Supporting Information
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Supporting Information

An Efficient Method for the Synthesis of Symmetrical Disiloxanes from Alkoxysilanes Using Meerwein’s Reagent

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General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Rhodium complex, [Rh(cod)(MeCN)2]BF4 was prepared according to procedure reported in the literature.1 Diethyl ether was distilled from sodium/benzophenone ketyl.2 All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) and iodine chamber. Flash column chromatography was performed with E. Merck silica gel 60 N (spherical, neutral 100–210 µm). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-EX270 (1H 270 MHz, and 13C 68 MHz) and JEOL JNM-EX400 (1H 400 MHz, and 13C 100 MHz) spectrometer. Chemical shifts for 1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm) and CD3CN (δ 1.94 ppm). Chemical shifts for 13C NMR are expressed in parts ppm relative to CDCl3 (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s =
singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. High resolution mass spectroscopy (HR MS) was recorded with JEOL JMS-700 spectrometer.

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1,1,1,3,3,3-Hexaphenyldisiloxane (7)

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Table S1. Optimization of the additive for the Synthesis of Disiloxanes<sup>a</sup>

![Chemical structure](image)

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<sup>a</sup> All reactions performed on 0.5 mmol reaction scale of (4-bromophenyl)ethoxydi(prop-2-enyl)silane 1a and Me<sub>3</sub>OBF<sub>4</sub> (1.0 equiv) and additive (1.0 equiv) in MeCN (2.5 mL) was heated at 100 °C. <sup>b</sup> Isolated yield.

**Typical Experimental Procedure for the Synthesis of Symmetrical Disiloxane (Table 1, entries 2/8/9):** A dry and nitrogen flushed 10 mL screw-capped vial was charged with alkoxy silane (1.0 mmol), acetonitrile (5.0 mL) followed by the addition of potassium carbonate (138.2 mg, 1.0 mmol) and trimethyloxonium tetrafluoroborate (148 mg, 1.0 mmol) or triethyloxonium tetrafluoroborate (190 mg, 1.0 mmol) or triethyloxonium hexafluorophosphate (248 mg, 1.0 mmol). The reaction mixture was stirred at 100 °C for 90 min and quenched by dropwise addition of water (1.0–2.0 mL). It was then
diluted with dichloromethane and the organic layer was washed with brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The crude mixture was purified by chromatography on silica gel (5% EtOAc/hexane as eluent) to give symmetrical disiloxane as colorless liquid.

**Typical Procedure for the Synthesis of Fluorosilanes.** A dry and nitrogen flushed 10 mL screw-capped vial was charged with alkoxysilane (1.0 mmol), acetonitrile (5.0 mL) followed by the addition of trimethyloxonium tetrafluoroborate (147.9 mg, 1.0 mmol) or triethyl oxonium tetrafluoroborate (189.9 mg, 1.0 mmol). The reaction mixture was stirred at 50 °C for 30 min and quenched by dropwise addition of water. It was then diluted with dichloromethane; the organic layer was washed with brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The crude mixture was purified by chromatography on silica gel (5% EtOAc/hexane as eluent) to give corresponding fluorosilanes as colorless liquid.

1,3-Bis(4-bromophenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2a): colorless liquid; \(^1\)H NMR (270 MHz, CDCl₃) \(\delta\) 1.87–1.93 (m, 8H), 4.86–4.88 (m, 4H), 4.90–4.94 (m, 4H), 5.64–5.80 (m, 4H), 7.37 (d, \(J\) = 8.37 Hz, 1H), 7.49 (d, \(J\) = 8.37 Hz, 1H); \(^{13}\)C NMR (68 MHz, CDCl₃) \(\delta\) 23.1, 115.3, 124.7, 130.9, 132.6, 134.8, 135.2; HR MS (FAB\(^+\)) [M-C₃H₅]\(^+\) calcd for C\(_{21}\)H\(_{23}\)Br\(_2\)OSi\(_2\) 504.9654, found 504.9651.
1,3-Diphenyl-1,1,3,3-tetra(prop-2-enyl)disiloxane (2b): colorless liquid; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.88–1.92 (m, 8H), 4.86–4.94 (m, 8H), 5.69–5.85 (m, 4H), 7.32–7.40 (m, 6H), 7.52–7.56 (m, 4H); $^{13}$C NMR (68 MHz, CDCl$_3$) δ 22.3, 114.8, 127.7, 129.7, 133.2, 133.7, 136.3; HR MS (EI$^+$) [M]$^+$ calcd for C$_{24}$H$_{30}$OSi$_2$ 390.1835, found 390.1839.

