

Tris(trimethylsilyl)methane and Tris(dimethylphenylsilyl)methane: Preparation and Comparison of some Alkene and Cyclopropane Derivatives

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(Received 14 September 2007, Accepted 13 November 2007)

It is known that metalation of $(RMe_2Si)_3CH$ ($R: a = Me, b = Ph$) with MeLi in THF yields $(RMe_2Si)_3CLi$, which when reacted with allyl bromide, $(RMe_2Si)_3C-CH_2-CH=CH_2$ (**1a**, **1b**) are produced. In this study, although $(PhMe_2Si)_3CLi$ does not react with benzyl bromide, under the same conditions $(Me_3Si)_3CLi$ does, giving the expected product. We found that the bromination of **1b** was unsuccessful and the reaction of **1a** occurs in low yield due to severe steric hindrance. This idea is supported by our results, which show that, when treated with dichlorocarbene and dibromocarbene, **1a** and **1b** yield the related dihalocyclopropanes. Furthermore, reduction of the obtained products gives the dehalogenated compounds.

Keywords: Tris(dimethylphenylsilyl)methane, Tris(trimethylsilyl)methane, Bulky ligands, Cyclopropane, Gem-dihalocyclopropane

INTRODUCTION

Organosilicon compounds containing bulky groups, such as $(Me_3Si)_3C$ (denoted by Tsi) or $(PhMe_2Si)_3C$ (denoted by Tpsi), exhibit unusual reactivity and have novel structures because of the severe steric hindrance produced at the centers to which they are attached [1-4]. There have been many fruitful studies of compounds in which the very bulky ligands, mainly $(Me_3Si)_3C$ or $(PhMe_2Si)_3C$, are attached to a functional silicon or other metal centers, although there are few references in the literature about the attachment of $(Me_3Si)_3C$ groups to carbon [5-10]. Furthermore, as far as we are aware, there has been hitherto no references in the literature about the attachment of $(PhMe_2Si)_3C$ groups to carbon. Thus, we are interested in comparing the reactivity of $(PhMe_2Si)_3C$ vs. that of $(Me_3Si)_3C$ toward several carbon electrophiles. In this work, some new derivatives bearing the $(PhMe_2Si)_3C$ and

$(Me_3Si)_3C$ ligands have been prepared to investigate the steric hindrance of these groups and certain reactions with various reagents are examined.

EXPERIMENTAL

Reactions involving lithium metal, organolithium reagents and $LiAlH_4$ were carried out under dry argon to exclude oxygen and moisture from the reaction systems. Solvents were dried by standard methods.

Materials and Measurements

$(Me_3Si)_3CH$ and $(PhMe_2Si)_3CH$ were prepared according to the literature methods [1-5]. For the preparation of $(Me_3Si)_3CLi$ and $(PhMe_2Si)_3CLi$, bromoform (Merck), chloroform (Merck), tetrahydrofuran (THF, Merck) and diethyl ether (Merck) were dried by standard methods and Me_3SiCl (Merck), Me_2SiCl_2 (Merck), PhBr (Merck), n-BuLi (1.5 M in hexane, Merck) methyl iodide (MeI, Merck) and Li (Merck) were used as received. The 1H NMR

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and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz NMR spectrometer at room temperature using CDCl_3 as a solvent. The mass spectra were obtained with a Finnigan-Mat model 8400, operating at 70 eV. The IR spectra were recorded on a DR.8001-Shimadzu FT-IR spectrometer. Elemental analyses were carried out with a Heareus CHN-RAPID instrument. Melting points were determined on an Electrothermal 9100 apparatus.

Synthesis of $(\text{Me}_3\text{Si})_3\text{CCH}_2(\text{cyclo-C}_3\text{H}_3\text{Cl}_2)$ (**2a**, $\text{C}_{14}\text{H}_{32}\text{Si}_3\text{Cl}_2$)

