PAPER

Highly reactive oligosilyltriflates—synthesis, structure and rearrangement[†]

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Received (in St. Louis, MO, USA) 7th June 2005, Accepted 17th October 2005 First published as an Advance Article on the web 3rd November 2005

The novel branched oligosilyltriflates of formula $[TfO(Me_3Si)_2Si]_2E$ (**2a–d**) [E = 0 (**2a**), $SiMe_2$ (**2b**), $GeMe_2$ (**2c**), $SiMe_2$ –SiMe₂ (**2d**)] and $[TfO(Me_3Si)_2SiSiMe_2]_3SiMe$ (**9**) have been prepared by the protodesilylation of $[Ph(Me_3Si)_2Si]_2E$ (**1a–c**), $[H(Me_3Si)_2Si]_2E$ (**5d**) and $[Ph(Me_3Si)_2SiSiMe_2]_3SiMe$ (**8**) using TfOH (CF₃SO₃H) as reagent in almost quantitative yields. The crystal structure of **2b** is reported.

Introduction

In recent years there has been a growing interest in well-defined polyfunctionalized oligosilanes as sources of materials with novel electronic properties.¹ The development of such compounds requires new synthetic methods for the manipulation of functional groups on the silicon backbone without Si–Si bond cleavage. One of such useful groups is the trifluoromethane-sulfonate group (TfO = CF₃SO₃), which can be selectively introduced by protodesilylation of hydrido, vinyl, allyl and phenyl silanes with trifluoromethanesulfonic acid (TfOH) giving the desired silyltriflates in high yields.²

Although the formation of multiple triflate functionalized oligosilanes, often obtained as thermally unstable oils, has been reported by protodesilylation of mainly perphenylated linear,³ cyclic⁴ and dendrimeric oligosilanes,⁵ nothing is known about their structures in the solid state. Herein we wish to report a rather straightforward and selective synthesis of a series of novel isolable and crystalline permethylated oligosilanes with two or three triflate functionalities and we report the first crystal structure of an oligosilylbis(triflate).

Results and discussion

Phenylsilanes, readily available and reactive derivatives towards the protodesilylation reaction, are ideal starting materials for the synthesis of oligosilyl triflates. Disadvantageous, however, is that in the presence of TfOH or related electrophilic reagents, linear oligosilanes with more electropositive substituents such as alkyl or silyl tend to rearrange under Si–Si bond cleavage or migration of substituents to branched structures.⁶ To avoid such unpredictable skeletal rearrangements, we primarily focused on the synthesis of already branched oligosilanes in which both phenyl groups, connected to tertiary silicon atoms, are separated from each other by different spacers groups.

The corresponding diphenyloligosilanes 1a-d (supporting information[†]) have been synthesized in good yields *via* salt

metathesis reactions by treatment of phenylbis(trimethylsilyl)silylpotassium with BrCH₂CH₂Br, Cl₂SiMe₂, Cl₂GeMe₂ and ClMe₂SiSiMe₂Cl, respectively.⁷ For the protodesilylation of **1a–d**, the progress of the reaction was monitored by ²⁹Si- and ¹⁹F-NMR spectroscopy.

When the oligosilanes **1a-c** were allowed to react with two equivalents of TfOH, immediately new fluorine signals for the triflate group appeared at around -75 ppm in the 19 F NMR spectrum and a significant shift for the tertiary silicon atom to lower field was observed: -70.9 (1a), -70.5 (1b) and -62.8ppm (1c) to 40.8 (2a), 39.3 (2b) and 44.8 ppm (2c).8 The remarkable changes in the chemical shift clearly indicate a complete Si-Ph bond cleavage under formation of the corresponding SiOTf functionality. The reaction proceeds facilely and highly selectively yielding the oligosilylbis(triflates) 2a-c in almost quantitative yields after removal of the solvent (eqn (1). The triflates so obtained are surprisingly thermally stable but highly moisture sensitive, colourless solids. They can be further purified by crystallization from pentane at low temperatures. The NMR spectra of the crystalline compounds are rather straightforward and are in full agreement with the structures proposed.



In addition, the molecular structure of **2b** has been confirmed by X-ray crystallography. Suitable crystals were grown from pentane solutions at RT. As seen in Fig. 1, the molecule has a total of 7 silicon atoms and a longest chain of 5 silicon atoms bearing two triflate groups at the 2- and 4-positions. Most of Si–Si bond lengths lie unremarkably within the range of 2.36–2.38 Å and the Si–Si–Si bond angles are variable but generally within the range 110–119°.

