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Convenient route to di- and triorganosilyl ethyl ethers and the corresponding di- and triorganosilanes

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Abstract

Tetraethoxysilane was treated with alkyl- and aryllithium reagents for the preparation of organosilyl ethyl ethers of the type R_3SiOEt, $R_2R'SiOEt$, and $R_2Si(OEt)_2$, that can be reduced to the organosilanes R_3SiH, $R_2R'SiH$, and R_2SiH_2, respectively. Compounds of the type $RR'R''SiOEt$ cannot be cleanly formed. The reduction procedure involves treatment of the silyl alkoxy ethers with diisobutylaluminium hydride (DIBALH) and hydrolysis of the remaining alkylaluminium compounds with $Na_2SO_4 \cdot 10H_2O$. This hydrolysis provides a convenient method for the isolation of R_3SiH, $R_2R'SiH$, and R_2SiH_2 compounds without hydrolysis of the Si–H moiety that often occurs in standard aqueous work-up procedures of unhindered silanes.

Introduction

Di- and triorganosilanes have become extremely important for the synthesis of various silicon-containing materials by metal-catalyzed hydrosilylation [1]. We became interested in preparing di- and trisubstituted silanes, some of which were required to have mixed substitution patterns, for example $R_2R'SiH$. Early reports indicated that formation of R_3SiCl or R_2SiCl_2 compounds by the addition of organolithium or Grignard reagents to silicon tetrachloride was not selective due to the high reactivity of the chlorides [2]. There were some reports of reactions of organolithium reagents with tetraalkoxysilanes to give compounds of the type R_3SiOEt and R_4Si. Only one case of a mixed tetra(aryl)silane ($R_2R'_2Si$) was reported [3]. Conversion of triorganosilyl alkoxy ethers, R_3SiOR', to the corresponding hydrido compounds or triorganosilanes, R_3SiH, has been reported using diisobutylaluminium hydride (DIBALH), however, the scope and limitations of this method and detailed experimental procedures were not disclosed [4]. More recently, the mechanism of addition of nucleophiles including hydrides to alkoxysilanes has been thoroughly investigated [5].

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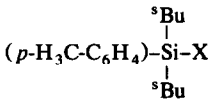
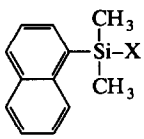
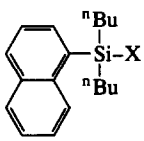
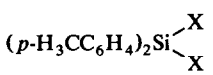
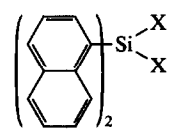
Table 1

Conversion of $(CH_3CH_2O)_4Si$ to organosilyl ethyl ethers ($X = OCH_2CH_3$) using organolithium reagents and to the corresponding silanes ($X = H$) using DIBALH [a]

Entry	Silane products	% yield for $X = OCH_2CH_3$	% yield for $X = H$ [b]
1	$(n\text{-}C_4H_9)_3Si\text{–}X$	66	60 (99)
2	$Ph(CH_3)_2Si\text{–}X$	52	– (65)
3	$(p\text{-}Br\text{-}C_6H_4)(CH_3)_2Si\text{–}X$	56	50 (73)
4		44	50 (76)
5		44	42 (83)
6		46	70 (82)
7	$Ph_3Si\text{–}X$	51	69 (89)
8		44	62 (85)
9		70	73

[a] See Experimental for details. [b] Yields are isolated yields of material obtained by distillation or crystallization. Yields in parentheses are GC yields determined using the response ratio of the product relative to an n-alkane internal standard.

Here we define methods for the addition of alkyl- and aryllithium reagents to tetraethoxysilane and their limitations. We also describe the procedures necessary for the reduction of the alkoxy moiety using DIBALH. This involves a method for the hydrolysis of excess DIBALH and alkylaluminium intermediates using $Na_2SO_4 \cdot 10H_2O$, a procedure that does not interfere with the Si–H linkage. This is especially important in unhindered triorganosilanes and diorganosilane products.

