Rational synthesis of asymmetric bicyclic siloxane†

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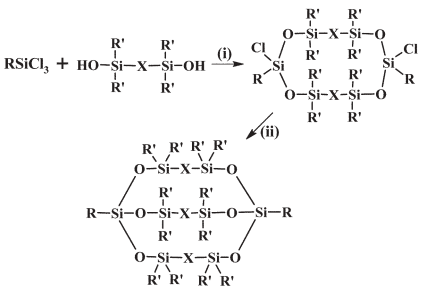
A rational and versatile method to synthesize bicyclosiloxane of design structures is presented. The method is used to synthesize a new, asymmetric bicyclo[7.5.3]octasiloxane and other bicyclosiloxanes.

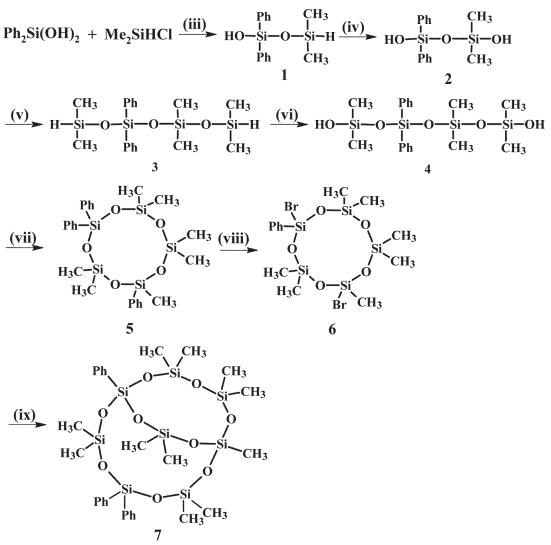
Siloxanes are building blocks for organosilicon hybrid materials and silicone rubber that have found applications in electronic[1] and medical devices.[2] Their properties depend on the nature of the organic ligands, length of the siloxane chain, and positions and nature of functional groups. However, in spite of the rather large number of siloxane compounds available, there are relatively few known siloxane bicyclic compounds. Furthermore, the procedures employed to synthesize the few known bicyclic compounds exert little control over the size or make-up of these structural units. Controlled synthesis of such compounds would enable their properties to be studied. Here we report a method that permits synthesis of bicyclosiloxanes where the three siloxane chains can be of different but controlled lengths.

Ladders and cages of silsesquioxane have been synthesized. Their preparation typically involves reaction of siloxanes with multiple but identical functional groups. Thus, when the precursor siloxanes hydrolytically condense with other siloxanes to form these structures, the products are always symmetric.[3–5] For the synthesis of highly symmetric bicyclosiloxanes, the reported methods offer little control of the reactions and/or result in very low yields because of multiple products and extensive purification steps.[5–11] This is illustrated with reactions (i) and (ii), which involve reaction of organotrichlorosilane with an organosilanediol to form a siloxane ring with chloro groups at the potential bridgehead positions (reaction (i)).[12–14] Then, the third bridge was added by reaction of a silanediol with the bridgehead chloro groups (reaction (ii)). In addition to the large number of products formed, the hygroscopic nature of the halosilanes causes additional difficulties in handling.[15,16]



In order to form asymmetric structures, siloxanes containing different functional groups of different reactivities need to be used. This was one of the synthesis strategies investigated by Masamune and coworkers,[17] employing hydrochlorosilane (*e.g.* α-hydro-ω-chlorooligosiloxane) and hydrosilanol for stepwise linear homologation and branched elongation and for building hyperbranched polysiloxanes and silicone dendrimers. The building blocks with different functional groups were synthesized by partial functionalization of a precursor, and consequently with low yield. They did not extend their investigation to asymmetric cyclic compounds.

Expanding on our earlier work in the synthesis of siloxanes,[18] we report here a strategy that exerts control of the reactions by exploiting the differences in reactivity of different functional groups. Selective reaction of one functional group of a bifunctional silane with a different silane would result in quantitative formation of a desired intermediate without byproducts. The remaining functional group then can be used in a different step of the synthetic process as desired. This concept is illustrated in Scheme 1 for the synthesis of an asymmetric bicyclosiloxane. The process is initiated by reacting chlorodimethylsilane with diphenylsilanediol (reaction (iii)). The different reactivities of the hydride and chloride substituents permit selective reaction of chloride with a silanol and ensure termination of the reaction at that stage,[17] thereby eliminating the formation of a wide range of byproducts due to simultaneous reaction of both substituents as in the case when dichlorosilane is used. Using excess diphenylsilane ensures that



Scheme 1 (iii) py, yield 86%; (iv) & (vi) H_2O, $Pd(OH)_2/C$, yield 93% for **2** and 98% for **4**: (v) Me_2SiHCl, py, yield 88%; (vii) $PhMeSiCl_2$, py, yield 74%; (viii) Br_2, a mixture of *cis*- and *trans*-isomers was obtained; (ix) **10**, py, yield 19% from **5**.