10.1039/b408573

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Published on 03 November 2005. Downloaded by University of Regina on 27/10/2014 12:09:53

[†] Electronic supplementary information (ESI) available: experimental details. See DOI: 10.1039/b408573f



Fig. 1 Molecular structure of **2b** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [A] and angles [°]: Si₂–O₁ 1.778(2), Si₃–O₄ 1.780(2), S₁–O₁ 1.520(2), S₂–O₄ 1.494(3), Si₁–Si₂ 2.3581(14), Si₁–Si₃ 2.3582(14), Si₃–Si₆ 2.3785(14), Si₂–Si₄ 2.3821(15), S₁–O₁–Si₂ 132.2(2), S₂–O₄–Si₃ 137.1(2), Si₂–Si₁–Si₃ 118.90(5), Si₁–Si₃–Si₆ 109.80(5).

The Si₄–Si₂–Si₁–Si₃–Si₆ pentasilane chain approximately adopts an all-*trans* conformation (T-T-T),⁹ which is known to be optimal for σ -conjugation.¹⁰ The geometry around the silicon atoms Si₂ and Si₃ attached to the triflate groups can be described as distorted tetrahedral. As a result of steric strain in the molecule the angles S₁–O₁–Si₂ [132.2°] and S₂–O₄–Si₃ [137.1°] are larger then in Ph₃SiOTf¹¹ with 129.06° but smaller than in (Bu^t)₃SiOTf¹² in which the bulky tertiary butyl groups force a significant widening of the angle to a value of 149.3°. The length of the Si–O bonds in **2b**, 1.778 Å and 1.78 Å, is not only significantly longer than those normally observed for Si–O bonds [1.64–1.66 Å],¹³ it is also longer than in (Bu^t)₃SiOTf [1.742 Å] and in Ph₃SiOTf [1.743 Å], implying that there is a significant ionic component in the bonding.¹⁴

Moreover, it is the longest so far observed for tetrahedral silyltriflates, ¹⁵ reflecting the strong electronic influence of the surrounding electropositive silyl substituents, which act as more electron donating groups than their carbon analogues in $(Bu^t)_3$ SiOTf. The silylium cation character in this compound is also reflected in the sum of the three Si–Si–Si bond angles (338.5° and 336.8°) around the two silyltriflate functionalities indicating a substantial flattening of the oligosilane backbone.

In striking contrast to the protodesilylation reactions described above, treatment of 1d with TfOH in dichloromethane yields a product which exhibits four signals in the ¹H-NMR spectrum, two for a SiMe₃ and two for a SiMe₂ group, instead of the two signals expected for bis(triflate) 2d. However, the structure of the liquid compound was clearly identified by means of NMR spectroscopy as the rearranged oligsilyl(bis)-triflate 3, which shows 6 signals in the ²⁹Si-NMR spectrum, two for a silyltriflate group, two for a primary silicon, one for a quaternary and one for a secondary silicon as well (Scheme 1). In addition, the proposed structure of 3 could be confirmed by hydrolysis, which gave the cyclic siloxane 4 exclusively (supporting information[†]).



The formation of **3** can be rationalized as a 1,2-oligosilyl rearrangement in the oligosilane backbone reflecting clearly the tendency of oligosilanes to undergo skeletal rearrangements under formation of highly branched structures as already could be shown by Ishikawa *et al.*^{6a} Attempts to avoid such a rearrangement by using the less polar solvent pentane led only to mixtures of **3** and the bis(triflate) **2d**, which could not be separated.

However, the reaction of the dihydrido compound **5d** with TfOH gave the desired bis(triflate) **2d** in almost quantitative yields according to the NMR spectra (eqn (2)). To our surprise, **2d** a stable crystalline solid does not tend to undergo a skeletal rearrangement into **3**, which, is in sharp contrast to the reaction of **1d** with TfOH.



The remarkable difference in the selectivity of the protodesilylation reaction of **1d** compared to **5d**, may be attributed to an intramolecular donor–acceptor interaction of the silyltriflate with the phenyl group. This may result in the transient formation of the bridged carbocationic species **7** after the first protodesilylation step (Scheme 2). Similar 1,5-bridged cationic systems with a thermodynamically more stable carbosilane backbone have already been characterized by NMR spectroscopy and are supported by quantum-mechanical calculations,¹⁶ and 1,3-bridged cationic carbosilanes are supposed to be intermediates in the solvolysis of silicon halides with the $[(Me_2ArSi)(Me_3Si)_2C]$ group.¹⁷ A hydrido group (X = H) being only a weak donor should not interact intramolecularly with the silyltriflate, thereby a rapid second protodesilylation occurs without a competitive skeletal rearrangement.



Scheme 2 Proposed mechanism for the skeletal rearrangement.



To summarise, the strong π -donor interaction of the phenyl group does not only significantly stabilize the transient bridged species 7, but leads to an increased reaction rate of the intramolecular 1.2-oligosilyl migration by anchimeric assistance.

