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Laddersiloxanes — silsesquioxanes with defined ladder structure

M Unno, A Suto, T Matsumoto

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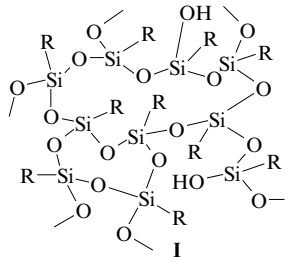
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Abstract. Data on the synthesis, structures, and properties of laddersiloxanes (silsesquioxanes with defined ladder structure) reported over the last 15 years are summarized. Synthetic methods applied to prepare tricyclic, pentacyclic, heptacyclic, and nonacyclic laddersiloxanes are considered. The structural features of laddersiloxanes determined by X-ray crystallography and the key properties (thermal stability, hydrophobicity, *etc*.) are analyzed. The bibliography includes 50 references.

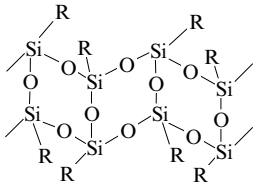
I. Introduction

Silsesquioxanes, or silicon compounds with the empirical formulas $RSiO_{3/2}$, where R is hydrogen or any alkyl or aryl group, have been intensively studied, and their properties, including thermal stability, water repellency, and low dielectric constant, have been revealed.[1] Several structures are possible for silsesquioxanes. Random (**I**), ladder (**II**), partially condensed (**III**), and cage (*e.g.*, $\mathbf{T_8}$, $\mathbf{T_{10}}$ and $\mathbf{T_{12}}$) types are known to date.[2] Among them, ladder-type silsesquioxanes are expected to present better properties because of (1) possible polymeric forms, (2) highly ordered structures, and (3) double-chain structures.

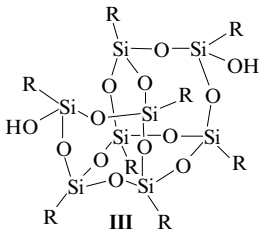
In 1960, Brown and co-workers reported[3] that the base-catalyzed polycondensation of the hydrolysate from phenyltrichlorosilane led to the formation of polyphenylsilsesquioxane $(PhSiO_{1.5})_n$. Using X-ray diffraction pattern and analyses of IR spectra, they proposed that the product possessed a stereoregular double-chain structure with a *cis*-syndiotactic conformation. This double-chain ladder polymer may be formed in equilibrium with lower-molecular-weight cage compounds that can be isolated from dilute solutions (Scheme 1, the Si – O – Si fragments are shown by straight line segments).[4, 5] The detected cage species included octa- ($\mathbf{T_8}$), deca- ($\mathbf{T_{10}}$), and dodecasilsesquioxanes ($\mathbf{T_{12}}$). Based on these findings, the polycondensation of the phenyltrichlorosilane hydrolysates is likely to proceed *via* the formation of *cis-trans-cis*-tetrahydroxycyclotetrasiloxane to yield ladder polysilsesquioxane (see Scheme 1). Despite several reports,[4–10] Frye and Klosowski[11] claimed in 1970 that maintenance of $(PhSiO_{1.5})_n$ in alkaline medium to equilibration did not yield ladder silsesquioxanes but yielded a randomly linked array of polycyclic cages. At present, it is believed that the proposed ladder structure was unsubstantiated, and further experimental work was required to demonstrate real ladder polysilsesquioxanes.[12]



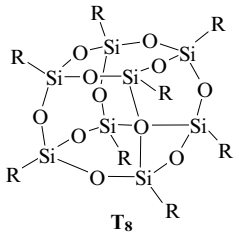
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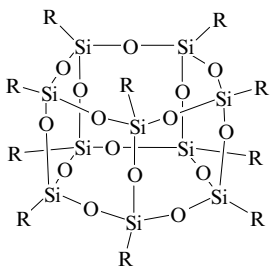
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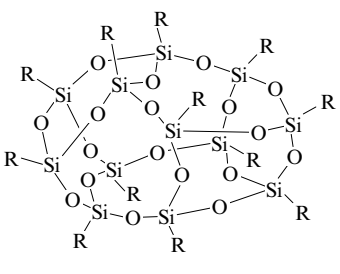
III



T_8



T_{10}

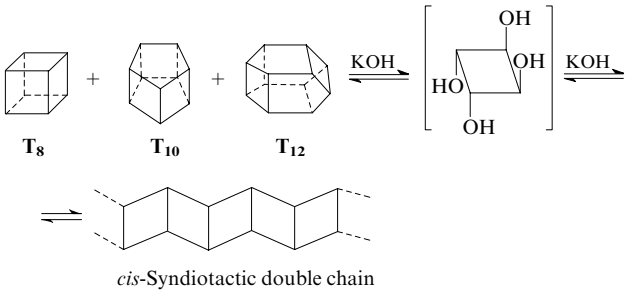


T_{12}

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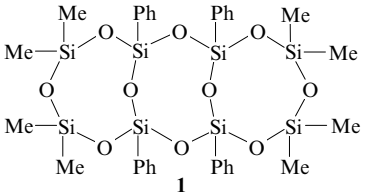
Scheme 1



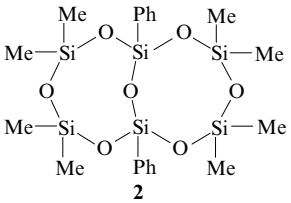
The interest in ladder-type silsesquioxanes has been growing in recent years, because of the demand for highly thermally stable materials for reducing the size of electronic devices. For example, recent developments of powerful light-emitting diodes result in demands for more stable silicone materials for the use as encapsulants (for lens assembly). The currently available silicone materials are not suitable for satisfying the specifications, and those with better quality are necessary. Well-defined structures without defects are always expected to show better physical properties. Therefore, silsesquioxanes with perfect ladder structures are considered promising materials. In addition, spectroscopic features and structure–property relationships of laddersiloxanes make them good models for determining the structures of various silsesquioxanes.

II. Synthesis of laddersiloxanes

Prior to our work, determination of the structures of three bicyclic and tricyclic laddersiloxanes had been reported. In 1965, Brown[13] reported the synthesis of the *syn*-tricyclic laddersiloxane, $Me_8Ph_4Si_8O_{10}$ (**1**), and Shklover *et al.*[14] determined the structure of **1** by X-ray crystallography in 1978. Later, Shklover *et al.*[15] reported the X-ray structure of the *anti*-isomer. The structure of bicyclic laddersiloxane $Me_8Ph_2Si_6O_7$ (**2**) was also described by the same group in 1980.[16] Shklover's group prepared these laddersiloxanes by the reactions of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (tricyclic) or 1,3-diphenyldisiloxanetetraol (bicyclic) with 1,3-dichlorotetramethyldisiloxane in the presence of a stoichiometric amount of pyridine. Brown's group performed a similar reaction using triethylamine instead of pyridine, and the yield was 26%.[13]



1

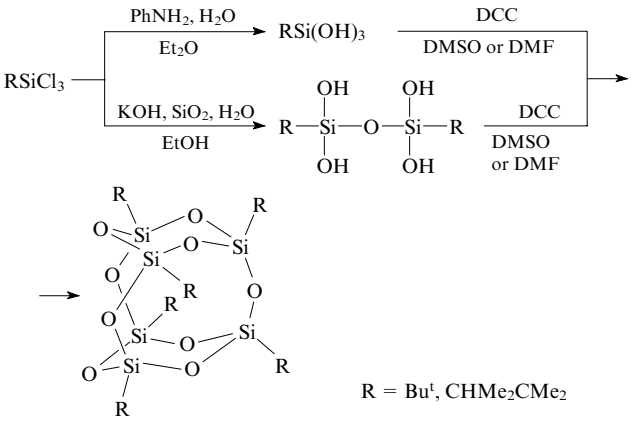


2

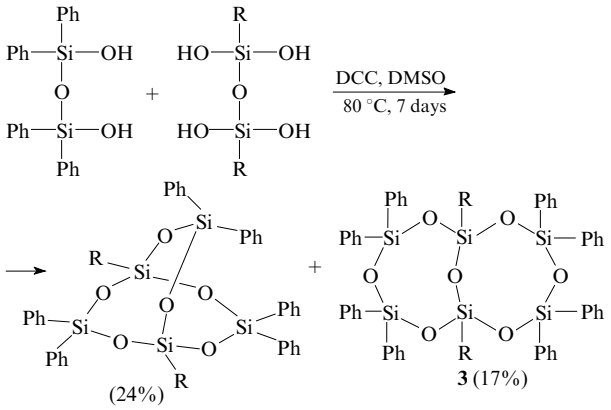
1. Bicyclic laddersiloxanes

In 1996, we reported the synthesis of cage hexasilsesquioxanes from respective silanols by dehydration with dicyclohexylcarbodiimide (DCC) as the dehydrating agent (Scheme 2).[17] With the same synthetic methods, we have obtained a bicyclic laddersiloxane **3** (Scheme 3).[18] The structures of the products were determined by X-ray crystallography.

