Preliminary communication

Derivatisation of octasilsesquioxane with alcohols and silanols [1]

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Abstract

The T_8 cage in $(HSiO_{3/2})_8$ has been successfully derivatised to give $(ROSiO_{3/2})_8$ and $(R_3SiOSiO_{3/2})_8$ by the reaction with alcohols and silanols in the presence of catalytic amounts of amines. The most effective catalyst is Et_2NOH.

Keywords: Silicon; Octasilsesquioxane; Dendrimers; Hydrosilylation

1. Introduction

Much attention has recently been paid to the synthesis and investigation of 'octopus' molecules which are based on cage octasilsesquioxane cores with eight pendant molecular 'arms' [1-8]. These compounds are of considerable interest because of their unusual molecular architecture and the great structural variety that is possible as the nature of the pendant groups is varied. Published studies to date have been limited to arms such as simple hydrocarbons [1,2], halocarbon [4], and metal substituted ligands [5]. There are very few examples of functionalised arms [5,7,9] and none of branched arms. One important aim of our work is to use the T_8 core in dendrimer synthesis, where the eight-fold symmetry poses interesting challenges and opportunities.

The usual methods of synthesis of such compounds are either direct methods, such as careful hydrolysis of $RSiCl_3$ or $RSi(OEt)_3$ [8], or hydrosilylation of alkenes using $(HSiO_{3/2})_8$ [1-3] or $(HSiMe_2OSiO_{3/2})_8$ [5]. Recent reports [9,10] have described the synthesis of $(ROSiO_{3/2})_8$ compounds by synthesis and subsequent derivatisation of the Q_8^- $(^-OSiO_{3/2})_8$ ion with, for example, chlorosilanes.

It is desirable to develop as many methods of synthesis of octopus molecules as possible, and those that are

effective under mild conditions are particularly valuable. In this communication we present a very simple procedure that can give high yields of octopus molecules at ambient temperature and in a short time.

2. Results and discussion

Our method is based on the well-established reaction of hydridosilanes with alcohols and silanols to form alkoxysilanes and siloxanes respectively [11].

$$R_3SiH + HOR^1 = R_3SiOR^1 + H_2$$

$$R_3SiH + HOSiR_3^1 = R_3SiOSiR_3^1 + H_2$$

Many catalysts are known for these reactions, including amines, metal salts and acids. In the case of the derivatisation of the silsesquioxane $(HSiO_{3/2})_8$ the reaction must take place with retention of the cage structure. Pyridine is usually an excellent catalyst for reactions of silanes with alcohols and silanols, but is unsuitable here because we found that the octasilsesquioxane cage $(HSiO_{3/2})_8$ rapidly degrades when catalytic amounts of pyridine are added to a solution of $(HSiO_{3/2})_8$ at ambient temperature. No identifiable products were isolated from the $(HSiO_{3/2})_8$–pyridine mixture and the infrared spectrum suggested a mixture of H–silsesquioxanes were present.

Initial experiments using catalytic amounts of Et_2NOH (10–20 μl in ca. 10 ml reaction mixtures) were much more promising as the silsesquioxane cage remained intact in the presence of the catalyst. When

Et$_2$NOH (10 μl) was added to a mixture of Me$_3$Si(OSiMe$_3$)$_3$OH (3.3 g, 10.7 mmol) and (HSiO$_{3/2}$)$_8$ (0.5 g, 1.2 mmol), infrared spectrocopy showed the complete disappearance of SiH on the first examination of the mixture after about 1 h of gentle heating (80°C). The product was shown by gel permeation chromatography (GPC) and ^{29}Si NMR spectroscopy (δ − 110, −21.3,− 21.2,− 19.1,+ 7.2) to be reasonably pure (Me$_3$Si(OSiMe$_3$)$_3$OSiO$_{3/2}$)$_8$. Similarly, but with a spontaneous exotherm immediately after adding the catalyst, hexanol reacted within 5 min with (HSiO$_{3/2}$)$_8$. The reaction was carried out without solvent and, although the ^{29}Si NMR spectrum showed only one major peak at δ − 103, GPC and ^{1}H NMR spectroscopy showed the presence of impurities. More control and substantially pure products, with no further purification, were possible if the reaction with alcohols was carried out in solution at ambient temperature and the loss of SiH was followed by infrared spectroscopy.

Other alcohols are also suitable for the synthesis of (ROSiO$_{3/2}$)$_8$ with no disruption of the cage structure. In the context of functionalisation of silsesquioxane cages for dendrimer synthesis or other further reaction we have been able to react CH$_2$=CH(CH$_2$)$_3$OH with (HSiO$_{3/2}$)$_8$ at either the alcohol or vinyl groups to make (CH$_2$=CH(CH$_2$)$_3$OSiO$_{3/2}$)$_8$ or (HO(CH$_2$)$_5$Si-O$_{3/2}$)$_8$ respectively.