Table 1 indicates several alkoxysilanes that were formed by treating tetraethoxysilane with organolithium reagents. Both alkyl- and aryllithium reagents add well to displace the alkoxide groups and trialkyl-, triaryl-, or diarylsilyl-ethyl ethers can be formed (entries 1, 7, 8, and 9). The corresponding Grignard reagents are far less effective for the substitution reactions [6]. Mixed trisubstituted ethers could also be formed by the addition of two equivalents of an organolithium reagent (RLi) followed by one equivalent of a second organolithium reagent (R'Li)

(eq. 1). The reverse mode of addition cannot be used since monoalkyl- or monoaryl(triethoxy)silane is more prone to attack by an organolithium reagent than is tetraethoxysilane (eq. 2).

$$2\ RLi + Si(OEt)_4 \longrightarrow R_2Si(OEt)_2 \xrightarrow{R'Li} R_2R'SiOEt \quad (1)$$

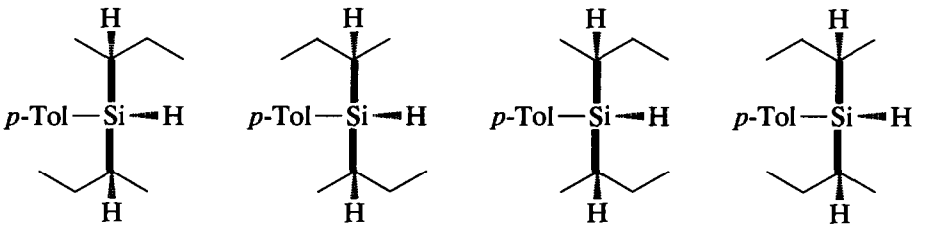
$$RLi + Si(OEt)_4 \longrightarrow 1/2\ R_2Si(OEt)_2 + 1/2 \text{ unreacted } Si(OEt)_4 \quad (2)$$

(R and R′ = alkyl or aryl)

This approach cannot therefore be used for clean formation of mixed silyl ethyl ethers of the types $RR'Si(OEt)_2$ or RR′R″SiOEt.

Reduction of the alkoxysilanes to the corresponding hydrido species was easily achieved with DIBALH in toluene at room temperature. The reaction times were generally 0.5–2.5 h using 1.9–2.0 equivalents of DIBALH per ethoxysilane bond. Reaction times of 5 min with one equivalent of reducing agent [4] could not be obtained with our systems. The reaction mixtures were quenched by adding $Na_2SO_4 \cdot 10H_2O$ to hydrolyze excess hydride and alkylaluminum. Upon cessation of bubbling, the slurry was filtered through a plug of silica gel, the solvent was removed and the silane distilled or crystallized directly. This avoids the standard aqueous work-up normally used for the quenching of excess DIBALH and alkylaluminum species. Consequently unhindered trialkylsilanes and diorganosilanes that are especially sensitive could be obtained with only limited hydrolysis of the Si–H moiety (Table 1, entries 1, 8, 9).

Interestingly, for entry 4, three isomers for both the ethoxy and hydrido compounds were observed by ^{13}C NMR. This is consistent with the formation of the enantiomeric pair **1** and **2**, and the two meso forms **3** and **4**, depicted using the hydrido species.



(1) (2) (3) (4)

In summary, a convenient approach to the di- and triorganosilylalkoxides has been developed and the limitations of this approach for the preparation of a symmetrical systems outlined. Additionally, a method for the conversion of the alkoxides to the corresponding silanes has been developed using DIBALH and a modified hydrolysis procedure.

Experimental

General

All operations were carried out under dry dinitrogen. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under dinitrogen from sodium benzophenone ketyl. Reagent grade toluene was distilled under dinitrogen from

calcium hydride. Bulk grade hexane was distilled prior to use. Tetraethoxysilane was purchased (Aldrich), distilled over calcium hydride, and stored under dinitrogen. n-Butyllithium, sec-butyllithium, and methyllithium were purchased (Aldrich) and titrated prior to use by the method of Watson and Eastham [7]. tert-Butyllithium was purchased (Aldrich, or Lithium Corporation of America) and titrated prior to use [7]. Proton NMR spectra were recorded at 300 or 500 MHz on Bruker AM-300 or Bruker AM-500 spectrometers respectively. The ^{13}C NMR spectra at 75 and 125 MHz were recorded on Bruker AM-300 and Bruker AM-500 spectrometers respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances were recorded using the 77.0 ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin–Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical 70SQ high resolution, double-focusing mass spectrometer with VG 11/250 data system. Combustion analyses were obtained from Atlantic Microlab, Norcross, GA. Capillary GC analyses were obtained using a Hewlett–Packard Model 5890 gas chromatograph and Hewlett–Packard 3396A integrator. Flash chromatography was carried out on 230–400 mesh silica gel (EM Science). In all experimental procedures, flash chromatography refers to chromatography with a dinitrogen head pressure as described by Still [8]. The GC yields were often greater than the isolated yields due to the difficulties in distilling or crystallizing the products on the small scales used. Larger scales should afford yields much closer to the GC values listed.