Scheme 2



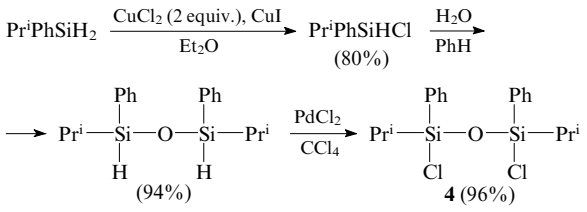
Scheme 3



R = $CHMe_2CMe_2$

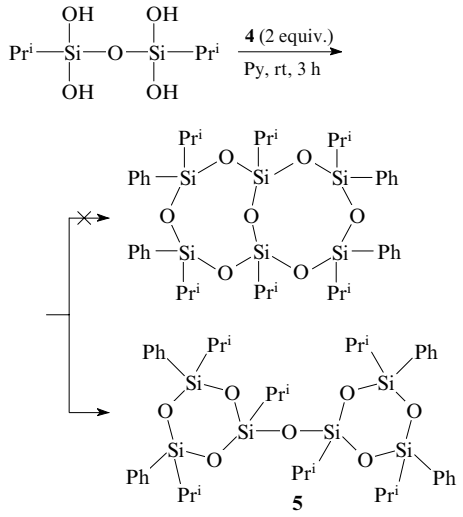
Although these reactions produced bicyclic laddersiloxanes, the yield was not satisfactory, and by-products generated by the disproportionation of starting silanols were also obtained. Therefore, we investigated cross-coupling reactions from silanols and chlorosilanes. Necessary 1,3-dichloro-1,3-diisopropyl-1,3-diphenyldisiloxane (**4**) was prepared as shown in Scheme 4.[19]

Scheme 4



The resulting dichlorodisiloxane **4** was treated with disiloxanetetraol (Scheme 5).

Scheme 5



Py is pyridine

Analysis by HPLC showed several peaks corresponding to isomers (Fig. 1, the yields are given in parentheses). We isolated each isomer and made single crystals, and their structures were determined by X-ray diffraction. Unexpectedly, all the products were not bicyclic laddersiloxanes but bicyclic siloxanes **5** with Si—O—Si bond between the rings (see Scheme 5). This clearly indicated that generation of laddersiloxanes is not easily accomplished even with monomers with well-defined structures.

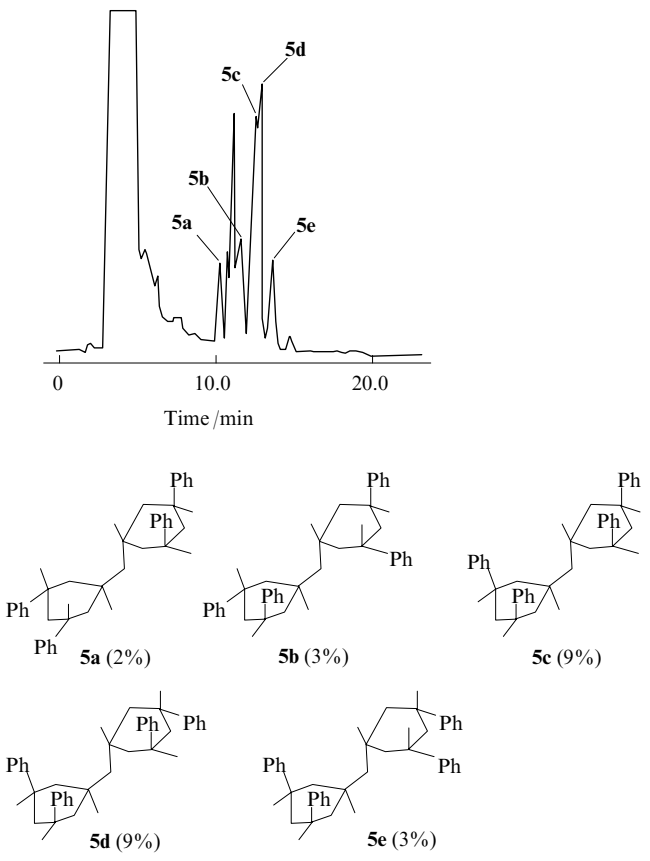


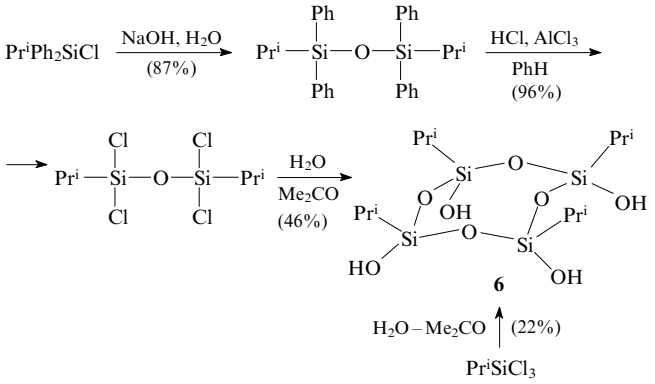
Figure 1. Chromatogram of an isomer mixture of glass-like siloxanes **5a**–**e** (O and Si atoms and Pr^i groups are omitted for clarity). HPLC: octadecylsilane (ODS), MeOH : THF = 9 : 1, detection at 250 nm.

2. Tricyclic laddersiloxanes

In order to minimize the possible generation of undesired products, we tried the synthesis of cyclic silanols. If we use these compounds to construct laddersiloxanes, eight-membered rings must be present in the products; therefore, generation of laddersiloxanes becomes more plausible. Regarding cyclotetrasiloxanetetraol or cyclic silanol $[RSi(OH)O]_4$, a phenyl- and cyclohexyl-substituted compound was previously reported by Brown's group.[13, 20] However, we chose phenyl groups for ring homologation and isopropyl groups for substituents.

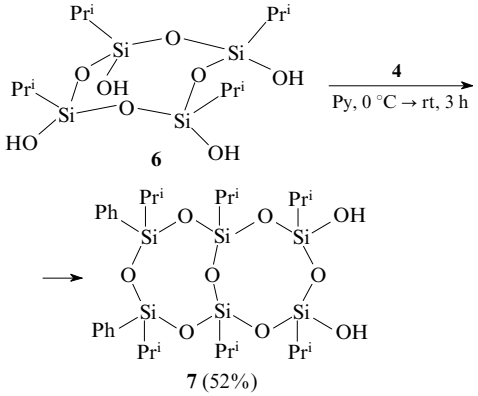
The isopropyl-substituted cyclic silanol $[Pr^iSi(OH)O]_4$ (**6**) can be formed by stepwise preparation [21] or by direct synthesis [22] (Scheme 6).The total yield of stepwise synthesis (38%) was better than that of the direct synthesis, but direct synthesis was more convenient. We [21, 23] and Feher's group [24] independently reported the crystal structures of **6** and $[PhSi(OH)O]_4$, respectively. The all-*cis* conformations were established for both compounds.

Scheme 6



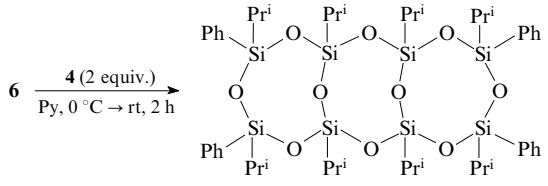
When cyclic silanol **6** was treated with dichlorosiloxane **4**, bicyclic silanol **7** was obtained as a mixture of isomers in a 52% total yield (Scheme 7). Previously, laddersiloxanes with terminal hydroxyl groups were prepared by hydrolysis of trichlorosilane as by-products together with completely condensed polyhedral oligosilsesquioxanes by Feher *et al.*[25] They also synthesized tetrahydroxy laddersiloxanes by base-catalyzed cleavage of cage silsesquioxane $Cy_6Si_6O_9$ (Cy is cyclohexyl) [26] These ladder silanols can serve as potential starting compounds for constructing well-defined siloxanes.

Scheme 7



On the other hand, when **6** was treated with two equivalents of dichlorosiloxane **4**, tricyclic laddersiloxane **8** was obtained as the sole product. The reaction conditions were optimized, and target tricyclic laddersiloxane was obtained as a mixture of stereoisomers **8a**–**e** in 85% total yield (Scheme 8).[19] The five isomers were isolated by recycle-type HPLC (Fig. 2), and all structures were determined by X-ray crystallography; each isomer was revealed to possess a *syn*-tricyclic structure reflecting the conformation of the starting cyclic silanol.