Finally, and with the intention of confirming the concept successfully applied for the triflates 2a-c mentioned above, we extended our studies to the synthesis of triflate functionalized dendritic oligosilanes. As substrate we used compound **8**, an oligosilane dendrimer of first generation with a longest chain of 7 silicon atoms, which was prepared analogously by reaction of three equiv. of Ph(Me₃Si)Si–K with (ClMe₂Si)₃SiMe in good yields (Scheme 3).

Whereas, the treatment of 8 with three equiv. of TfOH in dichloromethane gave a mixture of several rearranged products of unknown composition, a microcrystalline precipitate of the dendritic oligosilyltris(triflate) 9 was formed using pentane as solvent. Although we were not able to obtain single crystals of 9 suitable for X-ray diffraction studies, the structure proposed was unambiguously evidenced by means of elemental analysis and NMR spectroscopic data.

Conclusion

The branched oligosilyltriflates **2a–d** and **9** have been prepared by protodesilylation using TfOH as reagent. Although highly moisture sensitive, these oligosilyltriflates are thermally stable and easy to handle crystalline compounds which can be obtained even in larger amounts. Therefore, they might be of interest as Lewis acid catalysts for a variety of organic transformations and as reactive reagents for the protection of OH groups in sugars or other natural products. Investigations with regard to the latter are currently in progress.

Experimental

General remarks

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. TfOH (CF₃SO₃H) was distilled prior to use, Ph(Me₃Si)₂Si-K × 3 THF,¹⁸ (Me₃Si)₂SiPh–SiPh(SiMe₃)₂, (**1a**),¹⁹ and (Me₃Si)₂SiH–SiMe₂–SiMe₂–SiH(SiMe₃)₂, (**5d**),²⁰ were prepared as previously described. The full preparation and characterization of the oligosilanes **1b-d**, **4** and **8** is given in the supporting information[†].

General procedure for the protodesilylation of 1a–d, 5d and 8. In a typical experiment, TfOH (1.1 equiv.) was added to a stirred solution of 1a–d, 5d or 8 in pentane or CH_2Cl_2 at 0 °C. The mixture was allowed to warm up to RT within 2 h. After evaporation of the solvent the solid residue was dried under high vacuum to remove the excess TfOH. Analytically pure samples of **2a–d** and **9** were obtained by recrystallization from pentane at -40 °C.

1,1,4,4,4-Hexamethyl-2,3-bis(trifluoromethanesulfonato)-2,3-bis(trimethylsilyl)tetrasilane (2a). 1a (1.355 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and pentane (10 ml). Yield 1.36 g (78%); ¹H NMR (C₆D₆, 250 MHz): δ 0.33 (s, SiMe₃, 36H); ¹³C NMR (C₆D₆, 63 MHz): δ 0.0 (SiMe₃), 119.0 (q, ¹*J*_{C-F} = 318.1 Hz, CF₃); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -8.7 (SiMe₃), 40.8 (SiOTf); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -74.4 (CF₃); Anal. Calc. for C₁₄H₃₆F₆O₆S₂Si₆ (647.05): C, 25.99; H, 5.61. Found: C, 25.67; H, 5.65%.

1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trifluoromethanesulfonato)-2,4-bis(trimethylsilyl)pentasilane (2b). 1b (1.51 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH₂Cl₂ (*ca.* 10 ml). Yield 1.69 g (89%); ¹H NMR (C₆D₆, 250 MHz): δ 0.31 (s, SiMe₃, 36H), 0.44 (s, SiMe₂, 6H); ¹³C NMR (C₆D₆, 63 MHz): δ 0.1 (SiMe₃), -2.7 (SiMe₂), 119.1 (q, ¹J_{C-F} = 318.5 Hz, CF₃); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -10.0 (SiMe₃), -32.4 (SiMe₂), 39.3 (SiOTf); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -74.4 (CF₃); Anal. Calc. for C₁₆H₄₂F₆O₆S₂Si₇ (705.21): C, 27.25; H, 6.00. Found: C, 26.34; H, 6.30%.

1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trifluoromethanesulfonato)-2,4-bis(trimethylsilyl)-3-germa-pentasilane (2c). 1c (1.635 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH₂Cl₂ (*ca.* 10 ml). Yield 1.84 g (91%); ¹H NMR (C₆D₆, 250 MHz): δ 0.30 (s, SiMe₃, 36H), 0.60 (s, GeMe₂, 6H); ¹³C NMR (C₆D₆, 63 MHz): δ -0.2 (SiMe₃), -2.1 (GeMe₂), 119.1 (q, ¹J_{C-F} = 317.1 Hz, CF₃); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ -9.5 (SiMe₃), 44.8 (SiOTf); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -75.7 (CF₃); Anal. Calc. for C₁₆H₄₂F₆O₆S₂Si₆Ge (749.71): C, 25.63; H, 5.65; F, 15.20. Found: C, 25.03; H, 5.34; F, 14.93%.