![1,3-Diphenyl-1,1,3,3-tetra(prop-2-enyl)disiloxane](image)

1,3-Bis(4-methoxyphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2c): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.85–1.87 (m, 8H), 3.82 (s, 6H), 4.86–4.91 (m, 8H), 5.73–5.80 (m, 4H), 7.89 (d, $J$ = 6.8 Hz, 4H), 7.46 (d, $J$ = 6.8 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.4, 55.0, 113.4, 114.6, 127.3, 133.4, 135.2, 160.8; HR MS (EI$^+$) [M]$^+$ calcd for C$_{26}$H$_{34}$O$_3$Si$_2$ 450.2046, found 450.2049.

![1,3-Bis(4-methoxyphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane](image)

1,3-Bis(4-methylphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2d): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.86–1.88 (m, 8H), 2.35 (s, 6H), 4.86–4.92 (m, 8H), 5.73–5.80 (m, 4H), 7.17 (d, $J$ = 7.2 Hz, 4H), 7.43 (d, $J$ = 7.2 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.5, 23.4, 114.6, 128.5, 132.7, 133.4, 133.7, 139.5; HR MS (EI$^+$) [M]$^+$ calcd for C$_{26}$H$_{34}$OSi$_2$ 418.2148, found 418.2152.

![1,3-Bis(4-methylphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane](image)
1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane (2e): colorless liquid; $^1$H NMR (270 MHz, CDCl$_3$) δ 0.33 (s, 12H), 7.34–7.37 (m, 6H), 7.53–7.55 (m, 4H); $^{13}$C NMR (68 MHz, CDCl$_3$) δ 0.8, 127.7, 129.2, 133.0, 139.8; HR MS (EI$^+$) [M]$^+$ calcd for C$_{16}$H$_{22}$OSi$_2$ 286.1209, found 286.1205.

\[
\begin{array}{c}
\text{Ph} \quad \text{Si} \quad \text{O} \\
\text{Me} \quad \text{Me} \\
\end{array}
\]

1,3-Dimethyl-1,1,3,3-tetraphenyldisiloxane (4): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.67 (s, 6H), 7.36–7.42 (m, 12H), 7.60–7.62 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ -0.6, 127.7, 129.6, 134.0, 137.5; CAS Registry No. 807-28-3.

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\begin{array}{c}
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\text{Et} \quad \text{Et} \\
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1,3-Diethyl-1,1,3,3-tetraphenyldisiloxane (5): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.94 (t, $J$ = 7.2 Hz, 6H), 1.05 (q, $J$ = 7.2 Hz, 4H), 7.27–7.37 (m, 12H), 7.50–7.52 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 6.8, 7.4, 127.7, 129.5, 134.4, 136.5; CAS Registry No. 18858-60-1.

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\text{Et} \quad \text{Et} \\
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1,1,3,3-Tetraphenyl-1,3-di(prop-2-enyl)disiloxane (6): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.08–2.10 (m, 4H), 4.80–4.84 (m, 4H), 5.70–5.75 (m, 2H), 7.28–7.40 (m, 12H), 7.50–7.52 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.6, 115.1, 127.7, 129.8, 133.0, 134.5, 135.7; HR MS (EI$^+$) [M]$^+$ calcd for C$_{30}$H$_{30}$OSi$_2$ 462.1836, found 462.1839; CAS Registry No. 18842-38-1.
1,1,1,3,3,3-Hexaphenyldisiloxane (7): white solid; m.p. 222–224 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24–7.30 (m, 12H), 7.35–7.39 (m, 6H), 7.46–7.48 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.7, 129.8, 135.1, 135.4; CAS Registry No. 1829-40-9.

1,1,1,3,3,3-Hex(prop-2-enyl)disiloxane (8): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.62–1.68 (m, 12H), 4.90–4.95 (m, 12H), 5.75–5.81 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.6, 114.3, 133.4; HR MS (EI$^+$) [M]$^+$ calcd for C$_{18}$H$_{30}$OSi$_2$ 318.1835, found 318.1831.

2,2,5,5-Tetra(prop-2-enyl)-2,5-disila-1-oxacyclopentane (9): colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.60–1.75 (m, 8H), 4.85–5.00 (m, 8H), 5.70–5.89 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 5.2, 22.8, 114.4, 133.0; HR MS (Cl$^+$) [M+1]$^+$ calcd for C$_{14}$H$_{24}$OSi$_2$ 265.1366, found 265.1443.

