New, Effective Method of Synthesis and Structural Characterization of Octakis(3-chloropropyl)octasilsesquioxane

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*Summary: Our new synthesis of octakis(3-chloropropyl)octasilsesquioxane (***1***) is based on a two-stage hydrolytic condensation of 3-chloropropyltrimethoxysilane. This enables the selective formation of the desired product more rapidly (4 days), in comparison to methods used to date (5 weeks), while the yield (35%) is comparable. The process is conducted in methanolic solution, with the first stage being acid hydrolysis and the second stage condensation in the presence of di-n-butyltin dilaurate as a catalyst.*

The polyhedral oligomeric silsesquioxane (POSS) molecules are monodisperse, well-defined chemical compounds consisting of rigid silica cores surrounded by symmetrically distributed functional groups. The hybrid character of silsesquioxanes permits obtaining covalent organic–inorganic links on the nanoscale. They are characterized by a considerable chemical stability and specific physical properties;[1] thus, they have become the objects of much interest in view of the range of their possible applications.[1–4] Cubic octafunctional POSS molecules are an ideal nanosized starting material for the synthesis of inorganic–organic hybrid octaarmed dendritic polymers.[5] POSS molecules have also emerged as a new class of nanofillers for the preparation of nanostructured composites of high performance.[6] Properties of silsesquioxanes depend on their composition and, first of all, on the type of organic substituents on their silicon atoms.

One versatile method of introduction of organic functional groups onto the cubic silsesquioxane core is based on nucleophilic substitution of the halogen atom in ω-haloalkyl derivatives of the silsesquioxane. The starting material, used in this method, is the octakis(3-chloropropyl)-substituted cubic silsesquioxane, obtained by the hydrolytic condensation of commercially available (3-chloropropyl)trimethoxysilane.[7]

Due to the considerable importance of these compounds as starting materials for the synthesis of a wide range of materials, we sought alternative conditions for the hydrolysis and condensation processes that would permit a significant reduction in the time and improve the selectivity of the synthesis of octakis(3-chloropropyl)octasilsesquioxane in good yield.

Results and Discussion

The condensation of (3-chloropropyl)trimethoxysilane to obtain octakis(3-chloropropyl)silsesquioxane, (T-PrCl)$_8$, usually is conducted by the method described by Marsmann and coworkers,[7] which is based on the patent by Weidner et al.[8] This is a standard acid hydrolysis, characterized by a very long reaction time (5 weeks) and low yield (from 27 to 31%).[5,7] Another method uses hydrolysis in acidic medium (HCl), but with the subsequent condensation conducted in basic medium (NH_4OH). This method leads to yields of condensation products exceeding 90%. However, the reaction product is a mixture of various oligomeric silsesquioxanes, and the selectivity for the target product (T-PrCl)$_8$ is very low.[9,10]

In our study we have applied the method presented in the Scheme 1.

The hydrolysis of $Cl(CH_2)_3Si(OCH_3)_3$ was performed in methanol in the presence of concentrated hydrochloric acid. The condensation step was carried out in the presence of di-*n*-butyltin dilaurate catalyst,[11] Dibutyltin dicarboxylates are well-known catalysts in silicone condensation reactions [12a,b] (for a review, see ref 12c). Dibutyltin dilaurate catalyst has been recently used in the hydrolysis of (γ-glycidoxypropyl)trimethoxysilane[13] and the condensation of silanols.[13,14] The first stage of the process was carried out at room temperature for 2 days. A hydrolysis time of less than 2 days resulted in a drastic decrease of the final product yield. In the second stage, 1 h after the addition of di-*n*-butyltin dilaurate to the reaction mixture, formation of a turbid and opalescent solution was observed. After 2 days, a crystalline precipitate was obtained, which was pure (T-PrCl)$_8$ (**1**), as confirmed by analyses. If the second stage was carried out for a longer time, a higher yield was obtained, but mainly in the direction of formation of amorphous oligo- and polysilsesquioxanes. Therefore, longer condensation reaction times are not recommended, if high selectivity to (T-PrCl)$_8$ is desired.

The final yield of product **1** was 35%, which is comparable to the yields obtained using the methods known to date.

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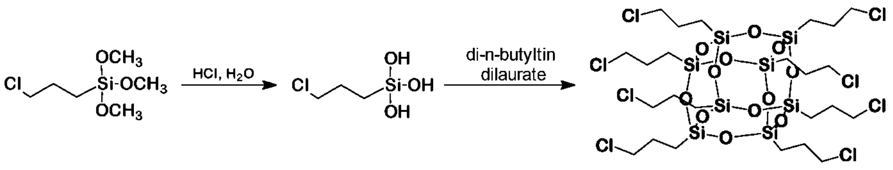
Scheme 1. Two-Step Synthesis of Octakis(3-chloropropyl)silsesquioxane, (T-PrCl)$_8$



However, it should be emphasized that our process is considerably faster (4 days) in comparison to previous methods (which required 5 weeks) and it enables the selective synthesis of (T-PrCl)$_8$ without admixtures of other silsesquioxanes. It is worth noting that $Cl(CH_2)_3Si(OCH_3)_3$, when used in methanol, can be used in higher concentrations (2.5 times higher than in previous methods). This increased volume efficiency makes scale-up of the synthesis more practical.[11]

As we have mentioned, product **1** is a crystalline solid. X-ray structure analysis as well as NMR and FT-IR spectroscopic analyses have confirmed the formation of the compound with the assumed structure.