1,1,3,3,4,4,6,6,6-Decamethyl-2,5-bis(trifluoromethanesulfonato)-2,5-bis(trimethylsilyl)hexasilane (2d). 5d (0.40 g, 0.86 mmol), TfOH (0.16 ml, 1.89 mmol) and pentane (*ca*. 5 ml). Yield 0.55 g (84%); ¹H NMR (C₆D₆, 250 MHz): δ 0.27 (s, SiMe₃, 36H), 0.50 (s, SiMe₂, 12H); ¹³C NMR (C₆D₆, 75 MHz): δ 0.0 (SiMe₃), -3.0 (SiMe₂), 119.1 (q, ¹J_{C-F} = 318.1 Hz, CF₃); ²⁹Si NMR (C₆D₆, 59.6 MHz): δ -32.8 (SiMe₂), -10.7 (SiMe₃), 42.1 (SiOTf); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -74.7 (CF₃); Anal. Calc. for C₁₈H₄₈F₆O₆S₂Si₈ (763.36): C, 28.32; H, 6.34. Found: C, 27.91; H, 6.22%.

1,1,1,3,3,5,5-Heptamethyl-2,5-bis(trifluoromethanesulfonato)-2,4,4-tris(trimethylsilyl)pentasilane (3). 1d (1.67 g, 2.7 mmol), TfOH (0.5 ml, 5.7 mmol) and CH₂Cl₂ (*ca.* 10 ml). Yield 1.98 g (96%); ¹H NMR (C₆D₆, 250 MHz): δ 0.27, 0.29 (2s, SiMe₃, 2×18H), 0.47, 0.71 (2s, SiMe₂, 2×6H); ¹³C NMR (C₆D₆, 63 MHz): δ 0.6, 1.4 (SiMe₃), 2.8 (SiMe₂), 119.1 (q, ¹ J_{C-F} = 320.4 Hz, CF₃); ²⁹Si NMR (C₆D₆, 59.6 MHz): δ -10.0, -9.3 (SiMe₃), -29.4 (SiMe₂), 55.9 (SiMe₂OTf), 43.3 (SiOTf), -122.5 (quart. Si); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -75.5, -74.1 (CF₃); Anal. Calc. for C₁₈H₄₈F₆O₆S₂Si₈ (763.36): C, 28.32; H, 6.34. Found: C, 27.78; H, 6.29%.

1,1,1,3,3,4,5,5,7,7,7-Undecamethyl-2,6-trifluoromethanesulfonato-2,6-bis(trimethylsilyl)-4-[1,1,3,3,3-pentamethyl-2-trifluoromethanesulfonato-2-trimethylsilyltrisilanyl]heptasilane (9). 8 (1.75 g, 1.8 mmol), TfOH (0.5 ml, 5.7 mmol) and pentane (*ca.* 10 ml). After a few minutes a white solid immediately precipitates out which was isolated by filtration and drying under vacuum to give pure 9 (1.3 g, 61%); ¹H NMR (C₆D₆, 250 MHz): δ 0.34 (s, SiMe₃, 54H), 0.63 (s, SiMe₂, 18H) 0.8 (s, SiMe, 3H); ¹³C NMR (C₆D₆, 63 MHz): δ 0.5 (SiMe₃), 0.2 (SiMe₂), 0.8 (SiMe), 127.0 (CF₃); ¹⁹F NMR (C₆D₆, 235.3 MHz): δ -74.1 (CF₃); Anal. Calc. for C₂₈H₇₅F₉O₉S₃Si₁₃ (1188.17): C, 28.30; H, 6.36. Found: C, 28.01; H, 6.13%.

X-ray crystallography

The data collection for **2b** was done on a STOE-IPDS diffractometer using a graphite monochromated Mo K α radiation. The structure was solved by direct methods (SHELXS-86) and refined by the full matrix least-squares method against F^2 (SHELXL-93)²¹ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions and refined using the riding model.

Crystal data. $C_{16}H_{42}F_6O_6S_2Si_7$, M = 705.25, colourless prism, monoclinic, space group $P2_1/c$, a = 8.992(2), b = 16.534(3), c = 23.992(5) Å, $\beta = 92.85(3)^\circ$, V = 3562.6(13) Å³, T = 200 K, Z = 4, μ (Mo-K α) = 0.443 mm⁻¹, 8670 reflections measured, 4657 reflections independent of symmetry, 3692 reflections observed [$I > 2\sigma(I)$], 334 parameters, R1 = 0.045, wR2 (all data) = 0.121.‡

Acknowledgements

We thank Prof. Dr H. Oehme for his generous support and we gratefully acknowledge the support of our research by the Fonds der Chemischen Industrie.

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