Ethoxy(tri-n-butyl)silane [9]. Tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL) was cooled to −78°C. n-Butyllithium (6.0 mL, 0.0149 mole, 2.48 *M* in hexane) was added and the reaction allowed to warm to room temperature for 1 h. The reaction was quenched with water and the organic phase dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude oily product purified by flash chromatography (silica gel, hexane → hexane/ether 20:1) to yield 0.80 g (66%) of the title compound as a clear colorless oil (95% GC purity). IR (neat): 2922.4, 1465.2, 1377.2, 1296.9, 1194.2, 1110.9, 1080.3, 944.9, 885.6, 762.5 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.64 (q, $J = 7.0$ Hz, 2 H), 1.30 (m, 12 H), 1.16 (t, $J = 7.0$ Hz, 3 H), 0.87 (m, 6 H), 0.57 (m, 9 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 58.35, 26.62, 25.42, 18.65, 13.77, 13.36. HRMS: Found: 244.2220. $C_{14}H_{32}SiO$ calcd.: 244.2222.

Dimethyl(ethoxy)(phenyl)silane [10]. Tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL) was cooled to −78°C. Methyllithium (7.1 mL, 0.00994 mole, 1.4 *M* in ether) was added and the reaction allowed to warm to room temperature for 30 min. Phenyllithium, prepared by adding bromobenzene (0.55 mL, 0.00522 mole) in ether (3 mL) to a solution of t-butyllithium (5.9 mL, 0.0100 mole, 1.7 *M* in pentane) in ether (2 mL) at −78°C and stirring for 1 h, was added at −78°C. After warming to room temperature for 1.5 h, the reaction was quenched with water (20 mL) and the organic phase dried over magnesium sulfate. The solvent was removed and the crude oily product distilled under vacuum (75°C, 0.8 mmHg, Kugelrohr) to yield 0.46 g (52%) of the title compound as a clear colorless oil (93% GC purity). IR (neat): 2970.6, 1427.9, 1251.4, 1116.4, 947.7, 826.6, 785.9, 699.1 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.56 (m, 2 H), 7.35 (m, 3 H), 3.65 (q, $J = 7.0$ Hz, 2 H), 1.16 (t, $J = 7.0$ Hz, 3 H), 0.36 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ

138.02, 133.45, 129.52, 127.81, 58.67, 18.42. HRMS: Found: 180.0968. $C_{10}H_{16}SiO$ calcd.: 180.0970.

4-Bromophenyl(dimethyl)(ethoxy)silane [11]. The title compound was prepared in a manner analogous to dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (11.2 mL, 0.0502 mole) in ether (50 mL), methyllithium (72.0 mL, 0.101 mole, 1.4 *M* in ether) and 4-bromophenyllithium, prepared by adding t-butyllithium (59 mL, 0.100 mole, 1.7 *M* in pentane) to a solution of 1,4-dibromobenzene (11.78 g, 0.0499 mole) in ether (30 mL) and THF (50 mL) at −78°C and stirred at −78°C for 1 h. After work-up, the crude, oily product was distilled under vacuum (70–80°C, 1.1 mmHg, Kugelrohr) to yield 7.23 g (56%) of the title compound as a clear colorless oil (94% GC purity). IR (neat): 2970.9, 1574.2, 1479.2, 1376.3, 1254.0, 1164.2, 1068.0, 1011.1, 948.8, 824.3, 783.4, 722.3 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.49 (1/2 ABq, $J = 8.2$ Hz, 2 H), 7.41 (1/2 ABq, $J = 8.2$ Hz, 2 H), 3.64 (q, $J = 6.9$ Hz, 2 H), 1.16 (t, $J = 7.0$ Hz, 3 H), 0.35 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.87, 135.04, 130.99, 124.39, 58.72, 18.40, −1.77. HRMS: Found: 258.0079. $C_{10}H_{15}Si^{79}BrO$ calcd.: 258.0076.