Scheme 8



8 (85%, isomer mixture)

More recently, Gunji's group reported [27] the synthesis of tricyclic laddersiloxane using reactive isocyanate substituents. Interestingly, as opposed to our case, both *anti*- and *syn*-tricyclic laddersiloxanes were obtained by this method, even though they started from *cis*,*trans*,*cis*-cyclotetrasiloxane. They explained this result by isomerization of the starting cyclotetrasiloxane and actually observed its base-induced isomerization. Later, the same research group prepared phenyl-substituted *syn*-tricyclic laddersiloxane **9** (Scheme 9).[28]

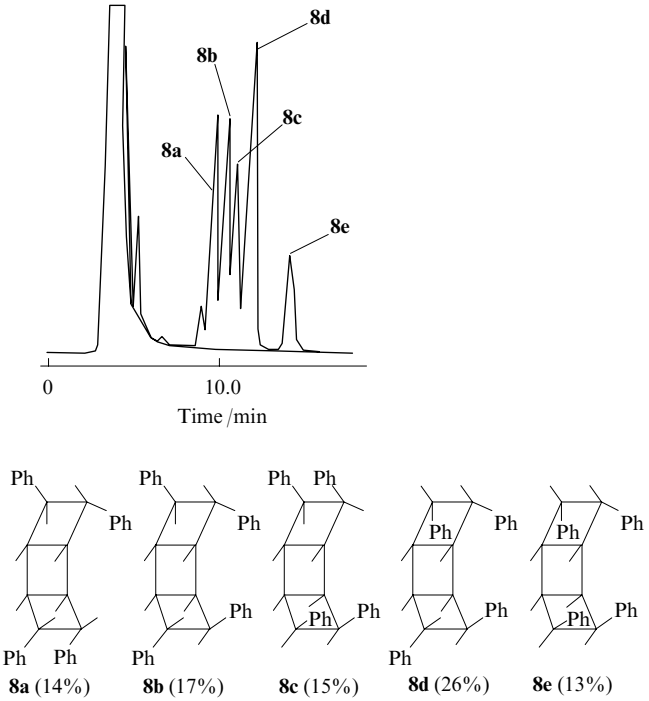
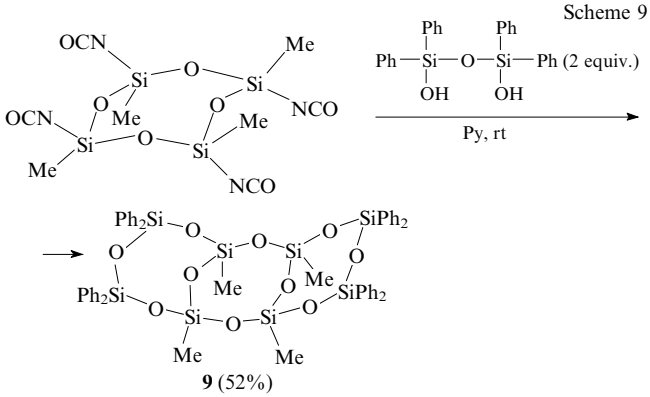


Figure 2. Chromatogram of an isomer mixture of tricyclic laddersiloxane **8a**–**e** (O and Si atoms and Pr^i groups are omitted for clarity).[19]
HPLC: ODS, MeOH : THF = 8 : 2, detection at 250 nm.

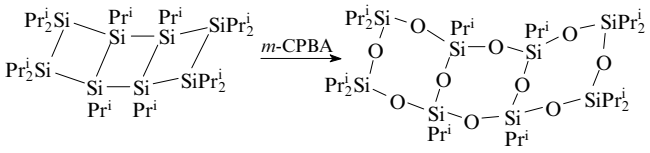
Scheme 9



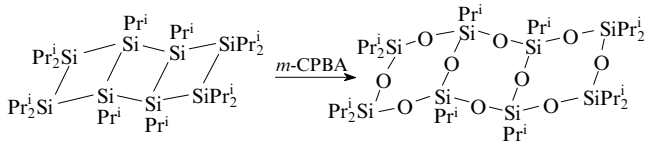
9 (52%)

In1987, Kyushin and Matsumoto's group described the synthesis of ladder polysilanes.[29] They isolated and determined the structure of tricyclic ladder oligosilanes in 1994.[30] Oxidation of tricyclic ladder oligosilanes with *m*-CPBA (*m*-chloroperbenzoic acid) produced respective tricyclic laddersiloxanes **10a**,**b** in good yields (Scheme 10). The original stereostructures were maintained in this reaction.[31]

Scheme 10



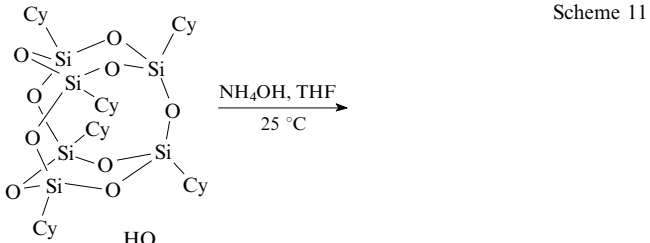
10a (73%)



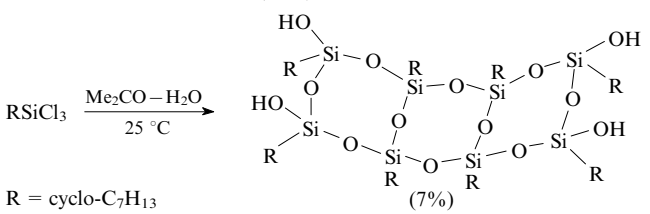
10b (25%)

As mentioned above, Feher's group reported the synthesis of a tricyclic ladder silanol by the reaction of

Scheme 11



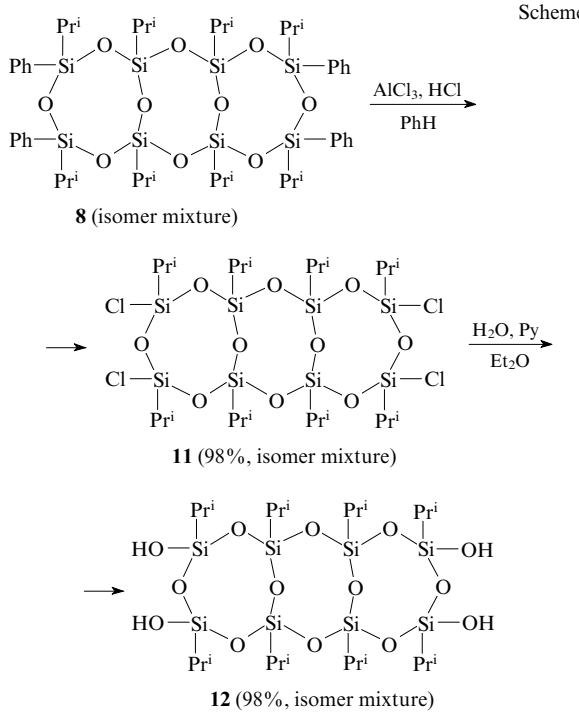
(63%)



R = cyclo-C_7H_{13}

(7%)

Scheme 12



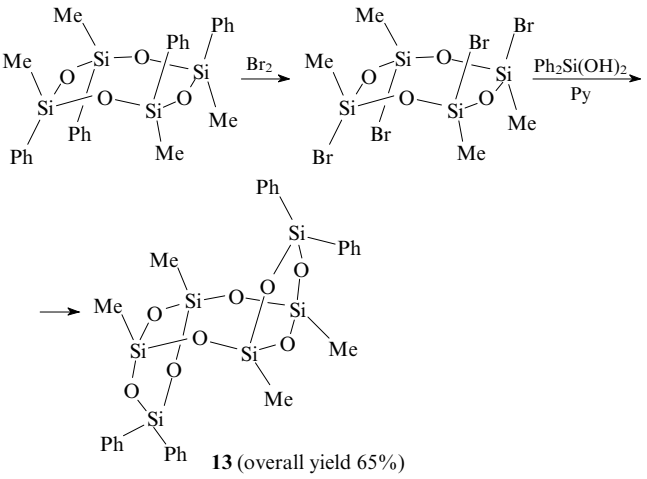
cage hexasilsesquioxanes or by room-temperature hydrolytic condensation of cycloheptyltrichlorosilane (Scheme 11).[25, 26] These reactions are beneficial because compounds that are the potential precursors to structurally regulated siloxanes can be produced in a single-step reaction.

Our tricyclic laddersiloxane **8** has an advantage in that phenyl groups can be transferred to hydroxyl groups *via* chloride. In this reaction, Si—O—Si skeletons remain intact, and phenyl groups can be replaced in almost quantitative yield. As shown in Scheme 12, laddersiloxane tetrachloride **11** was obtained in 98% yield and converted to tricyclic laddersiloxane tetraol **12** in the same yield. The structures of **11** and **12** were determined by spectroscopic methods. In addition, one of the isomers of **12** (*syn*-all-*cis*) was able to form single crystals, and X-ray diffraction analysis was performed. The molecular structure and packing diagram are shown in Fig. 3. Both intra- and intermolecular hydrogen bonds were observed.

A similar tricyclic laddersiloxane can also be prepared by the reaction of tetrachlorocylotetrasiloxane with disiloxanediol in pyridine. Details of this synthesis are provided in the next Section.

In addition to the tricyclic laddersiloxanes composed of three eight-membered rings, those with two terminal six-membered rings are also possible. As shown in Scheme 13, such a tricyclic laddersiloxane **13** can be synthesized by the reaction of 1,3,5,7-tetrabromo-1,3,5,7-tetramethylcyclotetrasiloxane and diphenylsilandiol. The structure was determined by X-ray crystallography, and again, in this case, the stereostructure of the starting cyclic tetrabromide was retained.[32] This skeleton can also be prepared by the reaction of cyclic silanol like **6** with dichlorosilanes R_2SiCl_2 in pyridine.

