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ORGANOBORON DERIVATIVES OF STEREOREGULAR PHENYLCYCLOSILSESQUIOXANES

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Abstract

This paper presents the synthesis of organoboron derivatives of stereoregular 4-, 6-, and 12-unit phenylcyclosilsesquioxanes. All the compounds obtained were isolated in good yields (70-80%) and were fully characterized by ^{1}H, ^{13}C, ^{29}Si, ^{11}B NMR, IR spectroscopy, HRMS ESI, and elemental microanalysis. The structure of key modifier, obtained for the first time, 4-(tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) dimethylvinylsilane was also confirmed by single-crystal XRD.

In the past decade, there has been intense work in the field of synthesizing and studying the properties of new supramolecular systems.[1-4] This motivated by the desire to create new, unique materials with a given set of properties. The production of such materials became possible due to the development of modern physicochemical methods of analysis that allow one to accurately determine the structure of compounds and identify the "structure-property" relationship.[5]

Of the wide variety of existing supramolecular systems, three large classes can be distinguished that differ in the type of bonding: hydrogen-bonded organic frameworks (HOF),[6] covalent organic frameworks (COF)[7] and metal-organic frameworks (MOF).[8] Each of these supramolecular classes offers promise for various applications.[9-15] In this paper, we focus on the precursors for producing HOFs because such systems are capable of reversible structure reorganization, which allows one to obtain materials that are sensitive to external effects, which, in turn, is relevant for the creation of smart materials.[16,17]

The search for new chemical compounds exhibiting specific interactions is an important task. Its solution would allow one to obtain materials with specified physical properties that can

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change depending on certain external effects. From this point of view, organosilicon compounds, namely siloxane systems, appear to be the most promising objects for solving such problems. This is due to the wide variety of siloxane forms frameworks and owing to their unique physicochemical properties.[18,19]

In the past decade, significant progress has been achieved in the development of new individual compounds with well-defined spatial structures. It should be noted, that since the discovery of dendrimers[20,21] and molecular brushes,[22-24] the field of organosilicon supramolecular chemistry has undergone a fast evolution due to the advantages of siloxane and carbosilane structures and the methods for their synthesis. Our group has developed a unique method for synthesizing functional, stereoregular organosilesesquioxane macrocycles (4, 6 and 12 Si-O units)[25-28] that could not be obtained using classical silicone chemistry methods. This class of compounds can compete with the currently popular derivatives of calixarenes[29] and cyclodextrins[30] in the field of the production of new supramolecular systems.

On the other hand, boric acid derivatives are also intensely studied in order to obtain supramolecular structures with various architectures, as reflected in review articles by Kubo and Dichtel.[31-33,7] This interest in boric acid derivatives is due to the fact that they can form intermolecular hydrogen or donor-acceptor bonds and that they easily change their chemical behavior depending on the environment and the nature of functional groups.[34,35] The use of boric acid derivatives for modifying siloxane polymers proved to be an efficient method for the production of new materials with various valuable properties. For example, the weak interchain interactions of B-O or B-N moieties cause formation of a physical network resulting in changes in the rheological properties of polyborosiloxanes.[36] It is worth noting separately that boric acid derivatives can be selectively bound to natural substrates, for example sugars,[37-39] which allows such molecules to be used as biosensors or specific sorbents.[40-42] We assume that combining a flexible siloxane framework with fragments of boric acid derivatives would allow one to create a new class of borosiloxane compounds.

In this paper, we present a method for synthesizing new organoboron derivatives of stereoregular phenylcyclosilsesquioxanes that contain 4, 6, or 12 Si-O units in the structure.

To solve this problem, we synthesized hydride-containing macrocycles **1**, **2**, and **3** as siloxane precursors (**Figure 1**).