Di-sec-butyl(ethoxy)(4-methylphenyl)silane. The title compound was prepared in a manner analogous to the preparation of dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (2.2 mL, 0.00986 mole) in ether (10 mL), sec-butyllithium (18.6 mL, 0.0197 mole, 1.1 *M* in cyclohexane) and 1-lithio-4-methylbenzene, prepared by adding 4-bromotoluene (1.69 g, 0.00988 mole) in ether (5 mL) to a solution of t-butyllithium (8.6 mL, 0.0198 mole, 1.7 *M* in pentane) in ether (5 mL) at −78°C and stirring at −78°C for 1 h. After work-up, the crude, oily product was distilled under vacuum (120°C, 0.7 mmHg, Kugelrohr) to yield 1.20 g (44%) of the title compound as a clear colorless oil (98% GC purity). IR (neat): 2959.2, 2870.6, 1604.4, 1459.7, 1390.3, 1160.2, 1107.0, 998.5, 945.3, 850.4, 799.8, 750.6, 699.9, 667.2 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, $J = 7.9$ Hz, 2 H), 7.16 (d, $J = 7.6$ Hz, 2 H), 3.76 (q, $J = 6.9$ Hz, 2 H), 2.33 (s, 3 H), 1.69–1.60 (m, 2 H), 1.22 (t, $J = 6.9$ Hz, 3 H), 1.11–0.88 (m, 16 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.86, 134.65, 134.62, 134.59, 131.48, 131.40, 131.31, 128.40, 59.39, 59.36, 59.33, 24.19, 24.11, 21.51, 19.77, 19.62, 19.60, 18.62, 13.56, 13.44, 13.40, 13.27, 13.26, 13.09, 13.07. HRMS: Found: 278.2060. $C_{17}H_{30}SiO$ calcd.: 278.2066.

Dimethyl(ethoxy)(1-naphthyl)silane. The title compound was prepared in a manner analogous to the preparation of dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL), methyllithium (7.1 mL, 0.00994 mole, 1.4 *M* in ether) and 1-naphthyllithium, prepared by adding 1-bromonaphthalene (0.70 mL, 0.00503 mole) in ether (2 mL) to a solution of t-butyllithium (5.9 mL, 0.0100 mole, 1.7 *M* in pentane) in ether (2 mL) at −78°C and stirring at −78°C for 1 h. After work-up, the crude, oily product was distilled under vacuum (115–125°C, 0.8 mmHg, Kugelrohr) to yield 0.50 g (44%) of the title compound as a clear colorless oil (96% GC purity). IR (neat): 3055.8, 2970.8, 1589.5, 1505.6, 1390.5, 1320.1, 1252.7, 1077.9, 985.6, 946.4, 783.7, 672.4, 636.9 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.32 (dd, $J = 8.1$, 0.9 Hz, 1 H), 7.87 (br d, $J = 8.2$ Hz, 1 H), 7.85 (dd, $J = 7.8$, 0.8 Hz, 1 H), 7.72 (dd, $J = 6.8$, 1.3 Hz, 1 H), 7.55–7.42 (m, 3 H), 3.67 (q, $J = 7.0$ Hz, 2 H), 1.18 (t, $J = 7.0$ Hz, 3 H), 0.54 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.90, 135.96, 133.78, 133.29, 130.37, 128.83, 128.26, 125.95, 125.50, 124.97, 58.73, 18.38, −0.52. HRMS: Found: 230.1127 $C_{14}H_{18}SiO$ calcd.: 230.1127.

