

Highly Reactive Oligosilyltriflates – Synthesis, Structure and Rearrangement

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Supporting Information

Experimental

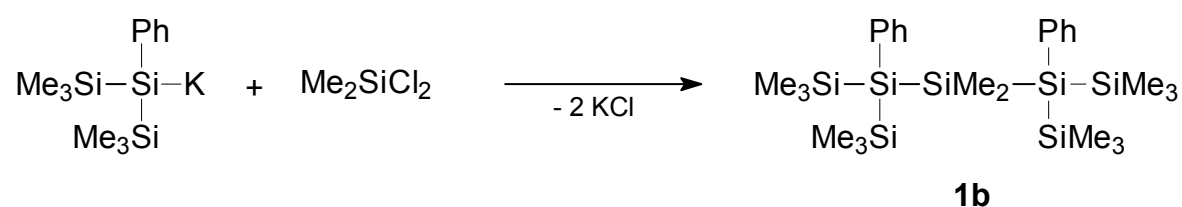
The manipulation of air and moisture sensitive compounds involved standard Schlenk line and dry box techniques. All solvents were freshly distilled under argon from alkali metals and also TfOH (CF₃SO₃H) was freshly distilled prior to use. Benzene-D₆ was dried over activated molecular sieves and stored in the glove box.

General procedure for the synthesis of the phenylogosilanes **1a-d** and **8**:

In a Schlenk type flask with magnetic stirrer were placed rapidly phenyltris(trimethylsilyl)silane (10 g, 30.8 mmol) and Bu^tOK (3.6 g, 32 mmol). The flask was evaporated and refilled with argon for three times, THF (100 mL) was added and the yellow-orange solution immediately formed was stirred overnight. Then, the solvent and other volatiles were removed under vacuum and the phenylbis(trimethylsilyl)silylpotassium x 3 THF obtained as a dark orange solid was suspended in pentane and cooled to -78°C. To this stirred suspension the related electrophile was added in one portion. Stirring was continued for 1 hour, and the mixture was allowed to warm up to room temperature within 2 hours. After addition of 40 ml (0.1 M) of hydrochloric acid, the organic phase was separated, dried with MgSO₄, and the solvent was evaporated. The raw products were purified as described below.

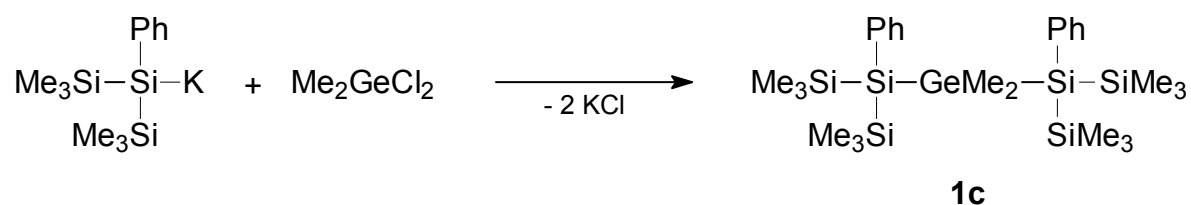
2,4-Diphenyl-1,1,1,3,3,5,5,5-octamethyl-2,4-bis(trimethylsilyl)pentasilane (**1b**)

Me_2SiCl_2 (1.9 ml, 15.7 mmol). The solid residue was re-crystallized from acetone to give **2a** (6.64 g, 77%); mp 126-128°C; ^1H NMR (C_6D_6 , 250 MHz): δ 0.20 (s, SiMe_3 , 36H), 7.11-7.57 (2m, SiPh, 10H). 0.70 (s, SiMe_2 , 6H); ^{13}C NMR (C_6D_6 , 63 MHz): δ 1.8 (SiMe_3), 1.9 (SiMe_2), 128.0, 128.2, 136.1, 137.3 (SiPh); ^{29}Si NMR (C_6D_6 , 79.5 MHz): δ -12.3 (SiMe_3), -33.2 (SiMe_2), -70.5 (SiPh). - MS: (70eV, m/z in %): 560 (1) [M^+], 545 (4) [$\text{M}^+ - \text{Me}$], 487 (3) [$\text{M}^+ - \text{SiMe}_3$]. - Anal. Calc. for $\text{C}_{26}\text{H}_{52}\text{Si}_7$ (561.29): C, 55.64; H, 9.34. Found: C, 54.60; H, 9.27.



2,4-Diphenyl-1,1,1,3,5,5,5-octamethyl-2,4-bis(trimethylsilyl)-3-germa-pentasilane (**1c**)