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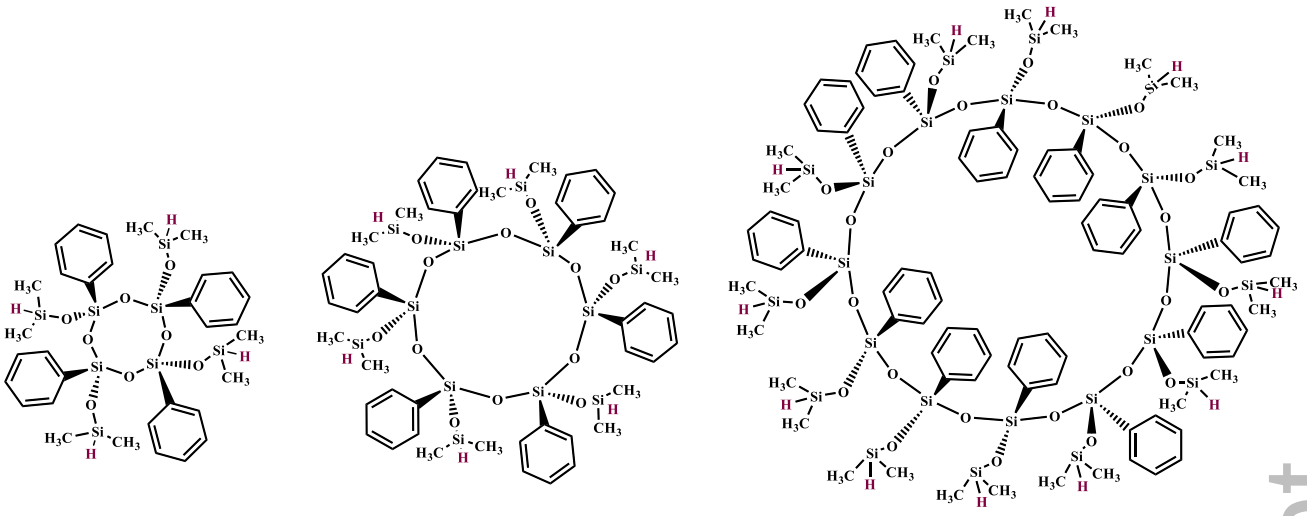
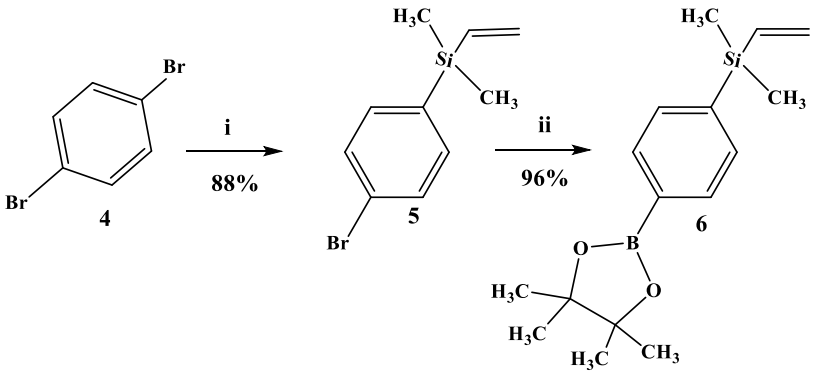


1 2 3

Figure 1. Structures of hydride-containing macrocycles

In order to modify cyclic precursors, compound **6** was synthesized by sequential substitution of bromine atoms in the starting 1,4-dibromobenzene **4** (Scheme 1). It should be noted, we previously[43] used an organoboron styrene derivative as a modifier incorporated by means of hydrosilylation. However, the use of this modifier is limited because it is liable to polymerization and necessitates a multi-stage synthesis. Therefore, for this work we developed its cheaper and more stable analogue, namely, the organosilicon modifier **6** containing a vinyl functional group capable of undergoing hydrosilylation.



Scheme 1. Reagents and conditions: i, 1. *n*-BuLi, THF, -78 °C, then ClSiVin(Me)$_2$; ii, *n*-BuLi, THF, -78 °C, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (IPTMDOB), then aqueous 1N HCl.

The structure of compound **6** was also confirmed by single-crystal XRD (the structure and description see Supporting Information).

The target compounds were synthesized by hydrosilylation in the presence of Karstedt's catalyst (**Figure 2**).