To a mixture of **1a** (1.0 g, 3.7 mmol), CHCl_3 (2.4 g, 20.1 mmol), aqueous NaOH (50%) solution (15 ml) and CH_2Cl_2 (15 ml), we added $[\text{PhCH}_2\text{NEt}_3]\text{Cl}$ (0.2 g). The mixture was stirred vigorously to give a thick emulsion. The temperature was gradually raised to 40 °C and then kept between 40-45 °C by cooling with an ice bath. After the exothermic reaction was complete (about 1 h), the dark brown reaction mixture was heated to 55-60 °C for 1 h, then allowed to cool to 30 °C with water (50 ml). The organic layer was separated and the aqueous phase extracted with Et_2O (2×15 ml). The organic fractions were combined and washed with water, dried (Na_2SO_4), filtered and the solvent was evaporated. The residue was purified by preparative TLC (silicagel, hexane as eluent) to give **2a** (74%). m.p.: 98 °C. FT-IR (KBr, cm^{-1}): 2960 (aliphatic C-H), 1255, 821 (C-Si), 555 (C-Cl). ^1H NMR (CDCl_3): 0.17 (s, 27H, Tsi), 1.05 (t, 1H, HCH-Tsi), 1.52-1.57 (dd, 1H, HCH-Tsi), 1.71-1.73 (m, 2H, HCH CCl_2 , CH CCl_2), 2.24-2.28 ppm (dd, 1H, HCH CCl_2). ^{13}C NMR (CDCl_3): 1.5 (Tsi), 5.7 (C-SiMe $_3$), 29.0, 29.6, 30.4 (CH $_2$ -Tsi, CH, CH $_2\text{CCl}_2$), 62.3 ppm (CCl $_2$). *m/z* (EI): 258 (10% [M-CH $_2\text{CCl}_2$] $^+$), 231 (10% [M-CH $_2\text{CHCH}_2\text{CCl}_2$] $^+$), 124 (50% [CH $_2\text{CHCH}_2\text{CCl}_2$] $^+$), 97 (45% [CH $_2\text{CCl}_2$] $^+$), 73 (100% [Me $_3\text{Si}$] $^+$). Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{Si}_3\text{Cl}_2$: C, 47.3; H, 9.0. Found: C, 47.3; H, 9.0%.

Synthesis of $(\text{Me}_3\text{Si})_3\text{CCH}_2(\text{cyclo-C}_3\text{H}_3\text{Br}_2)$ (**3a**, $\text{C}_{14}\text{H}_{32}\text{Si}_3\text{Br}_2$)

To a vigorously stirred mixture of bromoform (7.0 g, 27.6 mmol), **1a** (1.0 g, 3.7 mmol), $[\text{PhCH}_2\text{NEt}_3]\text{Cl}$ (0.2 g) and 0.5 ml of ethanol was added to 10 ml of an aqueous solution of NaOH (50%) over 10 min while the temperature was maintained at 40-45 °C by intermittent cooling in a cold water

bath. After the addition, the mixture was maintained at this temperature for 3 h and then CH_2Cl_2 (15 ml) was added so that the reaction mixture became very thick. The mixture was then poured into water (50 ml). The organic layer was extracted with CH_2Cl_2 (2×100 ml) the combined organic layer was washed with water and dried over Na_2SO_4 . The residue was purified by preparative TLC (silicagel, n-hexane eluent) to give **3a** (70%). m.p.: 115 °C. FT-IR (KBr, cm^{-1}): 2959 (aliphatic C-H), 1257, 841 (C-Si), 534 (C-Br). ^1H NMR (CDCl_3): 0.17 (s, 27H, Tsi), 1.22-1.26 (t, 1H, HCH-Tsi), 1.53-1.58 (dd, 1H, HCH-Tsi), 1.69-1.76 (m, 1H, CH-CBr $_2$), 1.93-1.97 (dd, 1H, HCH-CBr $_2$), 2.17-2.38 ppm (dd, 1H, HCH-CBr $_2$). ^{13}C NMR (CDCl_3): 1.7 (Tsi), 5.9 (C-SiMe $_3$), 29.8, 31.4, 31.5 (CH $_2$ -Tsi, CH, CH $_2\text{CBr}_2$), 33.0 ppm (1C, CBr $_2$). *m/z* (EI): 258 (10% [M-CH $_2\text{CBr}_2$] $^+$), 200 (10% [CH $_2\text{CHCH}_2\text{CBr}_2$] $^+$), 187 (20% [CH $_2\text{CBr}_2$] $^+$), 73 (100% [Me $_3\text{Si}$] $^+$). Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{Si}_3\text{Br}_2$: C, 37.8; H, 7.2. Found: C, 37.7; H, 7.2%.