Scheme 13



3. Pentacyclic laddersiloxanes

As shown in the previous section, with tricyclic laddersiloxane tetraol **11** in hand, a reaction similar to the one shown in Scheme 8 gave pentacyclic laddersiloxane **14** (Scheme 14).[19] Each stereoisomer was isolated by recycle-

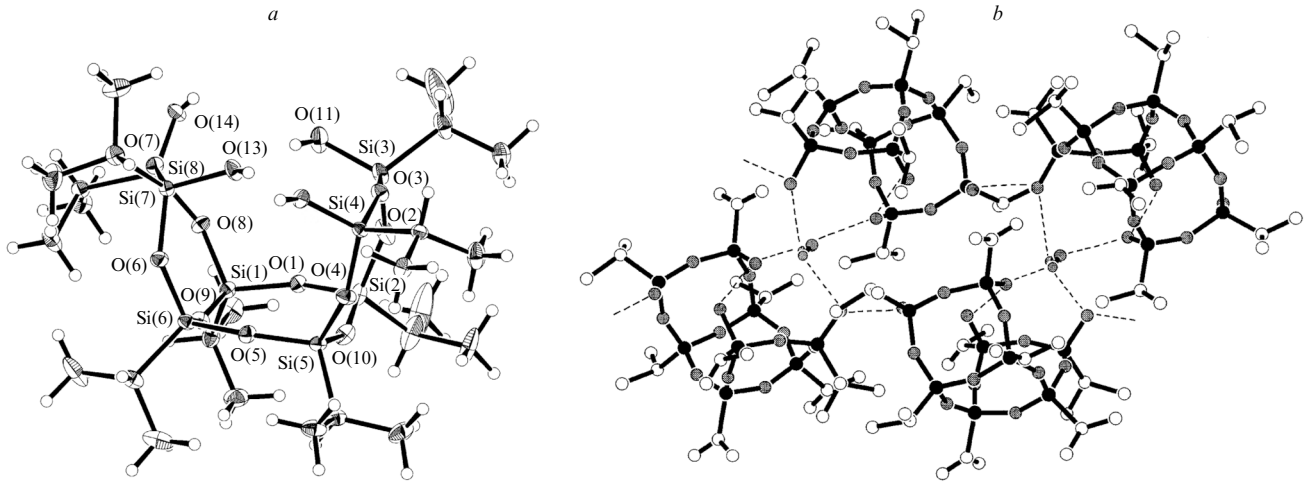
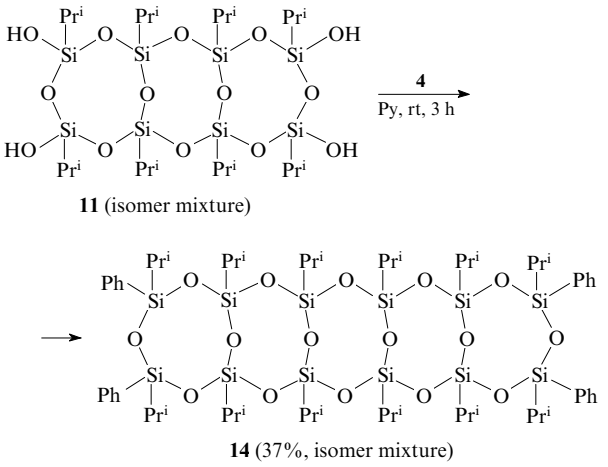
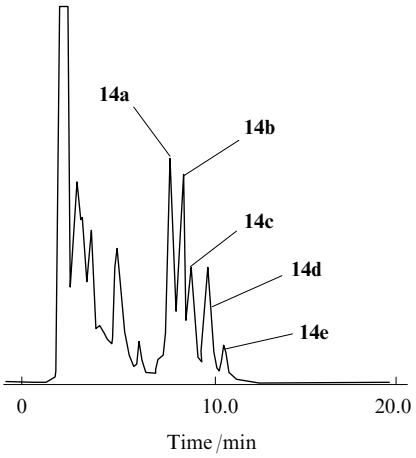


Figure 3. Molecular structure of silsesquioxane *syn*-all-*cis*-**12** (*a*) and packing of molecules in the crystal (*b*).[19]
Thermal ellipsoids are drawn at the 30% probability level, and possible hydrogen bonds are represented by dashed lines.

Scheme 14





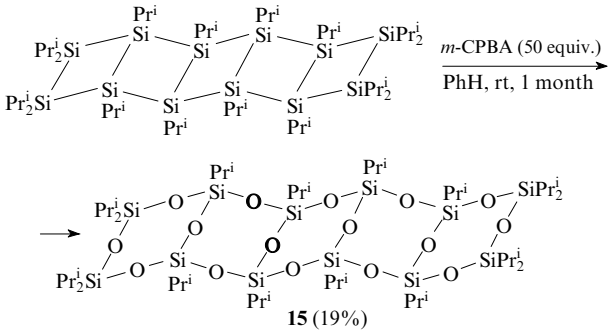
Compound	Yield (%)
14a	12
14b	9
14c	6
14d	7
14e	3

Figure 4. Chromatogram of an isomer mixture of pentacyclic laddersiloxane **14a–e**.[19]
HPLC: ODS, MeOH : THF = 7 : 3, detection at 250 nm.

type HPLC, and pentacyclic laddersiloxanes were obtained in 37% yield. Unlike the case of tricyclic laddersiloxanes, several peaks indicating the generation of lower-molecular-weight by-products were observed (Fig. 4). Fortunately, one of the isomers (**14b**) gave good single crystals, and X-ray crystallographic analysis was performed. The result unequivocally revealed the pentacyclic structure (Fig. 5). Because of the flexible Si–O–Si bonds, the other isomers of pentacyclic and longer (containing more rings) laddersiloxanes were all colourless, viscous oils.

The oxidation of pentacyclic silane (similar to the reacttion described in the previous Section, see Scheme 10) gave all-*anti* pentacyclic laddersiloxane **15** as a single isomer (Scheme 15). The reaction proceeded under harsh conditions, including considerable excess of *m*-CPBA and a long reaction time. The structure of **15** was also determined by X-ray crystallography.[31]

Scheme 15



Gunji's group also reported the synthesis and structure determination of pentacyclic laddersiloxanes.[33] They treated tetraisocyanatocyclotetrasiloxane with one equivalent of disiloxanediol. The resulting unstable bicyclic laddersiloxane was treated with water to yield *syn,anti,syn*-pentacyclic laddersiloxane **16** exclusively in 13% overall yield (Scheme 16). Again in this case, the structure of

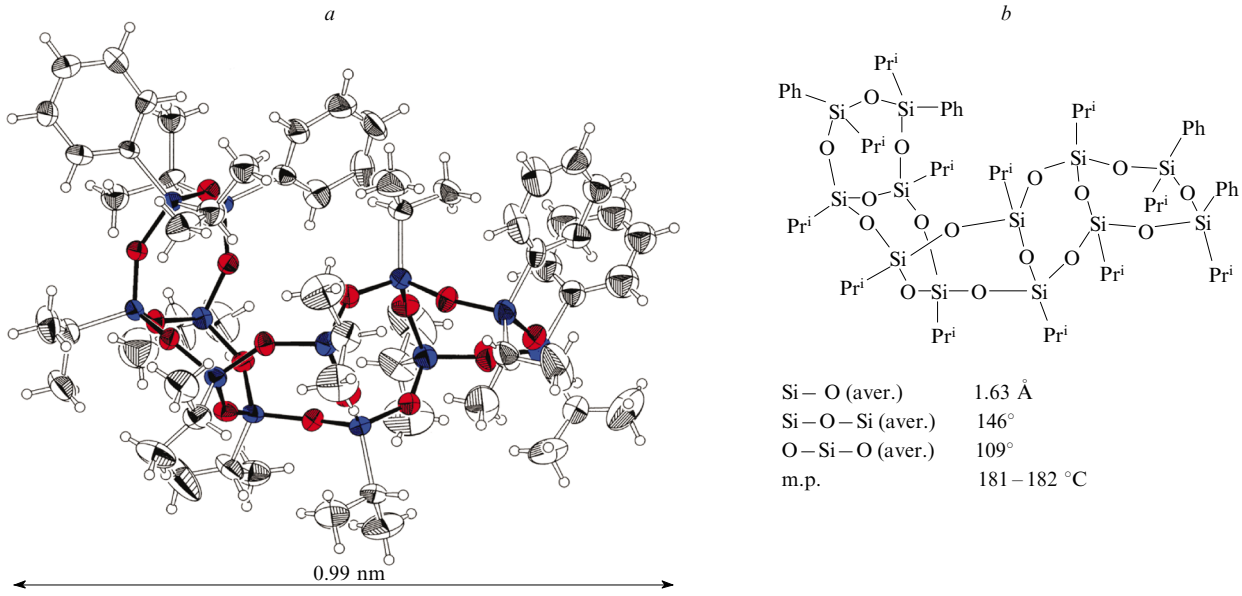
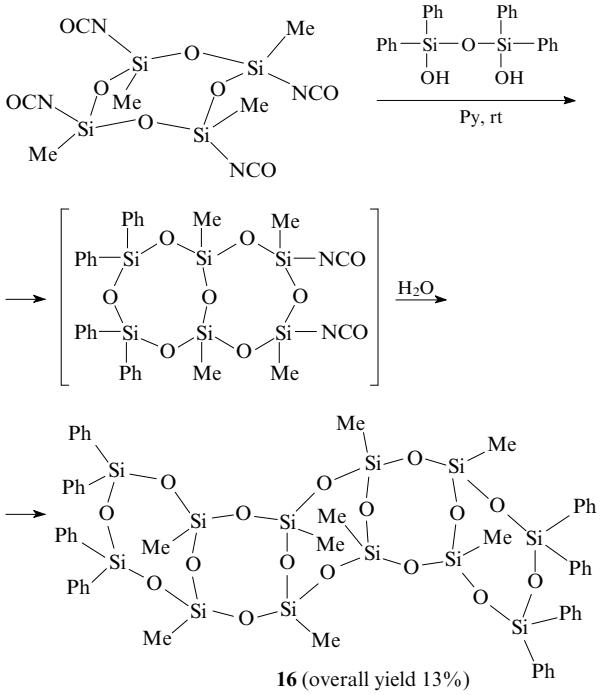


