbamates (TTOC Carbamates). Useful Precursors for Monoalkylaminium Cation Radicals

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Our group has demonstrated that Barton's powerful methodology for the production of carbon-centered radicals[1] from PTOC esters (**1**)[2] can be extended to dialkyl nitrogen-centered radicals.[3] Either neutral dialkylaminyl radicals or protonated dialkylaminium cation radicals can be produced from PTOC carbamates **2**.[2] The more reactive dialkylaminium cation radicals are synthetically useful, and good yields of products resulting from intramolecular 5-exo additions to unactivated double bonds[3b–d] or from intermolecular additions to electron-rich olefins[3e] can be realized under mild reaction conditions. We now report that nitrogen-centered radicals also can be produced from the title precursors, TTOC carbamates (**3**).[4] Dialkylaminium cation radicals are available from TTOC carbamates, but, more importantly, these precursors can be used for the

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[1] Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

[2] PTOC is the acronym for 2-thioxopyridinyloxycarbonyl. PTOC esters and PTOC carbamates are actually mixed anhydrides of the thiohydroxamic acid with a carboxylic acid and a carbamic acid, respectively.

[3] (a) Newcomb, M.; Deeb, T. M. *J. Am. Chem. Soc.* **1987**, *109*, 3163. (b) Newcomb, M.; Deeb, T. M.; Marquardt, D. J. *Tetrahedron* **1990**, *46*, 2317. (c) Newcomb, M.; Marquardt, D. J.; Deeb, T. M. *Ibid.* **1990**, *46*, 2329. (d) Newcomb, M.; Marquardt, D. J.; Kumar, M. U. *Ibid.* **1990**, *46*, 2345. (e) Newcomb, M.; Kumar, M. U. *Tetrahedron Lett.* **1990**, *31*, 1675.

[4] TTOC for thioxothiazolyloxycarbonyl.

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