Di-n-butyl(ethoxy)(1-naphthyl)silane. The title compound was prepared analogously to dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL), n-butyllithium (3.9 mL, 0.00983 mole, 2.52 *M* in hexane) and 1-naphthyllithium, prepared by adding 1-bromonaphthalene (0.70 mL, 0.00503 mole) in ether (3 mL) to a solution of t-butyllithium (5.9 mL, 0.0100 mole, 1.7 *M* in pentane) in ether (2 mL) at −78°C and stirring at −78°C for 1 h. After work-up, the crude, oily product was distilled under vacuum (175–200°C, 0.8–1.4 mmHg, Kugelrohr) to yield (0.71 g (46%) of the title compound as a clear colorless oil (97% GC purity). IR (neat): 2923.2, 1505.7, 1458.1, 1078.1, 944.9, 821.8, 777.4 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.32 (dd, $J = 7.8$, 0.9 Hz, 1 H), 7.85 (br d, $J = 8.2$ Hz, 1 H), 7.83 (dd, $J = 7.8$, 1.8 Hz, 1 H), 7.70 (dd, $J = 6.8$, 1.3 Hz, 1 H), 7.55–7.41 (m, 3 H), 3.70 (q, $J = 7.0$ Hz, 2 H), 1.40–1.30 (m, 8 H), 1.21 (t, $J = 7.0$ Hz, 3 H), 1.08 (t, $J = 7.8$ Hz, 4 H), 0.90 (t, $J = 7.2$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.27, 134.88, 134.24, 133.28, 130.16, 128.78, 128.30, 125.81, 125.41, 124.94, 58.82, 26.50, 25.39, 18.41, 14.21, 13.69. HRMS: Found: 314.2062. $C_{20}H_{30}SiO$ calcd.: 314.2066.

Ethoxy(triphenyl)silane [12]. Ether (10 mL) was cooled to −78°C and t-butyllithium (18.0 mL, 0.0306 mole, 1.7 *M* in pentane) was added. A solution of bromobenzene (1.60 mL, 0.0152 mole) in ether (5 mL) was prepared and added to the t-butyllithium solution. After stirring for 1 h at −78°C the prepared phenyllithium was added to tetraethoxysilane (1.10 mL, 0.00493 mole) in ether (5 mL) at −78°C. The reaction mixture was allowed to warm to room temperature over 1 h. After quenching with water (30 ml), the organic phase was dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude solid purified by flash chromatography (silica gel, hexane/methylene chloride 15 : 1) to yield 0.76 g (51%) of the title compound as a white crystalline solid (98% GC purity). IR (KBr): 3066.9, 2968.2, 1588.8, 1428.8, 1390.1, 1117.8, 1079.6, 949.1, 638.9 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.62–7.60 (m, 6 H), 7.43–7.34 (m, 9 H), 3.86 (q, $J = 7.0$ Hz, 2 H), 1.22 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.37, 134.43, 129.93, 127.82, 59.73, 18.37. HRMS: Found: 304.1281. $C_{20}H_{20}SiO$ calcd.: 304.1283. Anal. Found: C, 78.40; H, 6.60. $C_{20}H_{20}SiO$ calcd.: C, 78.90; H, 6.62%.

Diethoxy(di-4-methylphenyl)silane [13]. t-Butyllithium (17.4 mL, 0.0400 mole, 2.3 *M* in pentane) was added to ether (10 mL) and cooled to −78°C. 4-Bromotoluene (3.42 g, 0.0200 mole) in ether (10 mL) was added. The mixture was stirred for 1 h at −78°C and then added to tetraethoxysilane (2.2 mL, 0.00986 mole) in ether (10 mL) at −78°C. The reaction mixture was allowed to warm to room temperature for 2 h. After quenching with water (30 mL) the organic phase was dried over magnesium sulfate and the solvent was removed *in vacuo*. The crude oily product was distilled under vacuum (150–175°C, 0.8 mmHg, Kugelrohr) to yield 1.30 g (44%) of the title compound as a clear colorless oil. IR (neat): 2973.3, 2923.8, 1602.5, 1391.6, 1165.2, 1077.6, 955.3, 802.4, 781.6, 728.6, 653.9 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, $J = 7.9$ Hz, 4 H), 7.16 (d, $J = 7.4$ Hz, 4 H), 3.84 (q, $J = 7.0$ Hz, 4 H), 2.33 (s, 6 H), 1.22 (t, $J = 7.0$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.97, 134.89, 129.79, 128.57, 58.76, 21.55, 18.30. HRMS: Found: 300.1545. $C_{18}H_{24}SiO_2$ calcd.: 300.1546.