The perspective view of the molecule of **1** is presented in Figure 1. The crystal structures of two other octakis(3-halopropyl) derivatives were determined by earlier workers, namely bromo[15] and iodo[7] analoques. The molecular dimensions of these compounds are similar to those found for **1**. There are, however, differences in the conformation of the side chains: in **1** all Si−C−C−C torsion angles are close to 180° (all chains are in an extended conformation), while in the two other compounds, one of these angles is close to 75°.

Interestingly, in all three structures the molecules lie on symmetry centers, but all of them crystallize in different unit cells (bromo derivative in monoclinic $P2_1/c$, iodo derivative in triclinic $P\bar{1}$, but quite different from the chloro derivative **1**). The lack of isostructurality in this family of closely related compounds might be connected with the absence of specific, directional intermolecular interactions.

Experimental Section

Synthesis of Octakis(3-chloropropyl)silsesquioxane (1). A solution of 150 mL of dry methanol and 5 mL of concentrated hydrochloric acid was placed in a two-necked, round-bottomed flask equipped with a condenser, an addition funnel, and a magnetic stir bar. To this solution was added dropwise a portion of (3-chloropropyl)trimethoxysilane (15 g, 0.075 mol) through the addition funnel over a period of 10 min with vigorous stirring. The stirring was continued for 2 h until the solution had cooled to room temperature. The reaction mixture was kept at room temperature for another 48 h without stirring. After 2 days, di-*n*-butyltin dilaurate (0.15 g, 0.24 mmol), as a condensation catalyst, was added with stirring. The reaction mixture was maintained at room temperature for 2 days until a white crystalline precipitate appeared. The solution was filtered and the crystals were collected, washed several times with methanol, and dried under vacuum. The final product was obtained in 35% yield (3.68 g), mp 206 °C.

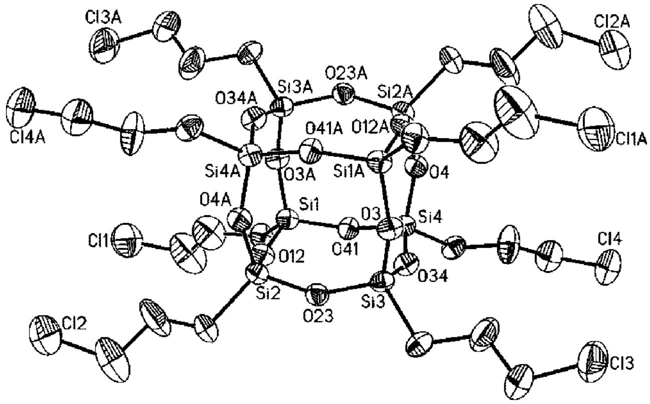


Figure 1. Perspective view of the molecule **1**. The thermal ellipsoids are drawn at the 30% probability level; atoms are shown as spheres with arbitrary radii. For clarity, hydrogen atoms are not shown. Only part of the molecule of greater occupancy is shown.

Spectroscopic data of **1** are as follows. ^1H NMR ($CDCl_3$, 298 K, 300 MHz; ppm): 0.78 (t, 16H, $SiCH_2$); 1.84 (qui, 16H, CH_2); 3.53 (t, 16H, CH_2Cl). ^{13}C NMR ($CDCl_3$, 298 K, 75.5 MHz; ppm): 9.88 ($SiCH_2-$); 26.38 ($-CH_2-$); 47.06 ($-CH_2Cl$). ^{29}Si NMR ($CDCl_3$, 298 K, 59.6 MHz; ppm): −67.28 (SiOSi). FT-IR (cm^{-1}): ν(CH) 2996–2875; δ(CH) 1457–1274; ν(SiOSi) 1230–940; δ(SiOSi) 552.

Details of the X-ray Crystal Structure Determination. Crystals of **1** were grown from methanol. Crystal data: $C_{24}H_{48}Cl_8O_{12}Si_8$, $M_r = 1036.94$, triclinic, space group $P\bar{1}$, $a = 10.020(1)$ Å, $b = 10.133(1)$ Å, $c = 12.855(1)$ Å, $V = 1217.7(3)$ Å^3, 14 128 reflections collected, 4278 independent reflections ($R_{int} = 0.037$), R1 ($I > 2\sigma(I)$) = 0.086. The final wR2 value was 0.198 (all data). CCDC-645879.

The molecule is symmetrical; it occupies the special position (at the center of symmetry) in the space group $P\bar{1}$. Some chlorine atoms are disordered over two alternative positions in the CH_2Cl groups. At lower temperatures, the structure probably undergoes a phase transition to another triclinic structure with two molecules occupying two different centers of symmetry. The bond lengths and angles are close to typical values; some discrepancies result, due to the relatively low quality of the crystals (caused by the vicinity of the phase transition).

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Supporting Information Available: A CIF file, giving crystallographic data that includes atomic coordinates, displacement parameters, and bond lengths and bond angles. This material is available free of charge via the Internet at http:/pubs.acs.org.

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