The silsesquioxane with eight vinyl groups available for further reaction was made by reaction of pentenol with (HSiO$_{3/2}$)$_8$ at ambient temperature, in ether solution, in the presence of a catalytic amount of Et$_2$NOH (product ^{29}Si NMR; δ − 103, CDCl$_3$). We have, to date, been unable to develop a method for rigorous purification of Q$_8$ silsesquioxane compounds as they appear to be unstable on silica chromatographic columns.

The silsesquioxane with eight hydroxy groups available for further reaction was prepared by hydrosilylation of the neat alkene using H$_2$PtCl$_6$ as catalyst, as previously reported [2]. When the reaction temperature was kept below 90°C there was no observable contamination of the product by formation of Q silicon by reaction of SiH with the OH group. In contrast to the Q silicon octopus molecules, we have been able to purify the T silicon octopus molecules (O$_3$SiC) by column chromatography using a silica column.

An attempt to synthesis a branched siloxane derivative of (HSiO$_{3/2}$)$_8$ was unsuccessful. Triallylpentaerythritol (HOCH$_2$C(CH$_2$OCH$_2$CH=CH$_2$)$_3$) was hydrosilylated by HMeSi(OSiMe$_3$)$_2$ in the presence of a catalytic amount of H$_2$PtCl$_6$ to give HOCH$_2$C(CH$_2$-O(CH$_2$)$_3$SiMe(OSiMe$_3$)$_2$)$_3$. This was then heated with (HSiO$_{3/2}$)$_8$ and no solvent in the presence of Et$_2$NOH, but the expected single molecule surrounded by 48 Me$_3$Si groups was not identifiable in the ^{29}Si NMR spectrum of the product mixture, which revealed many Q silicon resonances around δ − 100. The GPC analy-
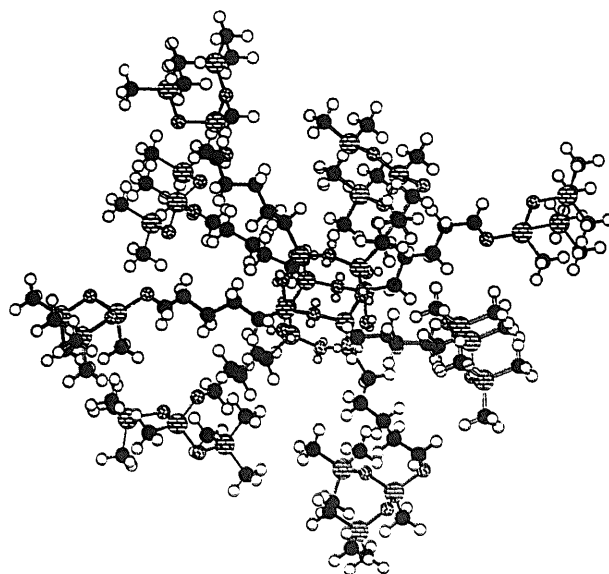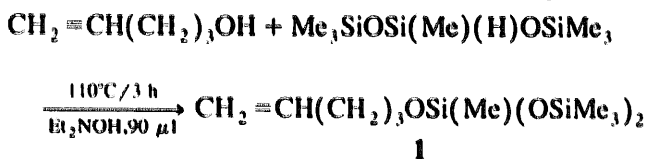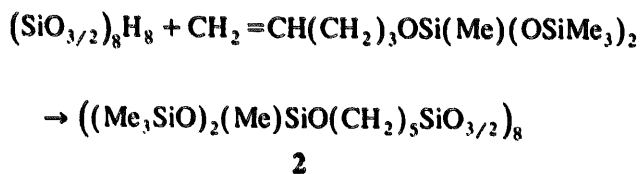

Fig. 1. Ball and stick model of the branched silsesquioxane 2.

sis also showed several higher molecular weight impurities.

By using a related but orthogonal route we did prepare a branched substituted cage octasilsesquioxane 2 (Fig. 1) with 16 Me$_3$Si groups around the surface, in high yield, pure by GPC and characterised by NMR (δ ^{29}Si NMR: − 66.7,− 57.1,+ 7.1, CDCl$_3$), infrared spectroscopy and mass spectrometry. The first step was to use the Et$_2$NOH-catalysed route to replace the hydroxyl hydrogen on pentenol by an Si(Me)(OSiMe$_3$)$_2$ group (60% isolated yield, 60 mmol scale) to give 1:

$$CH_2=CH(CH_2)_3OH + Me_3SiOSi(Me)(H)OSiMe_3$$

$$\xrightarrow[\text{Et}_2\text{NOH},90\ \mu\text{l}]{110°C/3\ h} CH_2=CH(CH_2)_3OSi(Me)(OSiMe_3)_2$$

$$\mathbf{1}$$

The branched siloxane 1 was then reacted with (SiO$_{3/2}$)$_8$H$_8$ in the presence of Karstedt's catalyst at 100–120°C for 4 h to give 2 as a clear viscous liquid in almost quantitative yield:

$$(SiO_{3/2})_8H_8 + CH_2=CH(CH_2)_3OSi(Me)(OSiMe_3)_2$$

$$\rightarrow ((Me_3SiO)_2(Me)SiO(CH_2)_5SiO_{3/2})_8$$

$$\mathbf{2}$$

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