Synthesis of (4-Bromophenyl)ethoxydi(prop-2-enyl)silane (1a): A dry and nitrogen flushed 100 mL two-necked flask, was charged with a solution of (4-bromophenyl)triethoxysilane (2.0 g, 6.26 mmol) in
diethyl ether (30 mL) was added allylmagnesium bromide (18.8 mL, 1.0M in ether, 18.8 mmol) in
diethyl ether at 0 °C. The reaction mixture was stirred at room temperature under nitrogen atmosphere
for 12 h and quenched with 10% HCl. It was then diluted with diethyl ether (50 mL) and the organic
layer was washed with a NaHCO₃ saturated solution (3 × 20 mL) and brine, dried over anhydrous
MgSO₄, and evaporated under reduced pressure. The crude mixture was purified by chromatography on
silica gel (5% EtOAc/hexane as eluent) to give 1.68 g (86%) of (4-bromophenyl)ethoxy di(prop-2-
enyl)silane (1a) as colorless liquid: ¹H NMR (270 MHz, CDCl₃) δ 1.21 (t, J = 6.7 Hz, 3H), 1.87–1.95 (m,
4H), 3.76 (q, J = 6.7 Hz, 2H), 4.89–4.98 (m, 4H), 5.71–5.87 (m, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.52 (d, J
= 8.4 Hz, 2H); ¹³C NMR (68 MHz, CDCl₃) δ 18.3, 21.1, 59.3, 115.0, 124.7, 130.9, 132.7, 133.9, 135.5;
HR MS (FAB⁺) [M-H]⁺ calcd for C₁₄H₁₇OBrSi 309.0311, found 309.0321. Anal. Calcd for C₁₄H₁₉OBrSi:
C, 54.02; H, 6.15. found: C, 53.93; H, 6.23; CAS Registry No. 959419-48-8.

Synthesis of Ethoxyphenyl di(prop-2-enyl)silane (1b): A dry and nitrogen flushed 100 mL two-
necked flask, was charged with a solution of triethoxyphenylsilane⁶ (5.0 g, 20.8 mmol) in diethyl ether
(100 mL) was added allylmagnesium bromide (62.4 mL, 1.0M in ether, 62.4 mmol) in diethyl ether at 0
°C. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h and
quenched with 10% HCl. It was then diluted with diethyl ether (50 mL) and the organic layer was
washed with a NaHCO₃ saturated solution (3 × 50 mL) and brine, dried over anhydrous MgSO₄, and
evaporated under reduced pressure. The crude mixture was purified by chromatography on silica gel
(5% EtOAc/hexane as eluent) to give 4.4 g (91%) of ethoxyphenyl di(prop-2-enyl)silane (1b) as
colorless liquid: ¹H NMR (270 MHz, CDCl₃) δ 1.21 (t, J = 7 Hz, 3H), 1.92–1.96 (m, 4H), 3.77 (q, J =
6.8 Hz, 2H), 4.89–5.00 (m, 4H), 5.75–5.91 (m, 2H), 7.37–7.41 (m, 3H), 7.56–7.60 (m, 2H); \(^{13}\)C NMR (68 MHz, CDCl\(_3\)) \(\delta\) 18.2, 21.1, 59.1, 114.6, 127.6, 129.6, 133.0, 133.9, 135.0; HR MS (FAB\(^+\)) [M-H]\(^+\) calcd for C\(_{14}\)H\(_{20}\)OSi 232.1283, found 232.1280; CAS Registry No. 881545-80-8.

**Synthesis of Ethoxy(4-methoxyphenyl)di(prop-2-enyl)silane (1c):** To triethoxy(4-methoxyphenyl)silane\(^6\) (0.5 g, 1.85 mmol) in Et\(_2\)O (20.0 mL) was added dropwise a solution of allylmagnesium bromide (5.55 mL, 1 M in Et\(_2\)O, 5.55 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10 h and quenched with 10% HCl. It was then diluted with Et\(_2\)O and the organic layer was washed with saturated NaHCO\(_3\) solution and brine, dried over anhydrous MgSO\(_4\), and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=20:1 as eluent) to give ethoxy(4-methoxyphenyl)di(prop-2-enyl)silane (0.442 g, 91%) as colorless liquid: \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 1.20 (t, \(J = 7.3\) Hz, 3H), 1.91–1.93 (m, 4H), 3.74 (q, \(J = 7\) Hz, 2H), 3.82 (s, 3H), 4.90–5.00 (m, 4H), 5.75–5.88 (m, 2H), 6.93 (d, \(J = 8.4\) Hz, 2H), 7.51 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (68 MHz, CDCl\(_3\)) \(\delta\) 18.4, 21.3, 54.9, 59.1, 113.5, 114.6, 125.9, 133.3, 135.6, 160.9; HRMS (EI\(^+\)) M\(^+\) calcd for C\(_{15}\)H\(_{22}\)O\(_2\)Si 262.1389, found 262.1385.