Synthesis of $(\text{Me}_3\text{Si})_3\text{CCH}_2(\text{cyclo-C}_3\text{H}_5)$ (**4a**, $\text{C}_{14}\text{H}_{34}\text{Si}_3$)

a) LiAlH_4 (0.53 g, 13.8 mmol) was gradually added to a stirred solution of **2a** (0.5 g, 0.2 mmol) in dry THF (10 ml). The reaction mixture was stirred at room temperature for 24 h. Aqueous saturated NH_4Cl solution was slowly added at 0 °C and the mixture was extracted with Et_2O . The extract was dried (Na_2SO_4), filtered and the solvent was evaporated. The residue was purified by preparative TLC (silicagel, n-hexane as eluent) to give **4a** (62%). m.p.: 80 °C. FT-IR (KBr, cm^{-1}): 2969 (aliphatic C-H), 1252, 835 (Si-C). ^1H NMR (CDCl_3): 0.11 (s, 27H, Tsi), 0.54-0.59 (m, 4H, cyclo-CH $_2$), 0.70-0.80 (m, 1H, CH), 1.66 (d, 2H, CH $_2$ -Tsi) ppm. ^{13}C NMR (CDCl_3): 1.6 (Tsi), 4.9 (C-SiMe $_3$), 8.4, 9.1 (cyclo-C $_3\text{H}_5$), 31.0 ppm (CH $_2$ -Tsi). *m/z* (EI): 286 (5% [M] $^+$), 213 (30% [M-Me $_3\text{Si}$] $^+$), 73 (100% [Me $_3\text{Si}$] $^+$). Anal. Calcd. for $\text{C}_{14}\text{H}_{34}\text{Si}_3$: C, 58.7; H, 11.8. Found: C, 58.6; H, 11.8%.

b) The reaction was repeated using **3a** and the results were identical to those mentioned above.

Synthesis of $(\text{PhMe}_2\text{Si})_3\text{CCH}_2\text{CH}=\text{CH}_2$ (**1b**, $\text{C}_{28}\text{H}_{38}\text{Si}_3$)

A solution of TpsiH (10.5 g, 25.1 mmol) was reacted with MeLi generated from MeI (4.1 g, 29.1 mmol) and Li (0.4 g, 57.1 mmol) in Et_2O (50 ml). After the lithiation of TpsiH was completed [13], a solution of allyl bromide (6 g, 49.6 mmol) in THF (10 ml) was added dropwise with stirring to the solution

at 0 °C and the mixture was stirred at the same temperature for 3 h. The solution was then poured into ice, extracted into Et₂O and the ethereal solution was dried with Na₂SO₄. After evaporation of Et₂O, the solid was recrystallized from EtOH to give **1b** (72%). m.p.: 136 °C. FT-IR (KBr, cm⁻¹): 3054 (Ar-H), 2950 (aliphatic C-H), 1592, 1481 (C=C), 1255, 821 (C-Si). ¹H NMR (CDCl₃): 0.18 (s, 18H, Tpsi), 3.0 (d, 2H, CH₂-Tpsi), 5.12-5.14 (dd, 1H, =HCH), 5.23-5.28 (dd, 1H, =HCH), 6.17-6.27 (m, 1H, =CH), 7.26-7.52 ppm (m, 15H, Ph). ¹³C NMR (CDCl₃): 0.0 (Tpsi), 9.4 (C-SiMe₂Ph), 34.1 (CH₂-Tpsi), 114.9 (=CH₂), 140.7 (=CH), 126.5, 127.6, 134.2, 139.7 ppm (Ph). *m/z* (EI): 443 (10% [M-Me]⁺), 135 [(100% [PhMe₂Si]⁺), 107 (35% [PhMe₂]⁺) 41 (42% [CH₂=CH-CH₂]⁺). Anal. Calcd. for C₂₈H₃₈Si₃: C, 73.7; H, 8.3. Found: C, 73.3; H, 8.4%.