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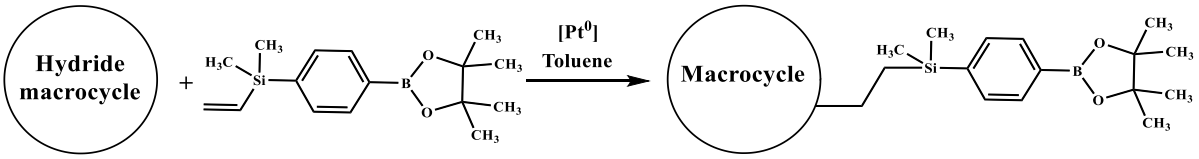

Figure 2. General scheme for synthesizing the new organoboron derivatives of stereoregular phenylcyclosilsesquioxanes.

The progress of the reaction was monitored by the disappearance of hydride (Si-H) signals in the ^{1}H NMR spectra. All the compounds obtained were purified by preparative chromatography. As a result, new organoboron derivatives of stereoregular phenylcyclosilsesquioxanes **7**, **8** and **9** were obtained in good yields (70-80%) **(Figure 3)**.

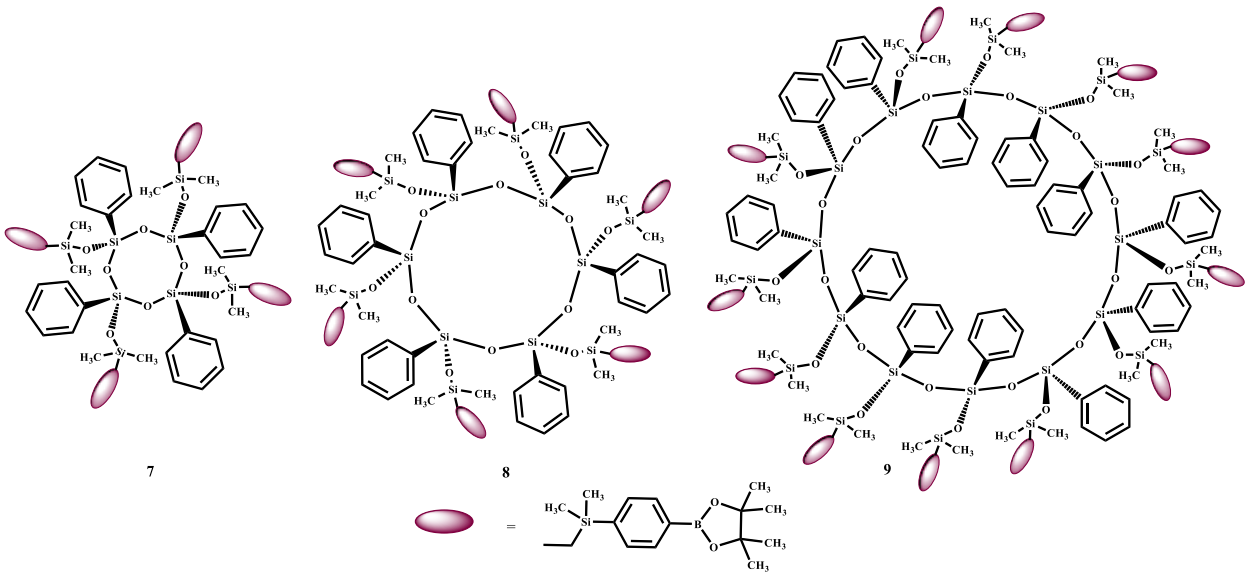

Figure 3. Proposed structures of new organoboron derivatives of stereoregular phenylcyclosilsesquioxanes.

The new compounds are a viscous liquid in the case of compound **7** and white powders for compounds **8** and **9**. These macrocycles very well soluble in such solvents as dichloromethane, toluene, benzene, chloroform, THF, hexane, and ethyl acetate.

Thus, we have suggested a simple and convenient method for synthesizing new organoboron derivatives of stereoregular phenylcyclosilsesquioxanes in high yields. The structure and purity of all the compounds obtained were confirmed by a set of methods of physicochemical analysis: ^{1}H, ^{13}C, ^{29}Si, ^{11}B NMR, IR spectroscopy, HRMS ESI, and elemental analysis. We intend to use all the organoboron macrocycle derivatives obtained as precursors for synthesizing new organo-inorganic hybrid systems. In addition, derivatives of this kind are interesting as macro initiators

and as starting compounds for synthesizing macromolecular scaffolds in Suzuki cross-coupling reactions.

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