**Synthesis of Ethoxy(4-methylphenyl)di(prop-2-enyl)silane (1d):** To triethoxy(4-methylphenyl)silane\(^6\) (1.0 g, 4.0 mmol) was added dropwise a solution of allylmagnesium bromide (12.0 mL, 1 M in Et\(_2\)O, 12.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10 h and quenched with
10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethoxy(4-methylphenyl)di(prop-2-enyl)silane (0.887 g, 90%): ¹H NMR (270 MHz, CDCl₃) δ 1.21 (t, 3H, J = 6.8 Hz), 1.91–1.95 (m, 4H), 2.37 (s, 3H), 3.76 (q, J = 6.8 Hz, 2H), 4.90–5.00 (m, 4H), 5.76–5.91 (m, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H); ¹³C NMR (68 MHz, CDCl₃) δ 18.4, 21.3, 21.5, 59.2, 114.6, 128.6, 131.4, 133.2, 134.0, 134.7, 139.7; HRMS (EI⁺) M⁺ calcd for C₁₅H₂₂OSi 246.144, found 246.142.

**Synthesis of Ethoxydimethylphenylsilane (1e)**: To triethoxyphenylsilane (0.96 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of methylmagnesium bromide (5.3 mL, 3 M in Et₂O, 16.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 25:1 as eluent) to give ethoxydimethylphenylsilane (0.68 g, 95%) as colorless liquid: ¹H NMR (270 MHz, CDCl₃) δ 1.20 (t, 3H, J = 7.0 Hz), 3.67 (q, J = 7.0 Hz, 2H), 7.36–7.39 (m, 3H), 7.56–7.60 (m, 2H); ¹³C NMR (68 MHz, CDCl₃) δ -1.8, 18.4, 58.6, 127.8, 129.5, 133.4, 138.0; CAS Registry No. 1825-58-7
Synthesis of Ethoxymethyldiphenylsilane (1f): To diethoxydiphenylsilane (1.09 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of methylmagnesium bromide (4.0 mL, 3 M in Et₂O, 12.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethoxymethyldiphenylsilane (1f, 0.95 g, 98%) as colorless liquid: ^1H NMR (400 MHz, CDCl₃) δ 0.64 (s, 3H), 1.22 (t, J = 6.8 Hz, 3H), 3.78 (q, J = 6.8 Hz, 2H), 7.35–7.41 (m, 6H), 7.58–7.61 (m, 4H); ^13C NMR (100 MHz, CDCl₃) δ -3.0, 18.4, 59.2, 127.8, 129.8, 134.3, 136.1; CAS Registry No. 1825-59-8.

Synthesis of Methoxy(methyldiphenyl)silane (1g): To dimethoxydiphenylsilane (0.98 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of methylmagnesium bromide (4.0 mL, 3 M in Et₂O, 12.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give methoxy(methyldiphenyl)silane (1g, 0.89 g, 98%) as colorless liquid: ^1H NMR (400 MHz, CDCl₃) δ 0.64 (s, 3H), 3.54 (s, 3H), 7.36–7.40 (m, 6H), 7.58–7.61 (m, 4H); ^13C NMR (100 MHz, CDCl₃) δ -3.6, 50.9, 127.9, 129.9, 134.3, 134.8; CAS Registry No. 18407-48-2.
**Synthesis of Ethoxyethyldiphenylsilane (1h):** To diethoxydiphenylsilane (1.09 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of ethylmagnesium bromide (4.0 mL, 3 M in Et₂O, 12.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethoxyethyldiphenylsilane (1h, 0.93 g, 90%) as colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 1.04 (t, J = 7.2 Hz, 3H), 1.14 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 6.8 Hz, 3H), 3.77 (q, J = 6.8 Hz, 2H), 7.35–7.41 (m, 6H), 7.58–7.61 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 5.6, 6.7, 18.4, 59.2, 127.8, 129.7, 134.7, 135.1; CAS Registry No. 17964-40-8

![Structure of Ethoxyethyldiphenylsilane](image)