Synthesis of (PhMe₂Si)₃CCH₂ (cyclo- C₃H₃Cl₂) (**2b**, C₂₉H₃₈Si₃Cl₂)

To a mixture of **1b** (1.0 g, 2.2 mmol), CHCl₃ (1.3 g, 11.0 mmol), aqueous NaOH (50%) solution (15 ml) and CH₂Cl₂ (15 ml) was added [PhCH₂NEt₃]Cl (0.2 g). The mixture was stirred vigorously to give a thick emulsion. The temperature was gradually raised to 40 °C and then kept between 40-45 °C using an ice bath. After the exothermic reaction was completed (about 1 h) the dark brown reaction mixture was heated to 55 °C for 1 h then allowed to cool to 30 °C with water (50 ml). The organic layer was separated and the aqueous phase extracted with Et₂O (2 × 100 ml). The organic fractions were combined and washed with water, dried (Na₂SO₄), filtered and the solvent was evaporated. The residue was purified by preparative TLC (silicagel, n-hexane and dichloromethane 1:1 as eluent) to give **2b** (65%). m.p.: 176 °C. FT-IR (KBr, cm⁻¹): 3061 (Ar-H), 2969 (aliphatic C-H), 1634, 1480 (C=C), 1251, 830 (C-Si), 550 (C-Cl). ¹H NMR (CDCl₃): 0.15 (s, 9H, Tpsi), 0.30 (s, 9H, Tpsi), 1.24-1.28 (t, 1H, HCH-Tpsi), 1.84-1.88 (dd, 1H, HCH-Tpsi), 1.93-1.98 (dd, 1H, HCHCl₂), 2.04-2.11 (m, 1H, CHCl₂), 2.86-2.90 (dd, 1H, HCHCl₂), 7.26-7.52 ppm (m, 15H, Ph). ¹³C NMR (CDCl₃): -0.4, -0.6 (Tpsi), 9.6 (C-SiMe₂Ph), 28.7, 30.0, 30.6 (CH₂-Tpsi, CH, CH₂CCl₂), 62.5 (CCl₂), 126.6, 127.8, 134.0, 139.3 ppm (Ph). *m/z* (EI): 406 (10% [M-PhMe₂Si]⁺), 135 (100% [PhMe₂Si]⁺) Anal. Calcd. for C₂₉H₃₈Si₃Cl₂: C, 64.3; H, 7.0. Found: C, 64.3; H, 7.1%.

Synthesis of (PhMe₂Si)₃CCH₂(cycloC₃H₃Br₂)(**3b**, C₂₉H₃₈Si₃Br₂)

To a vigorously stirred mixture of bromoform (4.3 g, 17.0 mmol), **1b** (1 g, 2.2 mmol), [PhCH₂NEt₃]Cl (0.2 g) and 0.5 ml of ethanol was added to 10 ml of an aqueous solution of NaOH (50%) over 10 min while the temperature was maintained at 40-45 °C by intermittent cooling with a cold water bath. After the addition, the mixture was maintained at this temperature for 3 h and then CH₂Cl₂ (15 ml) was added so that the reaction mixture became very thick. The mixture was then poured into water (50 ml). The organic layer was extracted with CH₂Cl₂ (2 × 100 ml), and the combined organic layer was washed with water and dried (Na₂SO₄). The residue was purified by preparative TLC (silicagel, n-hexane as eluent) to give **3b** (50%). m.p.: 185 °C FT-IR (KBr, cm⁻¹): 3067 (Ar-H), 2972 (aliphatic C-H), 1633, 1425 (C=C), 1257, 835 (C-Si), 530 (C-Br). ¹H NMR (CDCl₃): 0.14 (s, 9H, Tpsi), 0.28 (s, 9H, Tpsi), 1.42-1.49 (t, 1H, HCH-Tpsi), 1.93-1.98 (dd, 1H, HCH-Tpsi), 2.05-2.11 (m, 2H, CHCBr₂, HCHCBr₂), 2.80-2.84 (dd, 1H, HCHCBr₂), 7.22-7.54 ppm (m, 15H, Ph). ¹³C NMR (CDCl₃): -0.4, -0.7 (Tpsi), 10.0 (C-SiMe₂Ph), 30.5, 31.5, 32.6 (CH₂-Tpsi, CH, CH₂), 35.4 (CBr₂), 126.6, 127.3, 134.1, 139.4 ppm (Ph). *m/z* (EI): 453 (10% [M-Me-CH₂CHCBr₂]⁺), 135 (100% [PhMe₂Si]⁺) Anal. Calcd. for C₂₉H₃₈Si₃Br₂: C, 55.2; H, 6.0. Found: C, 55.3; H, 5.9 %.