Figure 5. Structure of the molecule of pentacyclic laddersiloxane **14b** in the crystal (*a*) and average geometric parameters (*b*).[19]

starting cyclotetrasiloxane (*cis*,*trans*,*cis*-form) was not maintained, probably because of the effect of pyridine.[33]

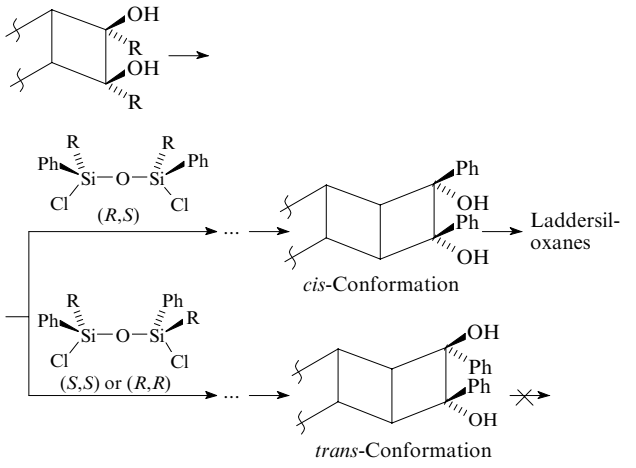
Scheme 16



16 (overall yield 13%)

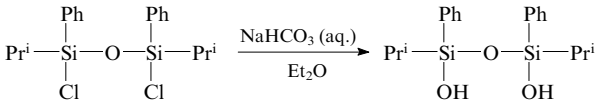
Although it seems possible to add more rings by repeating our procedure shown above, we could not prepare any further laddersiloxanes. This is explained by the generation of isomers incapable of ring homologation (Scheme 17, the Si – O – Si fragments are shown by straight line segments). As shown in the Scheme, if disilanol is treated with dichlorosiloxane, two stereoisomers with phenyl groups in *cis*- and *trans*-configurations at both terminal siloxane rings are obtained in 1 : 1 ratio, only *cis*-isomer being able to form further rings. This is the reason why the yield of pentacyclic laddersiloxanes is lower than that of tricyclic laddersiloxanes. This problem was solved by treating (*R*,*S*)-dichlorosiloxane instead of a diastereomeric mixture, and therefore, we tried to isolate the diastereomers.

Scheme 17



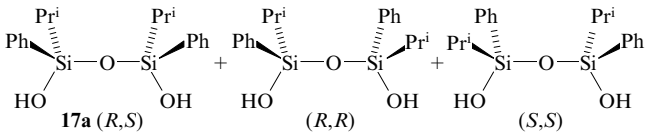
Our previous method with dichlorosiloxanes used as ring homologation units prevents the isolation of diastereomers because of their instability in water or silica gel. Therefore, we devised the reaction route shown in Schemes 18 and 19. The starting tetrasiloxane was obtained by hydrolytic condensation of $Pr^iPhSiCl_2$ followed by HPLC separation,[34] and the chlorination product obtained upon removal of phenyl groups was treated with (*R*,*S*)-dichlorosiloxanediol (**17a**) *in situ*. This reaction expectedly resulted in the formation of a tricyclic laddersiloxane **18** with phenyl groups in *cis*-configuration at both terminal siloxane rings for each isomer. The diastereomer of disiloxanediol **17a** was obtained in good yield by either recrystallization (Fig. 6) or HPLC (Fig. 7).[35] The ratio of the two diastereomers was easily identified by the ratio of Me peak areas in the ^1H NMR spectrum, as shown in Fig. 8. Additionally, the structure of (*R*,*S*)-**17** (**17a**) was determined by X-ray crystallography.

Scheme 18



4 **17a**,**b** (90%)

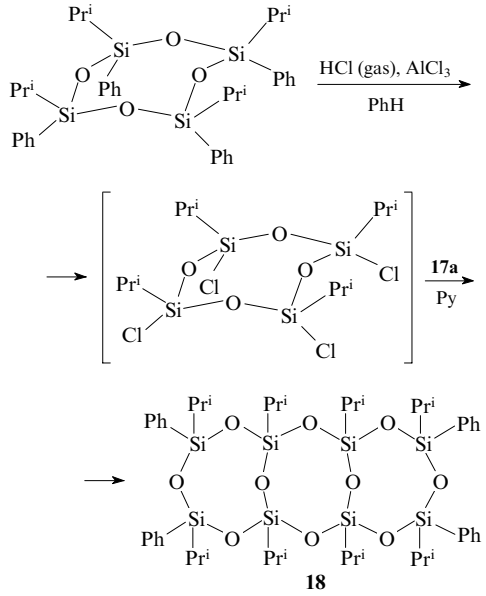
(*R*,*S*) : (*R*,*R*)/(*S*,*S*) = 50 : 50 **17a** : **17b** = 46 : 54



17a (*R*,*S*) (*R*,*R*) (*S*,*S*)

17b

Scheme 19



18

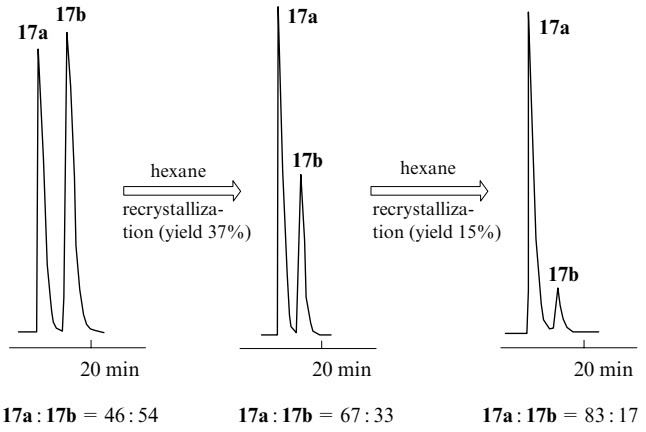


Figure 6. Preparation of compound **17** and isolation of diastereomer **17a** by recrystallization (here and in Fig. 7, chromatograms of the mixtures are given).[35]
HPLC: CHEMCOSORB 5Si, hexane : THF = 7 : 3, detection at 250 nm.

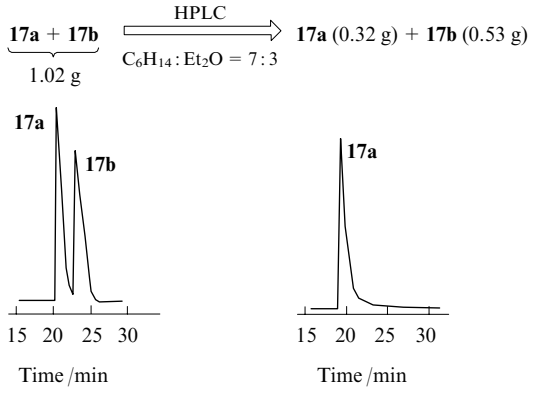


Figure 7. Isolation of diastereomer **17a** directly by HPLC.

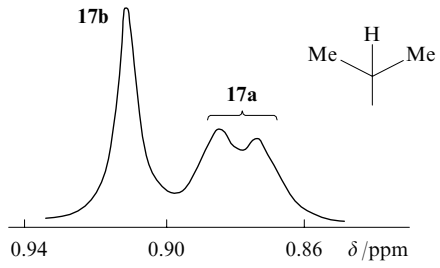
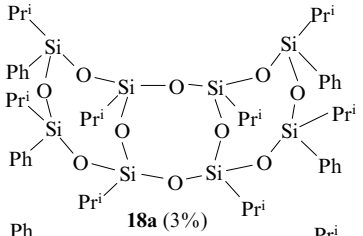
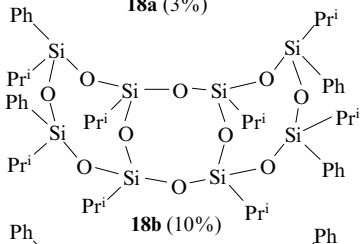


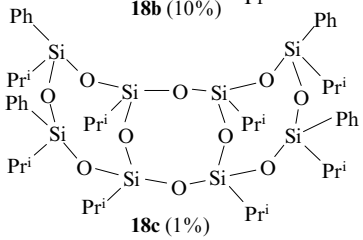
Figure 8. ^{1}H NMR spectrum of diastereomer mixture **17** in the methyl proton region.[35]

As expected, this reaction gave *cis*-Ph tricyclic laddersiloxanes **18**. The three isomers obtained were isolated by recycle-type HPLC, and the structures of these compounds were determined unequivocally by X-ray crystallographic analysis.[35]

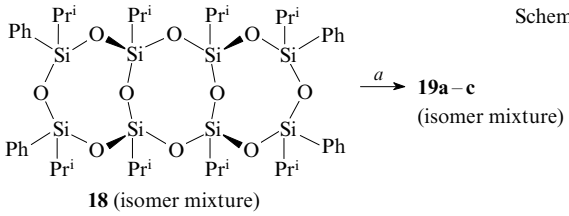
The subsequent reactions of **18** (mixture of isomers) with (*R,S*)-isomer **17a** yielded target pentacyclic laddersiloxanes **19** with *cis*-Ph groups in the terminal rings (Scheme 20).