**Synthesis of Ethylmethoxydiphenylsilane (1i):** To dimethoxydiphenylsilane (0.98 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of ethylmagnesium bromide (4.0 mL, 3 M in Et₂O, 12.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethylmethoxydiphenylsilane (1i, 0.92 g, 95%) as colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (t, J = 7.2 Hz, 3H), 1.14 (q, J = 7.2 Hz, 2H), 3.54 (s, 3H), 7.36–7.42 (m, 6H), 7.58–7.60 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 5.2, 127.9, 129.8, 134.6, 134.7; CAS Registry No. 112675-36-2
Synthesis of Ethoxydiphenyl(prop-2-enyl)silane (1j): To diethoxydiphenylsilane (1.09 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of allylmagnesium bromide (12.0 mL, 1 M in Et₂O, 12.0 mmol) in 25 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc=20:1 as eluent) to give ethoxydiphenyl(prop-2-enyl)silane (1j, 1.02 g, 95%) as colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 1.22 (t, J = 7.2 Hz, 3H), 2.18–2.20 (m, 2H), 3.80 (q, J = 6.8 Hz, 2H), 4.88–4.97 (m, 2H), 5.79–5.87 (m, 1H), 7.36–7.42 (m, 6H), 7.59–7.61 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 18.4, 21.9, 59.5, 115.0, 127.8, 129.9, 133.0, 134.6, 134.7; CAS Registry No. 75203-53-1.

Synthesis of Methoxydiphenyl(prop-2-enyl)silane (1k): To dimethoxydiphenylsilane (0.98 g, 4.0 mmol) in Et₂O (20.0 mL) was added dropwise a solution of allylmagnesium bromide (12.0 mL, 1 M in Et₂O, 12.0 mmol) in 25.0 mL of Et₂O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et₂O and the organic layer was washed with saturated NaHCO₃ solution and brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give methoxydiphenyl(prop-2-enyl)silane (1k, 0.92 g, 90%) as colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 2.18–2.20 (m, 2H), 1.20 (s, 3H), 4.90–5.00 (m, 2H), 5.81–5.87 (m, 1H), 7.37–7.43 (m, 6H), 7.58–7.61
(m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.4, 51.6, 115.1, 127.9, 130.0, 132.8, 134.0, 134.7; CAS Registry No. 324000-48-8.

Synthesis of Ethoxytriphenylsilane (1l)$^{13}$: To diethoxydiphenylsilane (1.09 g, 4.0 mmol) in Et$_2$O (20.0 mL) was added dropwise a solution of phenylmagnesium bromide (12.0 mL, 1 M in Et$_2$O, 12.0 mmol) in 25 mL of Et$_2$O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et$_2$O and the organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethoxytriphenylsilane (1l, 1.2 g, 98%) as colorless liquid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.30 (t, $J = 7.0$ Hz, 3H), 3.94 (q, $J = 7.2$ Hz, 2H), 7.42–7.56 (m, 9H), 7.68–7.70 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.1, 60.4, 128.5, 130.6, 135.2, 136.1; CAS Registry No. 1516-80-9.

Synthesis of Methoxytriphenylsilane (1m)$^{14}$: To dimethoxydiphenylsilane (0.98 g, 4.0 mmol) in Et$_2$O (20.0 mL) was added dropwise a solution of phenylmagnesium bromide (12.0 mL, 1 M in Et$_2$O, 12.0 mmol) in 25.0 mL of Et$_2$O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et$_2$O and the organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give
methoxytriphenylsilane (1m, 1.04 g, 90%) as colorless liquid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.79 (s, 3H), 7.42–7.55 (m, 9H), 7.71–7.73 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.5, 128.6, 130.7, 134.6, 136.1; CAS Registry No. 1829-41-0.

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\text{Synthesis of Ethoxytri(prop-2-enyl)silane (1n)}^{15}: \text{To tetraethoxysilane (2.08 g, 10.0 mmol) in Et}_2\text{O (40.0 mL) was added dropwise a solution of allylmagnesium bromide (60.0 mL, 1 M in Et}_2\text{O, 60.0 mmol) in 50 mL of Et}_2\text{O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et}_2\text{O and the organic layer was washed with saturated NaHCO}_3\text{ solution and brine, dried over anhydrous MgSO}_4\text{ and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give ethoxytri(prop-2-enyl)silane (1n, 1.67 g, 85%) as colorless liquid: \(^1\)H NMR (400 MHz, CDCl}\(_3\)) \(\delta\) 1.19 (t, \(J = 6.8\) Hz, 3H), 1.69–1.71 (m, 6H), 3.74 (q, \(J = 6.8\) Hz, 2H), 4.40–4.97 (m, 6H), 5.79–5.85 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.4, 20.8, 59.1, 114.4, 133.3; CAS Registry No. 17962-20-8.}