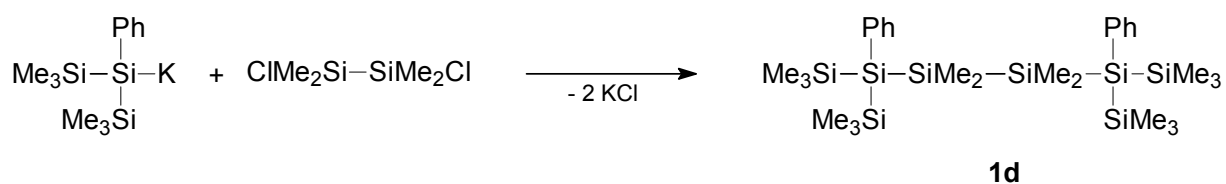
Me_2GeCl_2 (2.73 g, 15.7 mmol). Raw **1c** was suspended in cold ethanol, filtered off and dried under vacuum, yield 6.63 g (71%); mp 125°C; ^1H NMR (C_6D_6 , 250 MHz): δ 0.21 (2s, SiMe_3 , $2 \times 18\text{H}$), 0.82 (s, GeMe_2 , 6H), 7.11-7.14, 7.53-7.57 (2m, SiPh, 10H); ^{13}C NMR (C_6D_6 , 63 MHz): δ 1.6 (SiMe_3), 1.7 (GeMe_2), 127.9, 128.3, 136.5, 137.1 (SiPh); ^{29}Si NMR (C_6D_6 , 79.5 MHz): δ -12.1 (SiMe_3), -62.8 (SiPh). - Anal. Calc. for $\text{C}_{26}\text{H}_{52}\text{GeSi}_6$ (605.80): C, 51.55; H, 8.65. Found: C, 51.15; H, 8.58.



2,5-Diphenyl-1,1,1,3,3,4,4,6,6,6-decamethyl-2,5-bis(trimethylsilyl)hexasilane (**1d**)

$\text{ClMe}_2\text{Si}-\text{SiMe}_2\text{Cl}$ (2.91 ml, 15.6 mmol). The solid residue was re-crystallized from acetone to give 7.71 g (81 %) of **1d**; mp 155-162°C; ^1H NMR (C_6D_6 , 250 MHz): δ 0.31 (s, SiMe_3 , 36 H),

0.35 (s, SiMe₂, 12 H), 7.11-7.20, 7.61-7.64 (2m, SiPh, 10 H); ¹³C NMR (C₆D₆, 63 MHz): δ 2.0 (SiMe₃), -0.6 (SiMe₂), 128.1, 128.3, 136.1, 137.1 (SiPh); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -72.0 (SiPh), -34.2 (SiMe₂), -12.5 (SiMe₃). - MS: (70eV, m/z in %): 618 (3) [M⁺], 603 (5) [M⁺-Me], 367 (100) [M⁺-SiPh(SiMe₃)₂]. - Anal. Calc. for C₂₈H₅₈Si₈ (619.45): C, 54.29; H, 9.44. Found: C, 53.26; H, 9.15.



2,6-Diphenyl-1,1,1,3,3,4,5,5,7,7,7-undecamethyl-2,6-bis(trimethylsilyl)-4-[1,1,3,3,3-pentamethyl-2-phenyl-2-trimethylsilyl-trisilanyl]heptasilane (8)

(ClMe₂Si)₃SiMe (3.23 g, 10 mmol). The solid residue was re-crystallized from acetone to give 7.1 g (73%) of **8**; mp 180°C; ¹H NMR (C₆D₆, 250 MHz): δ 0.31 (s, SiMe₃, 54 H), 0.32 (s, SiMe₂, 18 H), 0.63 (s, Me, 3 H), 7.10-7.22, 7.59-7.74 (m, phenyl, 15 H); ¹³C NMR (C₆D₆, 62.9 MHz): δ 2.0 (SiMe), 2.1 (SiMe), 2.4 (SiMe), 128.4, 137.4 (arom. C-H); 136.5, 137.3 (arom. quart. C); ²⁹Si NMR (C₆D₆, 59.6 MHz): δ -68.5 (SiPh); -56.8 (SiMe); -29.9 (SiMe₂); -12.0, -11.5 (SiMe₃). - MS (CI isobutane / FAB): m/z (%) = 955 (16) [M⁺-Me]; 897 (11) [M⁺-SiMe₃]; 719 (100) [M⁺-PhSi(SiMe₃)₂]. - Anal. Calc. for C₄₃H₉₀Si₁₃ (972.29): C, 53.12; H, 9.33. Found: C, 52.33; H, 9.19.



2,2,4,4-Tetramethyl-3,3,5,5-tetrakis(trimethylsilyl)-1-oxa-tetrasilacyclobutane (4)

TfOH (0.5 ml, 5.7 mmol) was added at room temperature to a solution of oligosilane **1d** (1.67 g, 2.7 mmol) in CH₂Cl₂ (30 ml) and the mixture was stirred for 2 hrs. After addition of water (30 ml) to the stirred solution the organic phase was separated, dried with MgSO₄, and the solvent was evaporated. The solid residue was re-crystallized from acetone to give **4** (1.18 g, 86%); ¹H NMR (C₆D₆, 250 MHz): δ 0.31, 0.28 (2s, SiMe₃, 2 × 18H), 0.55, 0.44 (2s, SiMe₂, 2 × 6H); ¹³C NMR (C₆D₆, 63 MHz): δ 3.4 (SiMe₃), 6.6, 0.1 (SiMe₂); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -8.2, -15.5 (SiMe₃), 28.3 (OSiMe₂), -1.4 (OSi(SiMe₃)₂) -23.7 (SiMe₂), -145.7 (quart. Si). - MS: (70eV, m/z in %): 480 (90) [M⁺], 465 (20) [M⁺ - CH₃], 407 (80) [M⁺ - Si(CH₃)₃]. - Anal. Calc. for C₁₆H₄₈OSi₈ (481.246): C, 39.93; H, 10.05. Found: C, 39.89; H, 9.86.