18a (3%)

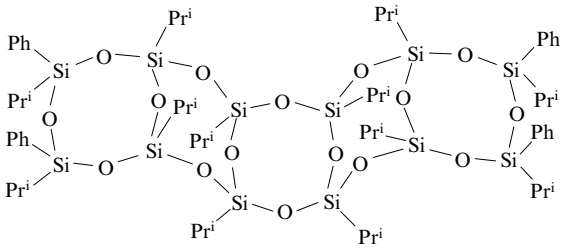

18b (10%)

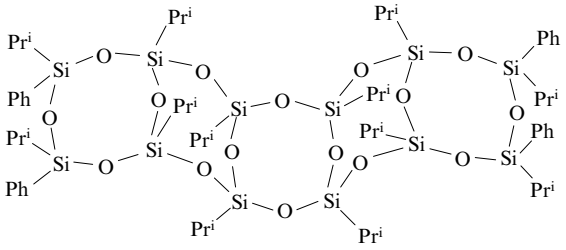

18c (1%)

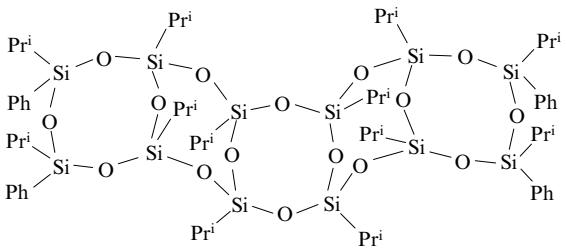
Scheme 20



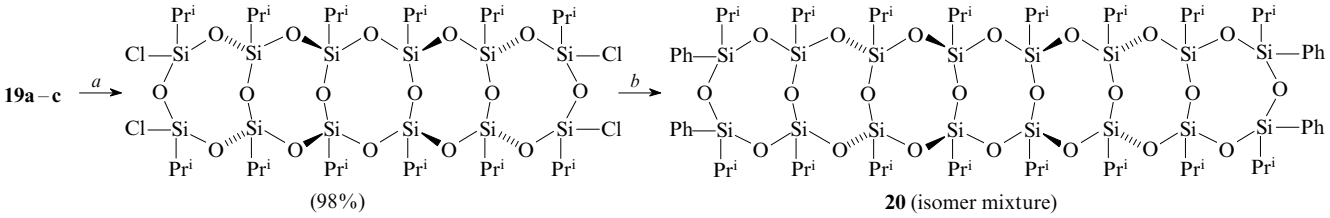
(*a*) 1) HCl (gas), $AlCl_3$, C_6H_{14}; 2) **17a**, Py


exo-all-*cis*-*anti*-*syn*-*anti*-**19** (**19a**)


endo,*exo*-all-*cis*-*anti*-*syn*-*anti*-**19** (**19b**)

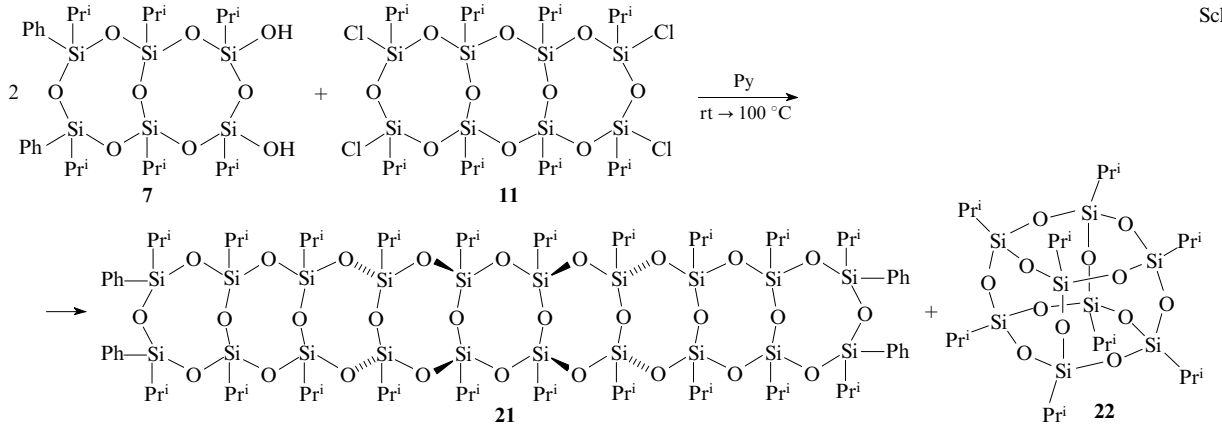

endo-all-*cis*-*anti*-*syn*-*anti*-**19** (**19c**)

Scheme 21



(*a*) HCl, $AlCl_3$; (*b*) **17a** (2 equiv.), Py, PhH

Scheme 22



Interestingly, the structures of **19** were all of *anti*,*syn*,*anti*-conformation, probably because of the steric congestion of other stereoisomers. The structures of **19** were determined by X-ray crystallography. The *cis*-configuration of the phenyl groups in the terminal rings enabled the production of heptacyclic laddersiloxanes from **19**.[35]

4. Heptacyclic laddersiloxanes

Synthesis of heptacyclic laddersiloxanes was only possible from pentacyclic **19**. Dephenylchlorination of a mixture of isomers of **19** gave a quantitative yield of tetrachloride. Treatment of the tetrachloride with **17a** gave heptacyclic laddersiloxane **20** in 6% yield (Scheme 21). Unfortunately, this compound was a viscous colourless oil, and no single crystals were obtained from any of isomers. The identification of heptacyclic **20** was performed using NMR and mass spectra. The ^{29}Si NMR spectrum of **20** shows peaks in the regions from −66.26 to −64.94 ppm and −34.36 to −33.22 ppm. This is in good agreement with the values for other laddersiloxanes. The mass spectrum shows a peak at m/z 1754 ($M^+ - Pr^i$) consistent with the structure of **20**.[36]

5. Nonacyclic laddersiloxanes

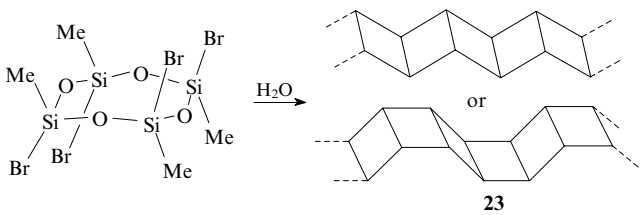
Nonacyclic laddersiloxanes were obtained from bicyclic ladder silanol **7**, which is easily obtained from cyclic silanol **6** by a single-step reaction. When dehydrochlorination of tricyclic laddersiloxane tetrachloride **11** and two equivalents of **7** was performed, nonacyclic laddersiloxane **21** was obtained as a mixture of isomers in 7% yield (Scheme 22). Cage octa(isopropylsilsesquioxane) **22** was formed as a by-product in 4% yield. The identification was performed using NMR and mass spectra as in the case of heptacyclic laddersiloxane.[37]

6. Ladder polysilsesquioxanes

Structure determination of ladder polysilsesquioxanes is rather difficult. All the laddersiloxanes described above may serve as good models for the spectroscopic analysis of ladder polysilsesquioxanes. Although NMR and IR spectra show several unique properties of ladder silsesquioxanes, other polymers, especially random ones with a part-ladder structure, also show similar spectra. Hence, identification is challenging and ambiguous. Nonetheless, there have been several reports on preparation routes of polymeric ladder structures.

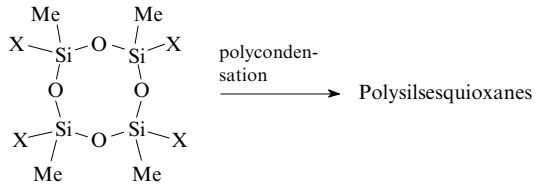
In 2005, we isolated *cis*,*trans*,*cis*-tetrabromotetramethylcyclotetrasiloxane (see Scheme 13).[32] This compound spontaneously decomposed under the action of air moisture to give a white solid compound **23**. Unfortunately, this polymer is insoluble in all common solvents; however, ^{29}Si NMR and IR spectra and considerable thermal stability observed by thermogravimetric (TGA) and differential thermal (DTA) analyses indicated that this polymer possesses a well-defined ladder-like structure (Scheme 23).[36] The 5% weight loss temperature Td_5 was 645 °C, and this value is higher than that of other ladder-like polysilsesquioxanes reported so far.

Scheme 23



Gunji's group also isolated cyclotetrasiloxane precursors and obtained soluble ladder polysilsesquioxanes.[38] They used three types of precursors (hydrido, ethoxy, isocyanato derivatives) and obtained polymers with different properties (Scheme 24). From their results, ethoxy-substituted cyclotetrasiloxane yielded less-ordered polysilsesquioxanes according to IR and NMR data. All three polymers show broad peaks in ^{29}Si NMR spectra at around −65.0 ppm, indicative of structure variation. However, the results of IR spectra and TGA (Td_5 temperature of 435 °C for the hydrido compound) indicated that they possess fairly well-defined structures.