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\text{Synthesis of Methoxymethyldiphenylsilane (1o): To tetramethoxysilane (1.52 g, 10.0 mmol) in Et}_2\text{O (40.0 mL) was added dropwise a solution of allylmagnesium bromide (60.0 mL, 1 M in Et}_2\text{O, 60.0 mmol) in 50 mL of Et}_2\text{O at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with 10% HCl. It was then diluted with Et}_2\text{O and the organic layer was washed with saturated NaHCO}_3\text{ solution and brine, dried over anhydrous MgSO}_4\text{ and evaporated under reduced pressure. The}
\]

S18
residue was chromatographed on silica gel (hexane/EtOAc = 20:1 as eluent) to give methylmethoxydiphenylsilane (10, 1.64 g, 90%) as colorless liquid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.69–1.73 (m, 6H), 3.51 (s, 3H), 4.91–5.00 (m, 6H), 5.79–5.85 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.4, 51.3, 114.5, 133.1; CAS Registry No. 17984-83-7.

References


The $^1$H NMR Experiment Procedure for Reaction A: A dry and nitrogen flushed Wilmad® NMR tube with J Young value was charged with ethoxytrimethylsilane ($1q$, 8.0 mg, 0.067 mmol), potassium carbonate (14.0 mg, 0.1 mmol), and CD$_3$CN (0.6 mL) followed by the addition of trimethyloxonium tetrafluoroborate (10.0 mg, 0.067 mmol). The reaction mixture was stirred at 80 °C for 4 h. The reaction mixture was then cooled and $^1$H NMR was recorded. The reaction A spectrum shows the formation of disiloxane 10 with the elimination of dimethyl ether and ethyl methyl ether.

**Reaction A $^1$H NMR (400 MHz, CD$_3$CN)**

![Spectrum 1](image)
Reaction A: $^1$H NMR Experimental Studies (400 MHz, CD$_3$CN)

\[
\begin{align*}
\text{Me} & \quad \text{Si} \quad \text{O} \quad \text{Me} \\
\text{Me} & \quad \text{Si} \quad \text{OEt} \quad \text{Me} \\
1q & \\
\end{align*}
\]

MeCN- $d_3$, 80 $^\circ$C, Me$_2$OBF$_4$, K$_2$CO$_3$

\[
\begin{align*}
\text{Me} & \quad \text{Si} \quad \text{O} \quad \text{Me} \\
\text{Me} & \quad \text{Si} \quad \text{Me} \quad \text{Me} \\
\text{Me} & \quad \text{Si} \quad \text{Me} \quad \text{Me} \\
\text{Me} & \quad \text{OEt} \\
10 \\
\end{align*}
\]

Spectrum 1: Reaction A $\delta$ 0.093 (s) ($2a$), 1.14 (t) ($6b$), 1.96 (m) ($X^1$), 2.17 (s) ($X^2$), 2.65 (d) ($X^3$), 3.20-3.35 (m) ($X^4$), 3.67 (q) ($X^5$)

Spectrum 2: Hexamethyldisiloxane (10) $\delta$ 0.084 (s) ($a$)

Spectrum 3: Trimethyloxonium tetrafluoroborate $\delta$ 4.38 (s) ($a$)

Spectrum 4: Dimethyl ether $\delta$ 3.24 (s) ($a$)

Spectrum 5: Diethyl ether $\delta$ 1.12 (t) ($b$), 3.42 (q) ($a$)

Spectrum 6: Ethyl methyl ether $\delta$ 1.11 (t) ($b$), 3.22 (s) ($c$), 3.35 (q) ($a$)

($X^1$- CH$_3$CN$-d_3$, $X^2$- uncharacterized singlet, $X^3$- disproportionation of Me$_2$OBF$_4$, $X^4$- merging of one singlet of –CH$_3$ of (CH$_3$)$_2$O, one singlet of –CH$_3$ of CH$_3$CH$_2$OCH$_3$ and one quartet of –CH$_2$CH$_3$ of CH$_3$CH$_2$OCH$_3$, $X^5$- speculated singlet of –CH$_3$ of disilylmethyloxonium intermediate)
Reaction A:

1. $\text{SiO}_2 \rightarrow \text{Si}$
2. $\text{BF}_3$
3. $\text{O}_3$
4. $\text{O}_5$
5. $\text{SiO}_2$
6. $X = \text{-CH}_3 (s) \text{ of CH}_3\text{I}$

$[\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_5\text{OCH}_3]$
The $^1$H NMR Experiment Procedure for Reaction B: A dry and nitrogen flushed Wilmad® NMR tube with J Young value was charged with ethoxytrimethylsilane ($1q$, 8.0 mg, 0.067 mmol) and CD$_3$CN (0.6 mL) followed by the addition of trimethyloxonium tetrafluoroborate (10.0 mg, 0.067 mmol). The reaction mixture was stirred at 50 °C for 30 min. The reaction mixture was then cooled and $^1$H NMR was recorded. The reaction B spectrum shows the formation of fluorosilane 11 with the elimination of dimethyl ether and ethyl methyl ether.