Diethoxy(di-1-naphthyl)silane [3b]. The title compound was prepared analogously to diethoxy(di-4-methylphenyl)silane using t-butyllithium (17.5 mL, 0.0403 mole, 2.3 *M* in pentane) in ether (10 mL), 1-bromonaphthalene (4.10 g, 0.0198

mole) in ether (10 mL), and tetraethoxysilane (2.2 mL, 0.00986) in ether (10 mL). After work-up, the crude product was recrystallized from hexane to yield 2.55 g (70%) of the title compound as white crystals. IR (KBr): 2970.0, 1504.9, 1388.9, 1218.0, 1074.8, 987.7, 829.0, 778.2, 738.8, 675.6, 552.6, 474.6 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.31 (dd, $J = 8.4$, 0.7 Hz, 2 H), 8.10 (dd, $J = 6.8$, 1.3 Hz, 2 H), 7.90 (br d, $J = 8.2$ Hz, 2 H), 7.80 (dd, $J = 8.6$, 1.3 Hz, 2 H), 7.48 (dd, $J = 8.2$, 6.8 Hz, 2 H), 7.39 (m, 4 H), 3.83 (q, $J = 7.0$ Hz, 4 H), 1.23 (t, $J = 7.0$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.07, 136.15, 133.23, 131.82, 130.93, 128.62, 128.44, 126.04, 125.44, 125.14, 59.14, 18.31. HRMS: Found: 372.1547. $C_{24}H_{24}SiO_2$ calcd.: 372.1546. Anal. Found: C, 77.37; H, 6.46. $C_{24}H_{24}SiO_2$ calcd.: C, 77.38; H, 6.49%.

Tri-n-butylsilane [14]. Ethoxy(tri-n-butyl)silane (0.53 g, 0.00217 mole) and hexadecane (0.15 mL, 0.000512 mole as an internal standard) were added to toluene (3 mL). The solution was cooled to −78°C and DIBALH (0.75 mL, 0.00421 mole) was added. After stirring for 30 min at −78°C, the reaction mixture was allowed to warm to room temperature for 30 min. The reaction was judged complete by GC. Sodium sulfate decahydrate was added and the mixture was stirred until the gas evolution had ceased. The salts were removed by filtration through a silica plug. After the solvent was removed *in vacuo*, the crude product was distilled under vacuum (100°C, 0.8 mmHg, Kugelrohr) to yield 0.26 g (60%, GC yield 99%) of the title compound as a clear colorless oil (96% GC purity). IR (neat): 2918.3, 2099.9, 1464.0, 1410.5, 1377.2, 1295.9, 1192.2, 1081.9, 963.1, 892.8, 808.0 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.64 (sept, $J = 3.2$ H, 1 H), 1.35–1.26 (m, 12 H), 0.87 (t, $J = 6.9$ Hz, 9 H), 0.59–0.53 (m, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 26.97, 26.38, 13.80, 11.06.

Dimethyl(phenyl)silane [15]. The title compound was prepared in a manner analogous to tri-n-butylsilane using dimethyl(ethoxy)(phenyl)silane (0.30 g, 0.00166 mole) and tetradecane (0.11 mL, 0.000423 mole as an internal standard) in toluene (3 mL) and DIBALH (0.60 mL, 0.00337 mole). After work-up, the crude product was distilled under vacuum (30 mmHg). However, the product could not be completely separated from toluene. Therefore identity of the product was established by GC with coinjection of commercial (Aldrich) phenyl(dimethyl)silane. The GC yield was 65% (100% GC purity). IR (neat): 2959.4, 2924.9, 2120.2, 1635.7, 1427.8, 1259.9, 1115.8, 879.8, 804.4, 709.0, 668.1 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55–7.51 (m, 2 H), 7.37–7.33 (m, 3 H), 4.41 (sept, $J = 3.8$ Hz, 1 H), 0.33 (d, $J = 3.8$ Hz, 6 H).

4-Bromophenyl(dimethyl)silane [16]. The title compound was prepared in a manner analogous to tri-n-butylsilane using 4-bromophenyl(dimethyl)(ethoxy)silane (1.30 g, 0.00502 mole) in toluene (5 mL) and DIBALH (2.70 mL, 0.0152 mole). After work-up, the crude product was distilled under vacuum (80°C, 0.7–0.9 mmHg, Kugelrohr) to yield 0.54 g (50%) of the title compound as a clear colorless oil (99% GC purity). To determine the GC yield, another reaction was run using 4-bromophenyl(dimethyl)(ethoxy)silane (0.42 g, 0.00162 mole) and hexadecane (0.15 mL, 0.000512 mole as an internal standard) in toluene (3 mL) and DIBALH (0.55 mL, 0.00309 mole). The GC yield was 73%. IR (neat): 2959.6, 2122.8, 1575.4, 1478.8, 1378.2, 1251.0, 1067.2, 1012.0, 878.2, 836.4, 809.6, 764.5, 722.2 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.47 (1/2 ABq, $J = 8.3$ Hz, 2 H), 7.37 (1/2 ABq, $J = 8.3$ Hz, 2 H), 4.37 (sept, $J = 3.7$ Hz, 1 H), 0.31 (d, $J = 3.7$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.19, 135.56, 130.99, 123.99, −3.87. HRMS Found: 212.9736. $C_8H_{10}Si^{79}Br$ $(M - H)^+$ calcd.: 212.9735.

