Poly(trifluoromethanesulfonatosilyl)methanes – Precursors to Polysilylmethanes

Sebastian Bommers, Hubert Schmidbaur*
Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-80747 Garching

Z. Naturforsch. 49b, 337 – 339 (1994); received December 14, 1993

Poly(silyl)methanes, Silanes, Trifluoromethanesulfonates

A new and efficient synthetic route to di- and tri(silyl)methane is presented. Starting from bis- and tris(phenylsilyl)methane, bis- and tris(trifluoromethanesulfonatosilyl)methane can be obtained by Si–Ph cleavage with equivalent quantities of trifluoromethanesulfonic acid (triflic acid). Their reduction with lithium aluminium hydride yields di- and tri(silyl)methane. Substitution of the previously employed liquid anhydrous hydrogen bromide by triflic acid thus offers an experimentally more simple alternative with shorter reaction times and high selectivity.

Introduction

Due to the growing interest in highly silylated methane derivatives (H₃Si)ᵣH₄₋ᵣC, n = 2,3,4, as feedstock gases for chemical vapour deposition of silicon carbon alloys [1–3] there is presently considerable effort to improve the synthetical pathways to these compounds. To date the most favourable route to di-, tri- and tetrasilylmethane is a three step synthesis via poly(arylsilyl)methanes (aryl = phenyl or p-tolyl) and poly(bromosilyl)methanes [4–6]. For the cleavage of the aryl groups from poly(arylsilyl)methanes treatment with an excess of anhydrous liquid hydrogen bromide at −78 °C in the absence of solvent is required in this process. To avoid Si–C cleavage in the resulting halosilanes, their reduction with lithium aluminium hydride has to be carried out in a two phase system employing a phase-transfer catalyst and with long reaction times of up to 96 hours at ambient temperature. As an alternative the “protodesilylation” [7–10] of bis- and tris(phenylsilyl)methane using trifluoromethanesulfonic acid (triflic acid) has now been introduced to replace the tedious hydrogen bromide procedure for which the handling and disposal of large amounts of HBr gas are indispensable.

Results

Bis- and tris(phenylsilyl)methane are readily available from standard chemicals [4–6]. Treatment of these two precursors with “triflic acid” CF₃SO₂OH leads to selective cleavage of the Si–Ph bonds. At 0 °C (see Experimental) the reaction time for quantitative conversion is less than one hour (eq. (1, 2)).

\[
\begin{align*}
\text{(1)} & \quad \text{CH}_2(\text{SiH}_2\text{Ph})_2 + 2\text{CF}_3\text{SO}_2\text{OH} \rightarrow 2\text{C}_6\text{H}_6 + \text{CH}_2(\text{SiH}_2\text{OSO}_2\text{CF}_3)_2 \\
\text{(2)} & \quad \text{CH}(\text{SiH}_2\text{Ph})_3 + 3\text{CF}_3\text{SO}_2\text{OH} \rightarrow 3\text{C}_6\text{H}_6 + \text{CH}(\text{SiH}_2\text{OSO}_2\text{CF}_3)_3
\end{align*}
\]

Bis(trifluoromethanesulfonatosilyl)methane, as well as tris(trifluoromethanesulfonatosilyl)methane, are colourless liquids, which fume in air and cannot be distilled without decomposition. However, spectroscopic data of the crude products are in accordance with the proposed formulae (see Experimental).

Upon storage at room temperature, both compounds slowly undergo isomerisation and decomposition. As derived from ¹H NMR and ²⁹Si NMR spectroscopic results, inter- and intramolecular H₂OSOF₃ exchange lead to compounds with SiH(OSO₂CF₃)₃ and SiH₃ fragments. Although the isomerisations do not necessarily affect the yield of the following reduction step, the rearranged tris- and especially tetrakis(trifluoromethanesulfonatosilyl)methane compounds un-

* Reprint requests to Prof. Dr. H. Schmidbaur.

Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen
0932–0776/94/0300–0337/S 01.00/0
undergo Si–C-cleavage reaction more readily, thus leading to silyltriflate SiH₃(OSO₂CF₃), which gives rise to the formation of inflamable silane gas in the final step of the process.

Only if the final conversion of bis- and tris(trifluoromethanesulfonatosilyl)methane into di- and trisilylmethane through the reduction with lithium aluminium hydride is carried out immediately after the “protodesilylation”, the yields obtained are around 80%. Under standard reaction conditions with common solvents the reaction time will not exceed 4 hours for completion (eq. (3, 4)).

\[
\begin{align*}
\text{CH}_3\text{(SiH}_2\text{OSO}_2\text{CF}_3)_2 + \text{LiAlH}_4 & \rightarrow \text{CH}_3\text{(SiH}_3)_2 \quad (3) \\
\text{CH(SiH}_2\text{OSO}_2\text{CF}_3)_3 + \text{LiAlH}_4 & \rightarrow \text{CH(SiH}_3)_3 \quad (4)
\end{align*}
\]

In the reaction of tetrakis(β-tolysilyl)methane with four equivalents of triflic acid the rearrangements preceding the decomposition mentioned above are even more rapid. Even at reaction temperatures as low as −78 °C only decomposition products are obtained. The reduction of the reaction mixture with lithium aluminium hydride does not afford tetrasyllmethane. Large amounts of gaseous self-inflammable silanes are generated.