**Reaction B $^1$H NMR (400 MHz, CD$_3$CN)**
Reaction B: $^1$H NMR Experimental Studies (400 MHz, CD$_3$CN)

![Chemical Reaction Diagram]

Spectrum 1: Reaction A $\delta$ 0.23 (d) (a, fluorosilane 11), 1.14 (t) (6b), 1.45 (t) (X$^1$), 1.96 (m) (X$^2$), 2.89 (d) (X$^3$), 2.98 (d) (X$^3$), 3.26 (s) (4a), 3.27 (s) (6c), 3.39 (q) (6a), 4.53 (q) (X$^1$)

Spectrum 2: Hexamethyldisiloxane (10) $\delta$ 0.084 (s) (a)

Spectrum 3: Trimethyloxonium tetrafluoroborate $\delta$ 4.38 (s) (a)

Spectrum 4: Dimethyl ether $\delta$ 3.24 (s) (a)

Spectrum 5: Diethyl ether $\delta$ 1.12 (t) (b), 3.42 (q) (a)

Spectrum 6: Ethyl methyl ether $\delta$ 1.11 (t) (b), 3.22 (s) (c), 3.35 (q) (a)

(X$^1$- triplet and quartet of –CH$_2$–CH$_3$– of speculated silyloxonium intermediate, X$^2$- MeCN-d$_3$, X$^3$- disproportionation of Me$_3$OBF$_4$)
X = -CH₃ (s) of CH₃I

[C₂H₅ONa + CH₃I → C₂H₅OCH₃]
Additional Experiments:

Reaction 1.

Procedure: A dry and nitrogen flushed 10 mL screw-capped vial was charged with silanol 12 (1.0 mmol), acetonitrile (5.0 mL) followed by the addition of potassium carbonate (207.3 mg, 1.5 mmol) and trimethyloxonium tetrafluoroborate (148 mg, 1.0 mmol). The reaction mixture was stirred at 100 °C for 90 min and quenched by dropwise addition of water (1.0–2.0 mL). It was then diluted with dichloromethane and the organic layer was washed with brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. ¹H NMR of the crude mixture showed no product.

![Chemical structure of reaction 1](image)

Reaction 2.

Procedure: A dry and nitrogen flushed 10 mL screw-capped vial was charged with fluorosilane 13 (1.0 mmol), acetonitrile (5.0 mL) followed by the addition of potassium carbonate (207.3 mg, 1.5 mmol) and trimethyloxonium tetrafluoroborate (148 mg, 1.0 mmol). The reaction mixture was stirred at 100 °C for 90 min and quenched by dropwise addition of water (1.0–2.0 mL). It was then diluted with dichloromethane and the organic layer was washed with brine, dried over anhydrous MgSO₄, and evaporated under reduced pressure. ¹H NMR of the crude mixture showed no product.