Synthesis of (PhMe₂Si)₃CCH₂(cyclo-C₃H₅) (**4b**, C₂₉H₄₀Si₃)

a) LiAlH₄ (0.5 g, 13.9 mmol) was gradually added to a stirred solution of **2b** (0.5 g, 0.2 mmol) in dry THF (10 ml). The reaction mixture was stirred at room temperature for 24 h. Aqueous saturated NH₄Cl solution was slowly added at 0 °C and the mixture was extracted with Et₂O. The extract was dried (Na₂SO₄), filtered and the solvent was evaporated. The residue was purified by preparative TLC (silicagel, n-hexane and dichloromethane 1:1 as an eluent) to give TpsiCH₂(cyclo-C₃H₅) (60%). m.p.: 118 °C. FT-IR (KBr, cm⁻¹): 3062 (Ar-H), 2972 (aliphatic C-H), 1588, 1472 (C=C), 1253, 835 (Si-C). ¹H NMR (CDCl₃): 0.20 (s, 18H, Tpsi), 0.30-0.75 (m, 4H, cyclo-CH₂), 0.60 (m, 1H, CH), 1.00-1.04 (d, 2H, CH₂-Tpsi), 7.23-7.53 ppm (m, 15H, Ph). ¹³C NMR (CDCl₃): 0.0 (Tpsi), 9.4 (CH), 9.7, 10.75 (cyclo-C₃H₅), 34.7 (Tpsi-CH₂), 126.4, 127.5,

134.1, 140.10 ppm (*Ph*). m/z (EI): 470 (5% $[M]^+$), 135 (100% $[\text{PhMe}_2\text{Si}]^+$) 107 (50% $[\text{PhMe}_2]^+$). Anal. Calcd. for $\text{C}_{29}\text{H}_{40}\text{Si}_3$: C, 73.7; H, 8.5. Found: C, 73.4; H, 8.7%.

b) The reaction was repeated using **3b** and the results were identical to those mentioned above.

Synthesis of $(\text{Me}_3\text{Si})_3\text{C}-\text{CH}_2-\text{CHBr}-\text{CH}_2\text{Br}$ (**7**, $\text{C}_{13}\text{H}_{32}\text{Si}_3\text{Br}_2$)

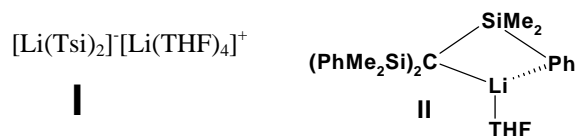
A solution of Br_2 (0.16 g, 1 mmol) in CCl_4 (15 ml) was added dropwise during a period of 30 min with stirring to solution of **1a** (1 g, 0.37 mmol) in CCl_4 (5 ml) at 0°C . The mixture was stirred for 1 h at room temperature, then the solvent was removed under reduced pressure and the residue was purified by TLC (silica gel, petroleum ether and dichloromethane 4:6) in 21% yield as a colorless liquid. FT-IR (KBr, cm^{-1}): 2953 (aliphatic C-H), 1250, 835 (Si-C), 510 (C-Br). ^1H NMR (CDCl_3): 0.27 (s, 27H, Tsi), 1.5-1.8 (2dd, 2H, CH_2 -Tsi), 3.3-3.5 (2dd, 2H, CH_2Br), 3.8 (m, 1H, CHBr) ppm. m/z (EI): 430 (5% $[M]^+$), 263 (30% $[\text{M}-\text{Br}-\text{Me}]$), 199 ($\text{M}-\text{Br}-\text{Me}_3\text{Si}-\text{Me}$), 73 (100% $[\text{Me}_3\text{Si}]^+$). Anal. Calcd. for $\text{C}_{13}\text{H}_{32}\text{Si}_3\text{Br}_2$: C, 36.1; H, 7.4. Found: C, 35.8; H, 7.4%.