In summary, the synthetic route to poly(silyl)methanes via the corresponding silyl triflates offers significant advantages over the previously applied silylhalides. Experimental difficulties associated with working with large amounts of liquid hydrogen bromide etc. can be avoided, and the reaction time required for the cleavage of the phenyl groups and for reduction can be reduced from several days to only several hours. This applies to both CH₂(SiH₃)₂ and CH(SiH₃)₃. However C(SiH₃)₄ is not obtained in appreciable yield owing to extensive C–Si cleavage by hydride in the last step of the process.

**Experimental**

All experiments were carried out under pure dry nitrogen. Glassware and solvents were purified, dried and kept under nitrogen. C₆D₆ and CDC₁₃ was used as solvents for NMR spectroscopy, and tetramethysilane as the reference compound (JEOL GX 270, GX 400 and Bruker WT 100 SY spectrometers).

**Bis(trifluoromethanesulfonatosilyl)methane:** To 4.56 g (20 mmol) of bis(phenylsilyl)methane 3.51 ml (40 mmol) triflic acid was added at 0 °C. No solvent was added. After 10 min the mixture was allowed to warm to room temperature, and the benzene formed in the reaction was removed under reduced pressure. The yield was almost quantitative. −¹H NMR (100 MHz, C₆D₆): δ = 4.5 ppm (t, SiH₃), ¼(J(HSi)) = 254 Hz, ¾(J(HSiCH)) = 3.3 Hz; δ = 0.07 ppm (qui, CH₃), ¼(J(HCSiH)) = 3.3 Hz. −¹³C (¹H) NMR (100.53 MHz, CDCl₃): δ = 116.7 ppm (q, CF₃), ¼(J(CF)) = 317 Hz; δ = 3.8 ppm CH₃. −²⁹Si NMR (79.43 MHz, CDCl₃): δ = −3.54 ppm (t*isi*si, SiH₃), ¼(J(SiH)) = 254 Hz, ¾(J(SiCH)) = 9.9 Hz, ¾(J(SiCSiH)) = 4.1 Hz.

**Tris(trifluoromethanesulfonatosilyl)methane:** To a solution of 2.6 g (8 mmol) tris(phenylsilyl)methane 10 ml of toluene, 2.1 ml (24 mmol) of triflic acid was added at −20 °C. After 10 min the mixture was allowed to warm to room temperature and stirred for 1 h at room temperature. The whole mixture was used in the following reduction step without any further purification. The yield was quantitative. −¹H NMR (100 MHz, C₆D₆): δ = 4.71 ppm (d, SiH₂), ¼(J(HSi)) = 265 Hz, ¾(J(HSiCH)) = 2.4 Hz; δ = −0.5 ppm (sept, CH), ¼(J(HCSiH)) = 2.4 Hz. −¹³C NMR (100.53 MHz, C₆D₆): δ = 118.8 ppm (q, CF₃), ¼(J(CF)) = 318 Hz; δ = −4.47 ppm (d*sept, CH), ¼(J(CH)) = 107 Hz, ¾(J(CSiH)) = 9.7 Hz. −²⁹Si NMR (79.43 MHz, C₆D₆): δ = −7.44 ppm (t*isi*qui, SiH₃), ¼(J(SiH)) = 265 Hz, ¾(J(SiCH)) = 10.2 Hz, ¾(J(SiCSiH)) = 4.3 Hz.

**Disilylmethane and trisilylmethane — general procedure:** To a suspension of lithium aluminium hydride in 1.2-dimethoxyethane (glyme), the freshly prepared silyltriflate dissolved in a small amount of glyme is added dropwise at 0 °C. The resulting mixture is stirred under reflux conditions for 4 h. Under reduced pressure the product is passed through a condenser cooled to −25 °C or 10 °C, respectively, and received in a Schlenk tube kept at liquid nitrogen temperature.

**Disilylmethane:** 4.56 g (20 mmol) of bis(phenylsilyl)methane, 3.51 ml (40 mmol) of triflic acid, and 0.46 g (12 mmol) of lithium aluminium hydride yield 1.21 g of the product (80%) b.p. 15 °C. −¹H NMR (100 MHz, C₆D₆): δ = 3.6 ppm (t, SiH₃), ¼(J(HSi)) = 197.8 Hz, ¾(J(HSiCH)) = 4.6 Hz; δ = −0.60 ppm (sept, CH₂), −²⁹Si-NMR (79.4 MHz, C₆D₆): δ = −60.0 ppm (q*isi*isi, SiH₂), ¼(J(SiH)) = 200.4 Hz, ¾(J(SiCH)) = 9.5 Hz, ¾(J(SiCSiH)) = 4.5 Hz.

**Trisilylmethane:** 2.6 g (8 mmol) of tris(phenylsilyl)methane, 2.1 ml of triflic acid, and 0.27 g (7.2 mmol) of lithium aluminium hydride gave 0.63 g of the product (74%). −¹H NMR (100
MHz, C₆D₆): δ = -1.17 ppm (dez, CH); δ = 3.71 ppm (d, SiH₃), ¹J(HSi) = 204 Hz, ²J(HSiCH) = 4.4 Hz. - ²⁹Si-NMR (79.4 MHz, C₆C₆): δ = -59.3 ppm (q*̄d*̄sept), ¹J(SiH) = 202.2 Hz, ²J(SiCH) = 9.2 Hz, ³J(SiCSiH) = 4.6 Hz.

This work has been supported by Bundesministerium für Forschung und Technologie, Bonn, and by Fonds der Chemischen Industrie, Frankfurt.