Di-sec-butyl(4-methylphenyl)silane. The title compound was prepared in a manner analogous to tri-n-butylsilane using di-sec-butyl(ethoxy)(4-methylphenyl)silane (0.40 g, 0.00144 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After workup, the crude product was distilled under vacuum (150°C, 1.3 mmHg, Kugelrohr) to yield 0.17 g (50%, GC yield 76%) of the title compound as a clear colorless oil. IR (neat): 2954.2, 2103.0, 1603.5, 1459.9, 1378.4, 1311.5, 1212.0, 1106.8, 1033.7, 1001.0, 792.1, 692.9, 636.1 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.48 (d, $J = 7.9$ Hz, 2 H), 7.14 (d, $J = 7.6$ Hz, 2 H), 3.99 (m, 1 H), 2.33 (s, 3 H), 1.53 (m, 1 H), 1.22 (m, 1 H), 1.03 (m, 4 H), 0.949 (d, $J = 7.3$ Hz, 3 H), 0.944 (d, $J = 7.3$ Hz, 3 H), 0.876 (t, $J = 7.5$ Hz, 3 H), 0.868 (t, $J = 7.5$ Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.79, 135.65, 135.57, 135.50, 130.89, 130.65, 130.46, 128.50, 25.95, 25.81, 25.62, 25.60, 21.49, 18.26, 18.18, 18.04, 14.90, 14.78, 14.75, 13.22, 13.20, 13.16.

Dimethyl(1-naphthyl)silane [17]. The title compound was prepared in a manner analogous to tri-n-butylsilane using dimethyl(ethoxy)(1-naphthyl)silane (0.35 g, 0.00151 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After work-up, the crude product was distilled under vacuum (110–120°C, 1.0 mmHg, Kugelrohr) to yield 0.12 g (42%, GC yield 83%) of the title compound as a clear colorless oil (97% GC purity). IR (neat): 3054.7, 2958.9, 2120.0, 1505.2, 1250.5, 1144.1, 985.2, 882.3, 839.2, 779.2, 737.9, 644.9 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.11 (dd, $J = 8.2$, 0.8 Hz, 1 H), 7.87 (d, $J = 8.2$ Hz, 1 H), 7.85 (dd, $J = 7.2$, 1.7 Hz, 1 H), 7.72 (dd, $J = 7.0$, 1.3 Hz, 1 H), 7.45 (m, 3 H), 4.84 (sept, $J = 3.7$ Hz, 1 H), 0.48 (d, $J = 3.8$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.93, 135.62, 133.61, 133.18, 129.98, 128.94, 127.59, 125.91, 125.52, 125.16, −3.26. HRMS: Found: 186.0855. $C_{12}H_{14}Si$ calcd.: 186.0865. Anal. Found: C, 76.53; H, 7.34. $C_{12}H_{14}Si$ calcd.: C, 77.35; H, 7.57%.