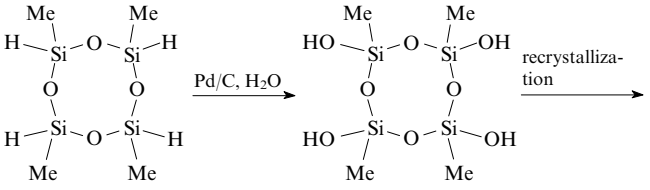
Scheme 24

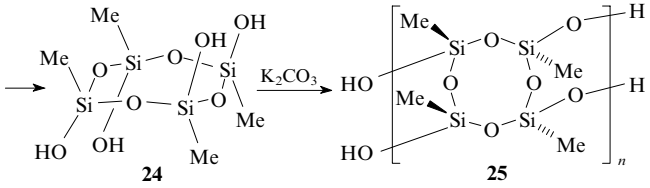


X = H, OEt, NCO

A synthetic approach from cyclic silanol was also reported by Lee and Hwang's group in Korea.[39] They isolated the methyl-substituted *cis*,*trans*,*cis*-isomer of cyclic silanol **24** by recrystallization and obtained ladder polysilsesquioxanes **25** by base-catalyzed dehydration of **24** (Scheme 25).[39] The ^{29}Si NMR spectra of the obtained polymer **25** exhibited signals for $\mathbf{T}^2$ groups (*i.e.*, silicon atoms connected by two bonds to the skeleton oxygen atoms, −O−Si−O−Si−, and to one OH group) in addition to the expected $\mathbf{T}^3$ signals (for silicon atoms not connected to OH groups but linked by three bonds to the skeleton). The authors also performed gel permeation chromatography and measured MALDI-TOF mass spectra. They concluded that polymer **25** comprises connected laddersiloxane segments (less in number than in hexacyclic laddersiloxanes). This polysilsesquioxane also showed enhanced thermal stability up to 700 °C, reflecting the ordered ladder structure.

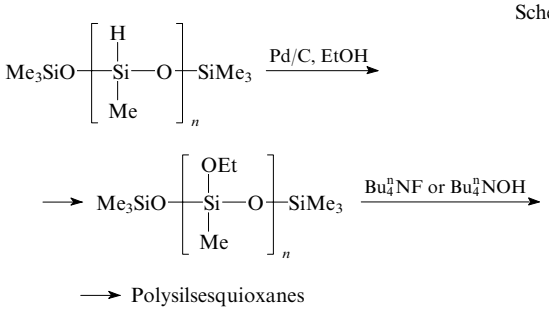
Scheme 25





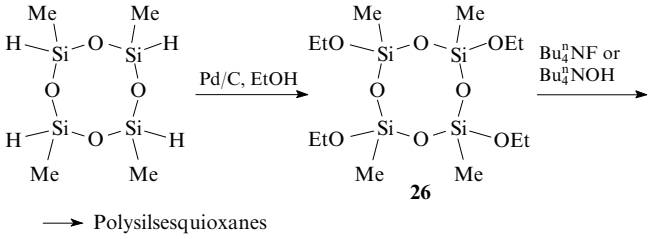
Handke's group in Poland devised a cross-linking method to yield ladder polysilsesquioxanes from acyclic siloxanes (Scheme 26).[40]

Scheme 26



The same researchers also isolated tetraethoxytetramethylcyclotetrasiloxane **26** (a mixture of four stereoisomers) and examined its condensation (Scheme 27).[41] Although the IR spectra of the polymer obtained according to Scheme 26 attested to some structural variations, TGA analysis indicated that the weight loss started at above 400 °C, indicative of ladder-like structures.

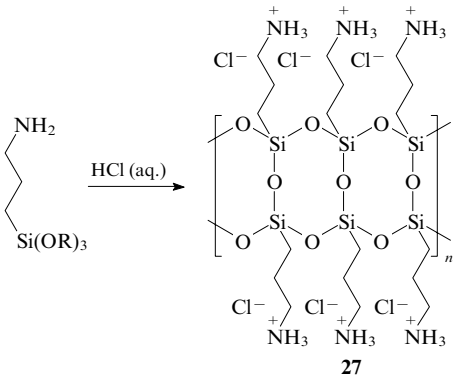
Scheme 27

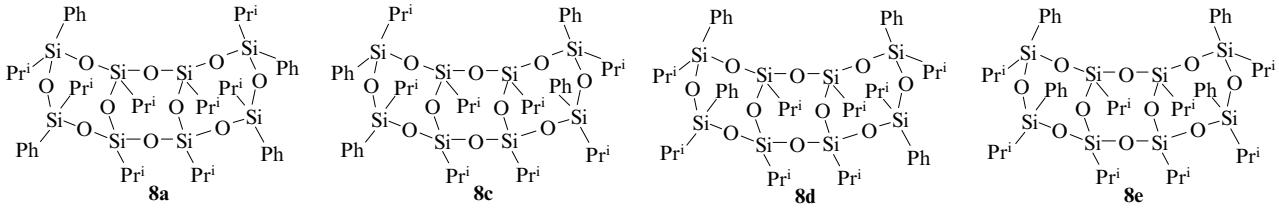


Another approach to producing ladder polysilsesquioxanes was developed by Zhang's group.[42] They organized the precursors by hydrogen bonding and then constructed structurally regulated silsesquioxanes.[42] Although the ladder structure was not fully supported, they obtained many valuable materials.

Quite recently, Kaneko's group in Japan took a unique approach by taking advantage of the ionic interaction at the end of the substituents.[43] As shown in Scheme 28, starting trialkoxysilanes were pre-organized by the interaction of the ammonium groups and chloride ions, and the subsequent hydrolysis and dehydration gave highly ordered structure **27**. The rod-like structures were observed by transmission and scanning electron microscopy, and X-ray diffraction measurements indicated that the diameter of the rod in polymer **27** was about 1.64 nm. With observation of $\mathbf{T}^3$ peaks in the ^{29}Si NMR spectra, the researchers concluded that highly ordered ladder structures were obtained.[44]

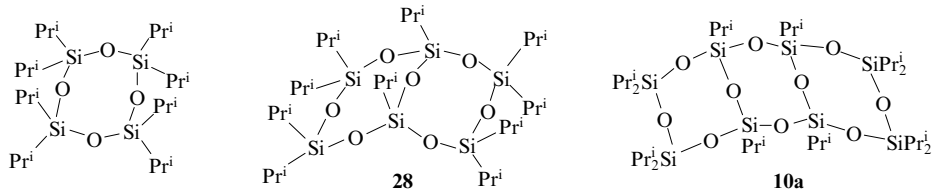
Scheme 28



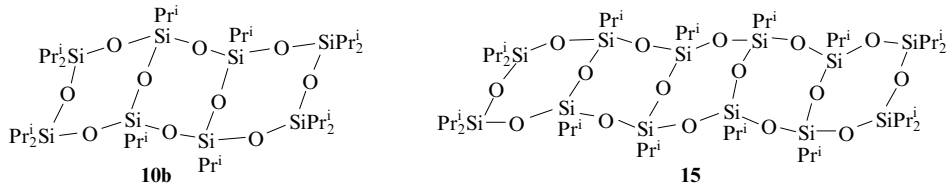


Sum of torsion angles /deg	29.7	25.0	31.3	30.6

Figure 9. Torsion angles of *syn*-tricyclic laddersiloxane **8**.[19]



Sum of torsion angles /deg	16.9	31.8	26.0



Sum of torsion angles /deg	36.1	0.1

Figure 10. Torsion angles of all-isopropyl laddersiloxanes.[31]

III. Structures and properties of laddersiloxanes

1. Structure of laddersiloxane

Because of the flexible Si – O – Si skeleton and steric repulsion of the substituents, the laddersiloxanes have intriguing double helix structures. As expected, all the laddersiloxanes showed helical structures. In Fig. 9, torsion angles of the terminal Si – O – Si bonds of *syn*-tricyclic laddersiloxanes are summarized.[19] Angles of 0° indicate the absence of helicity, and the larger the angles, the tighter the helical structure. In the cases examined, the torsion angles are similar to each other, and different configurations of terminal phenyl groups do not significantly affect the helical structure.

Figure 10 shows the torsion angles of all-isopropyl laddersiloxanes.[31] This data indicates that torsion angles of *anti*-laddersiloxanes increase up to tricyclic structures; however, pentacyclic laddersiloxane shows no helicity because of the centre of symmetry. In the case of all-*anti* ladder polysiloxanes, helical structures were also observed in the crystal, and more interestingly, both enantiomers could be detected by low-temperature ^{29}Si NMR spectroscopy.[45] Laddersiloxanes with fewer rings are much more flexible than the polymers, and since the steric repulsion of isopropyl groups is not significant, the separation of enantiomers was impossible.