† Electronic supplementary information (ESI) available: Preparatory procedures and NMR data. See http://www.rsc.org/suppdata/cc/b5/b500591d/

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only one of the hydroxyl groups in diphenylsilanediol was condensed. A small amount of bis-condensation side-product (less than 5%) could be separated by column chromatography.

The resulting organo-H-silanol (*e.g.* $HSiMe_2OSiPh_2OH$ **1**) can be oxidized to a linear silanediol (*e.g.* 1,3-dihydroxy-1,1-dimethyl-3,3-diphenylsiloxane **2**) using Pearlman's catalyst as described in the literature (reaction (iv)).[19] Since the Si atom containing the phenyl ligands will serve as a bridgehead, the two bridges that emanate from it will differ in length by one Si atom in this example. It can be seen that bridges that differ by other numbers of Si atoms can be formed readily by using different chlorosilanes in reaction (iii). For example, using $HSi(CH_3)_2OSi(CH_3)_2Cl$ would result in two bridges that differ by two Si atoms.

Other siloxane units can be added to compound **2** to lengthen the branches. For example, one cycle of reaction of R_2SiHCl with **2** followed by catalytic oxidation will add one Si unit to each of the two branches (reactions (v) and (vi)), and multiple cycles can be used. The reactions can be followed readily with ^1H, ^{13}C, and ^{29}Si NMR, and the products of these reactions are air-stable. Therefore, work-up is easy and the products could be obtained with over 90% yield.

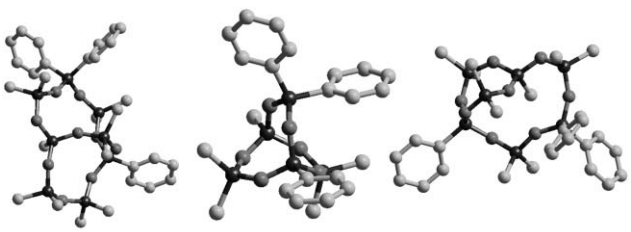
We have demonstrated the reactions shown in Scheme 1 to prepare two branches that differ by one Si atom, forming 1,7-dihydroxy-1,1,5,5,7,7-hexamethyl-3,3-diphenylsiloxane **4**. This compound in the pure form can be stored for several months at −18 °C, although it is sensitive towards self-condensation in solution. The ^{29}Si resonance of the $SiMe_2OH$ end groups appear at −9.10 and −10.28 ppm, and the Si in the $SiPh_2O_2$ and $SiMe_2O_2$ groups show their typical resonances around −47.67 and −18.90 ppm, respectively. The organo-H-siloxanes **1** and **3** are both liquid at room temperature. The characteristic signal of their ^1H NMR is a quadruple peak at 4.5–5.0 ppm, assigned to $Me_2Si\mathit{H}$. The terminal silicon resonances are at −3.19 for **1**, and −4.08 and −6.26 ppm for **3**.

The formation of cyclic 1,1,5-triphenyl-3,3,5,7,7,9,9-heptamethylcyclopentasiloxane **5** was achieved by condensation of **4** with dichloromethylphenylsilane in the presence of pyridine as an HCl acceptor (reaction (vii)). By mixing dilute solutions of the reactants slowly so as to minimize the formation of undesired, higher molecular weight products, a 74% yield of a racemic mixture of **5** was achieved. The mass spectrum of **5** showed the siliconium ion peak at m/z = 541, which was due to loss of a methyl group, a well-known behavior of organosiloxane compounds.[20]

Unlike previous preparations, the cyclic compound **5** is stable in air and contains no hydroxyl or chloride functional groups. Thus, it can be purified and handled easily. The asymmetric structure makes all six methyl groups of Me_2SiO_2 different, and their ^1H resonances were found at 0.18, 0.14, 0.11, 0.08, 0.07 and 0.01 ppm. The ^{29}Si NMR chemical shift of the Me_2SiO_2 moiety was in the range −18.73 to −19.92 ppm, the Ph_2SiO_2 moiety at −47.85, and the $MePhSiO_2$ group at −34.26 ppm. The detailed preparation procedure, the yields, and the NMR spectra of these compounds and others described later are provided in the electronic supplementary information (ESI).†