Di-n-butyl(1-naphthyl)silane. The title compound was prepared in a manner analogous to tri-n-butylsilane using di-n-butyl(ethoxy)(1-naphthyl)silane (0.47 g, 0.00149 mole) in toluene (2 mL) and DIBALH (0.80 mL, 0.00449 mole). After work-up, the crude product was distilled under vacuum (185°C, 0.7–1.0 mmHg, Kugelrohr) to yield 0.28 g (70%) of the title compound as a clear colorless oil (98% GC purity). To determine the GC yield, another reaction was run using di-n-butyl(ethoxy)(1-naphthyl)silane (0.42 g, 0.00134 mole) and tetradecane (0.10 mL, 0.000385 mole as an internal standard) in toluene (3 mL) and DIBALH (0.45 mL, 0.00252 mole). The GC yield was 82%. IR (neat): 3055.4, 2921.3, 2111.4, 1588.5, 1505.4, 1463.7, 1409.4, 1376.7, 1217.8, 1190.2, 1144.0, 1081.4, 1023.5, 983.1, 892.1, 793.1, 733.2 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.09 (dd, $J = 7.2$, 1.7 Hz, 1 H), 7.85 (d, $J = 7.6$ Hz, 1 H), 7.83 (dd, $J = 6.7$, 1.9 Hz, 1 H), 7.70 (dd, $J = 6.7$, 1.3 Hz, 1 H), 7.45 (m, 3 H), 4.67 (p, $J = 3.6$ Hz, 1 H), 1.41–1.29 (m, 8H), 1.02–0.96 (m, 4 H), 0.88 (t, $J = 7.1$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.32, 134.55, 134.48, 133.24, 129.83, 128.91, 127.80, 125.80, 125.46, 125.11, 27.11, 26.22, 13.73, 12.22. HRMS: Found: 270.1802. $C_{18}H_{26}Si$ calcd.: 270.1804.

Triphenylsilane [18]. The title compound was prepared in a manner analogous to tri-n-butylsilane using ethoxy(triphenyl)silane (0.46 g, 0.00151 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After work-up, the crude product was distilled under vacuum (170°C, 1.0 mmHg, Kugelrohr) to yield 0.27 g (69%, GC yield 89%) of the title compound as a clear colorless oil (99% GC purity). IR (neat): 3067.8, 3010.6,

2123.5, 1588.0, 1485.8, 1428.2, 1328.5, 1186.7, 1114.3, 998.1, 804.0, 729.1, 696.8 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.58–7.55 (m, 6 H), 7.43–7.33 (m, 9 H), 5.45 (s, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.80, 133.32, 129.80, 128.04. HRMS Found: 260.1017. $C_{18}H_{16}Si$ calcd.: 260.1022.

Di-4-methylphenylsilane [19]. The title compound was prepared in a manner analogous to tri-n-butylsilane using diethoxy(di-4-methylphenyl)silane (0.64 g, 0.00213 mole) and decane (0.15 mL, 0.000770 mole as an internal standard) in toluene (3 mL) and DIBALH (1.45 mL, 0.00814 mole). After work-up, the crude product was distilled under vacuum (135°C, 0.8 mmHg, Kugelrohr) to yield 0.28 g (62%, GC yield 85%) of the title compound as a clear colorless oil (99% GC purity). IR (neat): 3012.8, 2920.5, 2134.2, 1601.4, 1391.9, 1114.1, 937.9, 850.3, 794.4, 628.8 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.47 (d, $J = 7.9$ Hz, 4 H), 7.17 (d, $J = 7.9$ Hz, 4 H), 4.87 (s, 2 H), 2.34 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.77, 135.68, 128.93, 128.03, 21.51. HRMS: Found: 212.1015. $C_{14}H_{16}Si$ calcd.: 212.1022.

Di-1-naphthylsilane [20]. The title compound was prepared in a manner analogous to tri-n-butylsilane using diethoxy(di-1-naphthyl)silane (1.12 g, 0.00301 mole) and tetradecane (0.25 mL, 0.000961 mole as an internal standard) in toluene (4 mL) and DIBALH (1.90 mL, 0.0107 mole). After work-up, the crude product was recrystallized from hexane to yield 0.31 g (72%) of the title compound as a white crystalline solid. IR (KBr): 3047.5, 2159.7, 2133.8, 1503.6, 1327.8, 1217.5, 1141.0, 1021.8, 988.5, 938.8, 847.0, 782.8, 640.7, 597.0, 522.9, 508.8, 489.2 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (br d, $J = 8.7$ Hz, 2 H), 7.93 (br d, $J = 8.2$ Hz, 2 H), 7.87 (dd, $J = 7.3$, 1.8 Hz, 2 H), 7.76 (d, $J = 6.7$ Hz, 2 H), 7.48 (m, 4 H), 7.43 (br t, $J = 7.5$ Hz, 2 H), 5.69 (s, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.38, 136.48, 133.14, 130.89, 129.65, 128.84, 127.89, 126.37, 125.84, 125.38. Anal. Found: C, 83.45; H, 5.82. $C_{20}H_{16}Si$ calcd.: C, 84.45; H, 5.67.

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