![Chemical structure of reaction 2](image)
(4-bromophenyl)ethoxydi(prop-2-enyl)silane (1a) $^1$H NMR (270 MHz, CDCl$_3$)
(4-bromophenyl)ethoxydi(prop-2-eny)silane (1a) $^{13}$C NMR (68 MHz, CDCl$_3$)
1,3-Bis(4-bromophenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2a) $^1$H NMR (270 MHz, CDCl$_3$)
1,3-Bis(4-bromophenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2a) $^{13}$C NMR (68 MHz,
Ethoxyphenyl[di(prop-2-enyl)]silane (1b) $^1$H NMR (270 MHz, CDCl$_3$)
Ethoxyphenyl[di(prop-2-enyl)]silane \((\textbf{1b})\) \(^{13}\text{C}\) NMR (68 MHz, CDCl\(_3\))
1,3-Diphenyl-1,1,3,3-tetra(prop-2-enyl)disiloxane (2b) $^1$H NMR (270 MHz, CDCl$_3$)
1,3-Diphenyl-1,1,3,3-tetra(prop-2- enyl)disiloxane (2b) $^{13}$C NMR (68 MHz, CDCl$_3$)
Ethoxy(4-methoxyphenyl)di(prop-2-enyl)silane (1c) $^1$H NMR (270 MHz, CDCl$_3$)
Ethoxy(4-methoxyphenyl)di(prop-2-enyl)silane (1c) $^{13}$C NMR (68 MHz, CDCl$_3$)
1,3-Bis(4-methoxyphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2c) $^1$H NMR (400 MHz, CDCl$_3$)
1,3-Bis(4-methoxyphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2c) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxy(4-methylphenyl)di(prop-2-enyl)silane (1d) $^1$H NMR (270 MHz, CDCl$_3$)
Ethoxy(4-methylphenyl)di(prop-2-enyl)silane (1d) $^{13}$C NMR (68 MHz, CDCl$_3$)
1,3-Bis(4-methylphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2d) $^1$H NMR (400 MHz, CDCl$_3$)
1,3-Bis(4-methylphenyl)-1,1,3,3-tetra(prop-2-enyl)disiloxane (2d) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxydimethylphenylsilane (1e) $^1$H NMR (270 MHz, CDCl$_3$)
Ethoxydimethylphenylsilane (1e) $^{13}$C NMR (68 MHz, CDCl$_3$)
1,1,3,3-Tetramethyl-1,3-diphenydisiloxane (2e) $^1$H NMR (400 MHz, CDCl$_3$)
1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane (2e) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxy(methyldiphenyl)silane (1f) $^1$H NMR (400 MHz, CDCl$_3$)
Ethoxy(methyldiphenyl)silane (1f) $^{13}$C NMR (100 MHz, CDCl$_3$)
Methoxy(methyldiphenyl)silane (1g) $^1$H NMR (400 MHz, CDCl$_3$)
Methoxy(methyldiphenyl)silane (1g) $^{13}$C NMR (100 MHz, CDCl$_3$)
1,3-Dimethyl-1,1,3,3-tetraphenyldisiloxane (4) $^1$H NMR (400 MHz, CDCl$_3$)
1,3-Dimethyl-1,1,3,3-tetraphenyldisiloxane (4) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxyethyldiphenylsilane (1h) $^1$H NMR (400 MHz, CDCl$_3$)
Ethoxymethylphenyldiphenylsilane (1h) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethylmethoxydiphenylsilane (1i) $^1$H NMR (400 MHz, CDCl₃)
Ethylmethoxydiphenylsilane (1i) $^{13}$C NMR (100 MHz, CDCl$_3$)
1,3-Diethyl-1,1,3,3-tetraphenyldisiloxane (5) $^1$H NMR (400 MHz, CDCl$_3$)
1,3-Diethyl-1,1,3,3-tetraphenyldisiloxane (5) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxydiphenyl(prop-2-enyl)silane (1j) $^1$H NMR (400 MHz, CDCl$_3$)
Ethoxydiphenyl(prop-2-enyl)silane (1j) $^{13}$C NMR (100 MHz, CDCl$_3$)
Methoxydiphenyl(prop-2-enyl)silane (1k) $^1$H NMR (400 MHz, CDCl$_3$)
Methoxydiphenyl(prop-2-enyl)silane (1k) $^{13}$C NMR (100 MHz, CDCl$_3$)
1,1,3,3-Tetraphenyl-1,3-di(prop-2-enyl)disiloxane (6) $^1$H NMR (400 MHz, CDCl$_3$)
1,1,3,3-Tetraphenyl-1,3-di(prop-2-enyl)disiloxane (6) $^{13}$C NMR (100 MHz, CDCl$_3$)
1,1,3,3,3-Hexaphenyldisiloxane (7) $^1$H NMR (400 MHz, CDCl$_3$)
1,1,3,3,3-Hexaphenyldisiloxane (7) $^{13}$C NMR (100 MHz, CDCl$_3$)
Ethoxy[tri(prop-2-enyl)]silane (1n) $^1$H NMR (400 MHz, CDCl$_3$)
Ethoxy[tri(prop-2-enyl)]silane (1n) $^{13}$C NMR (100 MHz, CDCl$_3$)
Methoxymethyldiphenylsilane (10) $^1$H NMR (400 MHz, CDCl$_3$)
Methoxymethyldiphenylsilane (1o) $^{13}$C NMR (100 MHz, CDCl$_3$)
1,1,3,3,3-Hex(prop-2-enyl)disiloxane (8) \( ^1H \) NMR (400 MHz, CDCl\(_3\))
1,1,3,3,3-Hex(prop-2-enyl)disiloxane (8) $^{13}$C NMR (100 MHz, CDCl$_3$)
2,2,5,5-Tetra(prop-2-enyl)-2,5-disila-1-oxacyclopentane (9) $^1$H NMR (400 MHz, CDCl$_3$)
2,2,5,5-Tetra(prop-2-enyl)-2,5-disila-1-oxacyclopentane (9) $^{13}$C NMR (100 MHz, CDCl$_3$)