The helical structure of laddersiloxanes is induced by the repulsion of substituents. As depicted in Fig. 11, when the cyclotetrasiloxane ring is planar, all the adjacent groups are in the same plane (eclipsed conformation) and the steric repulsion is highest. In order to minimize the energy, two substituents tend to acquire the *gauche* conformation, which results in smaller dihedral angels characterizing folding of the rings along the Si···Si line and larger torsion angles. In the inner rings, steric hindrance is not large in the *anti*-conformation because only two substituents are in the *cis*-positions, whereas the *syn*-conformation with four *cis*-substituents experiences more pronounced repulsion.

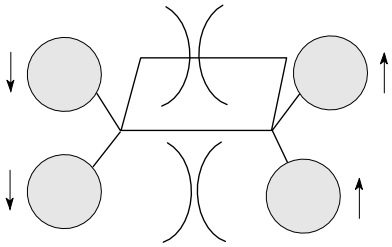


Figure 11. Schematic of the steric repulsion of substituents resulting in increased torsion angles.

2. Spectroscopic properties

One of the main aims for synthesizing laddersiloxanes is to use them as the model compounds for characterization of ladder-type polysilsesquioxanes. Here, we summarize the details of IR and NMR spectra of laddersiloxanes.

The ^{1}H and ^{13}C NMR spectra of laddersiloxanes show signals for substituents and provide no information for identification of the ladder structures. The ^{29}Si NMR spectra usually show signals characteristic of T fragments (SiO_3), and no data about the spatial srtructure of the molecule can be derived from the chemical shift. For example, the cage silsesquioxane, $\mathbf{T_8}$ with isopropyl substituents shows its ^{29}Si-NMR peak at -66.26 ppm in $CDCl_3$.[22] Meanwhile, isopropyl-substituted *anti*- and *syn*-tricyclic laddersiloxanes **10a**,**b** (Scheme 10) show peaks at -66.77 and -67.16 ppm in $CDCl_3$.[31] As clearly seen from this result, ^{29}Si NMR chemical shifts are basically independent of the stereostructure. Nevertheless, chemical shifts combined with the half-widths of the ^{29}Si NMR peaks are still good indicators for a ladder structure. The ^{29}Si NMR chemical shifts for some laddersiloxanes are listed in Table 1. It can be seen that chemical shifts of laddersiloxanes exist within a narrow range that is dependent on the substituents.

IR spectroscopy is also useful in the case of laddersiloxanes, because it can be employed for solid materials. Figure 12 *a* shows parts of the IR spectra of laddersiloxanes; for comparison, Fig. 12 *b* presents the same parts of the spectra of cyclic and cage silsesquioxanes. The latter tend to exhibit a broad single peak around 1050–1100 cm^{-1}, whereas laddersiloxanes show two sets of overlapping peaks around 1030 and 1130 cm^{-1}. Because of the several non-equivalent Si–O bonds present in bicyclic and tricyclic laddersiloxanes, several different peaks occur around 1130 cm^{-1}, giving rise to one broad flat peak.

Table 1. ^{29}Si NMR chemical shifts of laddersiloxanes.

Compound	δ /ppm	Ref.
28	−72.0	31
9	−62.8	28
10a	−67.2	31
8	−67.1 to −65.8	19
10b	−66.8	31
16	−64.2, −64.1	33
15	−65.8, −65.2	31
14b	−66.0 to −63.4	19
19	−66.2 to −64.9	35
23 (solid)	−64.5	32
Me-substituted polymer	−66.4 to −65.0	38
The same	−66.0	46

Meanwhile, the laddersiloxanes comprising more than five rings clearly show two peaks. The spectra of ladder polysilsesquioxane contain two symmetrical narrow peaks.

In 2008, Yoon's group reported[47] a theoretical IR study for ladder silsesquioxanes and predicted two peaks at 1050–1150 cm^{-1}. Our results experimentally supported their calculation. These peaks were also observed in ladder-type polysilsesquioxanes by Hwang's group,[48] Gunji's group,[38] and Handke's group.[40]

3. Thermal properties

As expected, all the laddersiloxanes showed interesting thermal properties. The results of TG analysis of laddersiloxanes, cage silsesquioxanes, and ladder polysilsesquioxanes are summarized in Table 2. Laddersiloxanes (except polymers) sublimed in the temperature range from 390 to 567 °C. The Td_5 value increased with the length of the

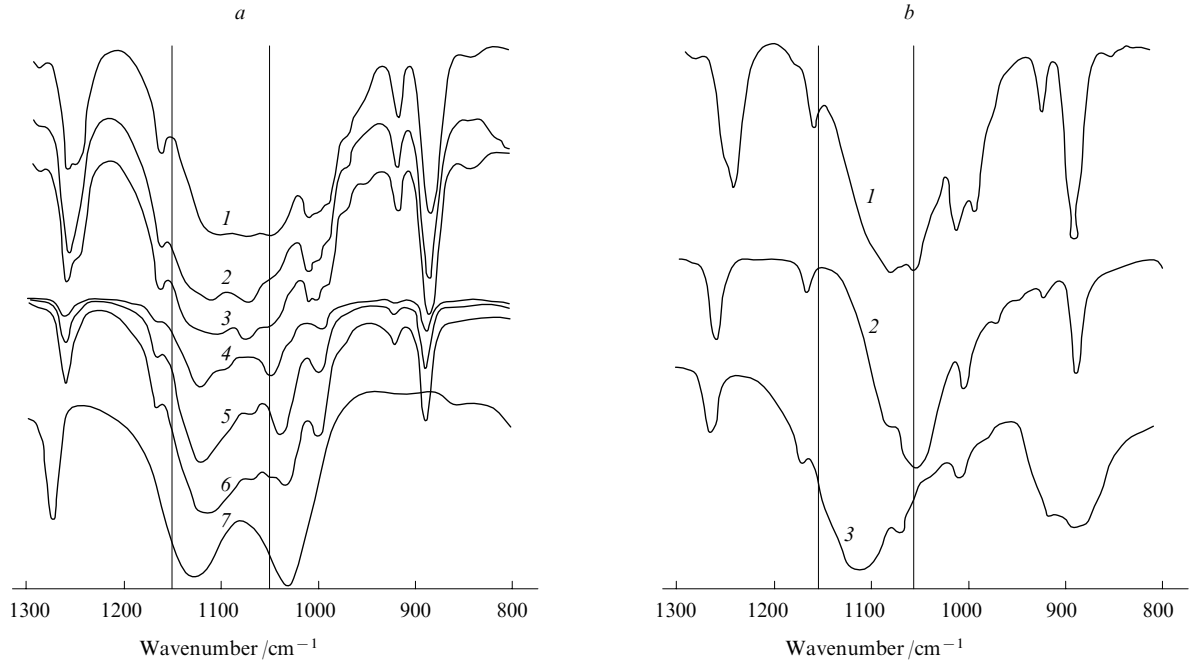


Figure 12. IR spectra of laddersiloxanes **28** (*1*), **10a** (*2*), **10b** (*3*), **14b** (4), isomer mixture **20** (*5*), isomer mixture **21** (*6*), Me-substituted polymer (*7*) (*a*); and cyclic and cage silsesquioxanes $(Pr^{i}{}_2SiO)_4$ (*1*), $(Pr^{i}SiO_{1.5})_6$ (*2*), $(Pr^{i}SiO_{1.5})_8$ (*3*) (*b*).[31, 36, 37]

Table 2. Thermogravimetric analysis data for laddersiloxanes, cage silsesquioxanes, and ladder polysilsesquioxanes.

Compound	Td_5 /°C	Notes [a]	Ref.
$(Pr^i_2SiO)_4$	205	T_{subl} = 345 °C	49
10a	260	T_{subl} = 390 °C	22
14b	296	T_{subl} = 423 °C	19
$(Pr^i_2SiO_{1.5})_6$	190	T_{subl} = 252 °C	17
$(Pr^i_2SiO_{1.5})_8$	200	T_{subl} = 282 °C	22
20	326	T_{subl} = 567 °C	36
23	645	Td_{12} = 1000 °C	36
Ladder polymer (from $MeSiCl_3$)	523 (in air)	M_w = 380 – 2000	49
The same	400 (in nitrogen)	M_w = 2000 – 6000	50

[a] T_{subl} is sublimation point, Td_{12} is the 12% weight loss temperature.

laddersiloxane molecule, and heptacyclic laddersiloxanes were remarkably stable up to 300 °C. Comparison of cage and laddersiloxanes also offers an interesting contrast. The tricyclic laddersiloxane had Td_5 and sublimation temperatures higher by 60 °C and 108 °C, respectively, than an octasilsesquioxane with the same number of silicon atoms.

Well-defined ladder polysilsesquioxanes showed significantly better thermal properties. Indeed, ladder polysilsesquioxane **23** exhibited 120 to 250 °C higher Td_5 temperature than polysilsesquioxanes prepared directly from methyltrichlorosilane.

* * *

Investigation of potential practical applications of laddersiloxanes has just started; however, the expected high thermal stability, transparency, and low dielectric constants are believed to be a great advantage in the production of novel materials in the future. It is possible to use ladder polysilsesquioxanes as pure materials, but it is more advantageous to use them after modification upon reactions with other compounds or polymers. It is possible to introduce vinyl groups or Si—H moieties into the laddersiloxane structures, and those compounds may serve as valuable precursors of polymeric silsesquioxanes having ladder structures.

In the future, laddersiloxanes or ladder polysilsesquioxanes may find use in the manufacture of electronic devices, surface functionalization, additives for higher thermal stabilization, development and so on.

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