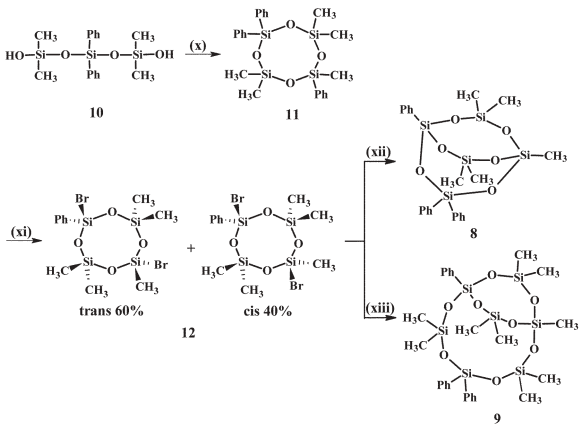
The phenyl groups at the potential bridgeheads in the cyclosiloxanes formed in this manner can be converted to bromide groups by treatment with bromine at room temperature, thereby functionalizing the Si atoms to anchor the third bridge.[19] Thus, **5** was converted to1,5-dibromo-1-phenyl-3,3,5,7,7,9,9-heptamethylcyclopentasiloxane **6** (reaction (viii)). The reaction was quantitative, and only one phenyl group in the Ph_2SiO_2 unit was converted, because the electron density of the silicon atom was significantly decreased by the electron-withdrawing effect of the bromine atom.[21] A mixture of *cis* and *trans* isomers was produced, and could be used directly for subsequent steps without purification, except for pumping off the excess bromine, although only the *cis* isomer will produce the bicyclic compound. **6** is an interesting intermediate as it contains two reactive groups. Thus, it can be used for other purposes as well, such as a building unit to form metal organic frameworks.

A bicyclosiloxane can be synthesized by reacting a dibromocyclosiloxane, such as **6**, with a silanediol to form the third bridge. The size of the silanediol determines the length of this bridge. For example, 1,5,5-triphenyl-3,3,7,7,9,11,11,13,13,16,16-undecamethylbicyclo[7.5.3]octasiloxane **7**, which contains three bridges of different lengths, was synthesized by reacting **6** with 1,5-dihydroxy-1,1,5,5-tetramethyl-3,3-diphenylsiloxane **10** (reaction (ix)). After purification by evacuation and chromatography, **7** was recovered as a colorless, viscous liquid with a yield of 19% starting from **5**. The major factor that lowers the yield is the formation of the *trans* isomer of **6**. The purity of **7** was confirmed by NMR, mass spectrometry, and elemental analysis (see ESI for details).† Although the compound contains two optical centers, because of the constraint of the bridges, only two of the four stereoisomers are expected. The Si atoms in all five Me_2SiO_2 groups yield resonances at different chemical shifts: −19.49, −19.83, −20.49, −20.56 and −21.32 ppm. The Si in Ph_2SiO_2 appears at −48.33, in $MeSiO_3$ at −66.65, and in $PhSiO_3$ at −80.52 ppm.



7 **8** **9**

Two other bicyclosiloxanes, 1,3,3-triphenyl-5,7,7,10,10-pentamethylbicyclo[3.3.3]pentasiloxane **8**, and 1,5,5-triphenyl-3,3,7,7,9,11,11,14,14-nonamethylbicyclo[7.3.3]heptasiloxane **9**, were synthesized to illustrate the versatility of this method (Scheme 2). In these two compounds, two of the siloxane bridges are identical, but the third is different. The reaction of 1,5-dihydroxy-1,1,5,5-tetramethyl-3,3-diphenylsiloxane **10**[19] with dichloromethylphenylsilane results in the symmetric cyclosiloxane 1,1,5-triphenyl-3,3,5,7,7-pentamethylcyclotetrasiloxane **11** with 92% yield (reaction (x)). The phenyl groups in the potential bridgehead positions were functionalized with bromine to form a mixture of *cis* and *trans* 1,5-dibromo-1-phenyl-3,3,5,7,7-pentamethylcyclotetrasiloxane **12** (reaction (xi)). ^1H NMR showed a *cis* to *trans* ratio of 2 : 3. The mixture was used to form **8** (reaction (xii)), but only the *cis* isomer was expected to be able to condense with diphenylsilanediol to form the desired product. Indeed, **8** was obtained quantitatively from the *cis* isomer, whereas the *trans* isomer reacted with silanediol to produce a mixture of high



Scheme 2 (x) $PhMeSiCl_2$, py, yield 92%; (xi) Br_2, yield 98%; (xii) $Ph_2Si(OH)_2$, py, yield 97%; (xiii) **10**, py, yield 97%.

molecular weight compounds that were easily separated from the desired product **8** by column chromatography.

9 was synthesized similar to **8** except that a larger silanediol was used in the reaction with **12** (reaction (xiii)). In this case, 1,5-dihydroxy-1,1,5,5-tetramethyl-3,3-diphenylsiloxane **10** was used. Again, the *cis* isomer of **12** reacted quantitatively to form **9**. Thus, we have demonstrated a general method that can be used to synthesize bicyclosiloxanes of arbitrary bridge lengths and bridgehead positions.

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