RESULTS AND DISCUSSION

The compound $(\text{PhMe}_2\text{Si})_3\text{CH}$, obtained via the reaction of PhMe_2SiCl and CHBr_3 in the presence of *n*-BuLi at -78°C , was metalated with MeLi under the same conditions used for $(\text{Me}_3\text{Si})_3\text{CH}$ in a previous study [11]. The former study indicates that $(\text{PhMe}_2\text{Si})_3\text{CLi}$ is, indeed, produced in good yield, but has abnormally low reactivity. For example, $(\text{PhMe}_2\text{Si})_3\text{CLi}$ does not react with some silane electrophiles, such as Me_2SiCl_2 , Me_3SiCl , Et_2SiCl_2 , Et_2SiF_2 , EtMeSiHCl , PhMe_2SiCl , PhMe_2SiF , PhMeSiHCl or Ph_2SiF_2 , whereas all of them react satisfactorily with $(\text{Me}_3\text{Si})_3\text{CLi}$ [11].

In the present study, the first goal is to examine the possibility of the reaction of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ with benzyl bromide and allyl bromide as carbon electrophiles. It is noteworthy that, when a solution of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ was refluxed with benzyl bromide for 24 h during which no trace of precipitate of LiBr or color change was observed, such a precipitate did appear immediately upon subsequent addition of allyl bromide with a gradual change in solution color from red to yellow. The carbon-carbon double bond remained

unchanged during the reactions when the experimental conditions were carefully chosen. The much lower reactivity of $(\text{PhMe}_2\text{Si})_3\text{CLi}$, compared to that of $(\text{Me}_3\text{Si})_3\text{CLi}$, was attributed to marked steric hindrance resulting from the presence of the phenyl group. In the case of the benzyl bromide, probably because of the aforementioned steric hindrance, nucleophilic substitution does not occur. The lower reactivity of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ could also be associated with the fact that the Li-C bond is shielded from attack by this Ph group and possibly by the other Ph groups, but probably the more important reason is that the negative charge on the $[\text{Li}(\text{Tsi})_2]^-$ anion (I) makes it more reactive toward electrophiles than the neutral $(\text{PhMe}_2\text{Si})_3\text{CLi}$ (II) [11].

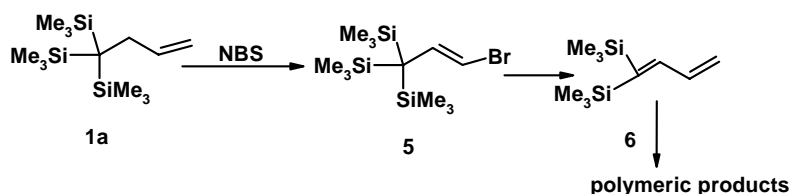


It was shown previously that compound **1a** reacts with *N*-bromosuccinimide, giving the halogenated allyl silane (**5**). In addition, compound **5** is unstable and decomposes to produce polymeric products, presumably by the way of 1,1-bis(trimethylsilyl)butadiene (**6**) (Scheme 1) [12,13].

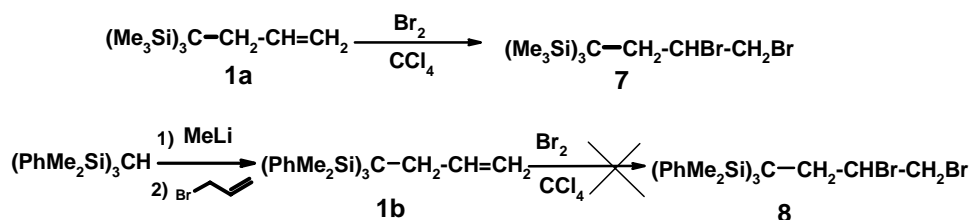
We were interested in studying the reactivity of the double bond in compounds **1a** and **1b**. It has been found that the reactivity of the carbon-carbon double bond in **1a** and **1b** are very different. For instance the bromination of **1a** led to compound **7**, but the preparation of compound **8** was unsuccessful (Scheme 2). However, olefines of all types can be converted to cyclopropane derivatives by a dichlorocarbene reaction, though difficulty may be encountered with those that are sterically hindered [12].

Compounds **1a** and **1b** react with the dichlorocarbene generated from the reaction of chloroform with 50% aqueous NaOH in the presence of a catalytic amount of the quaternary ammonium salt $[\text{PhCH}_2\text{NEt}_3]\text{Cl}$ to give **2a** and **2b** as new cyclopropane derivatives of **1a** and **1b**, respectively. In a similar manner, the treatment of dibromocarbene, generated from the reaction of bromoform with 50% aqueous NaOH in the presence of the same phase transfer catalyst and a trace amount of ethanol, with compounds **1a** and **1b** gives compounds **3a** and **3b**. It is evident from these results that the

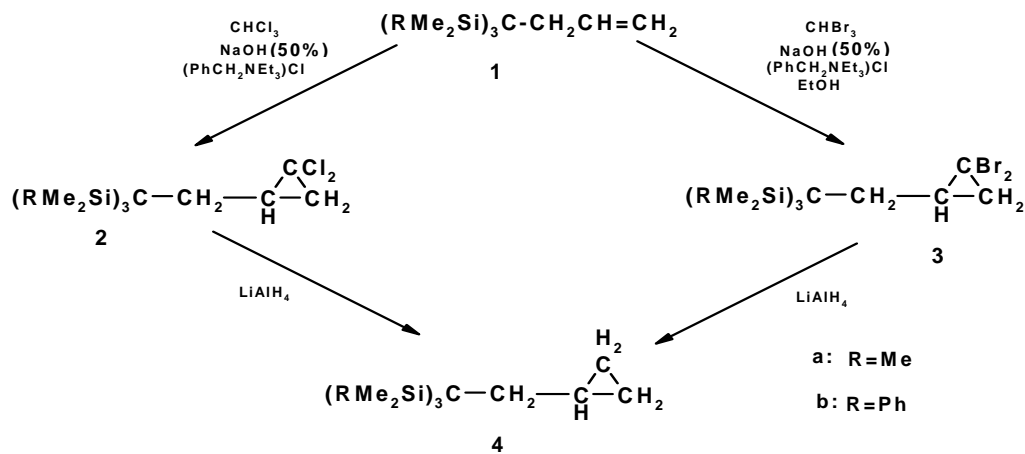
Tris(trimethylsilyl)methane and Tris(dimethylphenylsilyl)methane



Scheme 1



Scheme 2



Scheme 3

increased steric factor presented by the $(\text{PhMe}_2\text{Si})_3\text{C}-$ group does not cause a decrease in yield. Each of the above gem-dihalocyclopropanes undergoes reduction when allowed to react with an excess amount of LiAlH_4 in THF to produce the dehalogenated products **4a** and **4b**, as shown in this study for the first time (Scheme 3).

The ^1H NMR spectra of **1b** and **4b** show singlets corresponding to 18 protons of silyl methyls while doublets in the **2b** and **3b** spectra are obtained for the same protons of

silyl methyls. It is clear that the presence of halogen atoms and their stereo configuration toward silyl methyl groups is likely the reason for the obtained results, because, when **2b** and **3b** are reduced, the product **4b** also shows a singlet for 18 protons of silyl methyls. These results are not obtained for Tsi derivatives possibly because of the lower steric hindrance of $(\text{Me}_3\text{Si})_3\text{CLi}$ compared to that of $(\text{PhMe}_2\text{Si})_3\text{CLi}$.

A comparison of the reactivity of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ with that of $(\text{Me}_3\text{Si})_3\text{CLi}$ toward carbon electrophiles is very interesting.

Perhaps the severe steric hindrance in the $(\text{PhMe}_2\text{Si})_3\text{C}$ groups reduces the favorability of the reaction between $(\text{PhMe}_2\text{Si})_3\text{CLi}$ and benzyl bromide. The reactivity of the $(\text{Me}_3\text{Si})_3\text{C}$ -terminated alkenes differs from that of $(\text{PhMe}_2\text{Si})_3\text{C}$ -terminated alkenes. The failure of the bromination of $(\text{PhMe}_2\text{Si})_3\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ by bromine is an impressive illustration of the steric hindrance of the $(\text{PhMe}_2\text{Si})_3\text{C}$ group that affects even the reactivity of the adjacent double bond. It is clear, however, that the Ph group provides much greater steric hindrance than the Me group, but there is relatively little difference in the reaction of dihalocarbenes with $(\text{PhMe}_2\text{Si})_3\text{CLi}$ versus that with $(\text{Me}_3\text{Si})_3\text{CLi}$.

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