# Silacrown Ethers: Synthesis of Macrocyclic Diphenylpolyethyleneglycol Mono- and Disilanes

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**Abstract:** The synthesis of new mono- and disilacrown ethers ($[k]O_lSi_m$: (k,l,m) = (8,3,1); (11,4,1); (16,6,2); (22,8,2)) was achieved by reacting $Ph_2SiCl_2$ with $HO-(CH_2CH_2O)_n-H$ (n= 2, 3) in the presence of base. Variation of the later revealed that cations could act as templates and thus orient the synthesis towards the mono- or the disilanes.

Since the discovery of macrocyclic polyethers by Pedersen some two decades ago[1a], considerable attention has been focused on crown ethers and their analogues.[1b-1c] The synthesis of medium ring cyclic polyethers containing one or two endocyclic silane groups was first reported by Krieble and Burkhard as early as 1947.[2] However, since then only few investigations dealing with the synthesis[3-5] and properties[6] of macrocyclic poly(alkeneoxy)silanes containing one silane functionality and designed as silacrowns have been published. To our knowledge, no report dealing with the synthesis of macrocyclic polyethers bearing two silane functionalities is available in the literature.

Incorporation of two silane groups within the structure of a crown ether, in an endocyclic mode, offers the following advantages: 1) these compounds may show binding abilities towards large cations; 2) they may act as phase transfer catalysts and may be further used as extracting agents for large cations; 3) since disilacrowns may be considered as doubly contracted analogues of crown ethers, their structural investigation and their conformational analysis may be of interest for designing new structures; 4) further functionalization of the crown compound may lead, after polymerization, to new materials possessing ionophoric properties; 5) their possible immobilisation on the surface of polymers should yield new functionalized polymers.

We report here a systematic investigation of the synthesis of new large disilacrown ethers. Our first target molecules were compounds **6-8**. In these molecules two diphenylsilane groups are connected together by two polyethyleneglycol chains. The choice of diphenylsilyl group was made because the phenyl moieties should increase the lipophilicity of these compounds when used for extraction purposes and furthermore the phenyl groups may be substituted by hydroxy functionality leading to bis cyclic silanediols which in their term should permit further functionalization. In terms of size compounds **6, 7** and **8** may be compared to their parent crownethers. The 8,8',16,16'-tetraphenyl-1,4,7,9,12,15-hexaoxa-8,16-disila-cyclohexadecane **6** ($[16]O_6Si_2$) may be considered as a doubly contracted analogue of 18-crown-6. Whereas **7**, the 11,11',22,22'-tetraphenyl-1,4,7,10,12,15,18,21-octaoxa-11,22-disila-cyclodocosane ($[22]O_8Si_2$) may be compared to 24-crown-8. Finally, compound **8**, the 13,13',28,28'-tetraphenyl-1,4,7,10,13,15,18,21,24,27-decaoxa-13,28-disila-cyclooctacosane ($[28]O_{10}Si_2$) may be seen as an analogue of 30-crown-10.

Our first attempt to prepare compounds **6-8** was based on a directed stepwise strategy (Scheme 1).
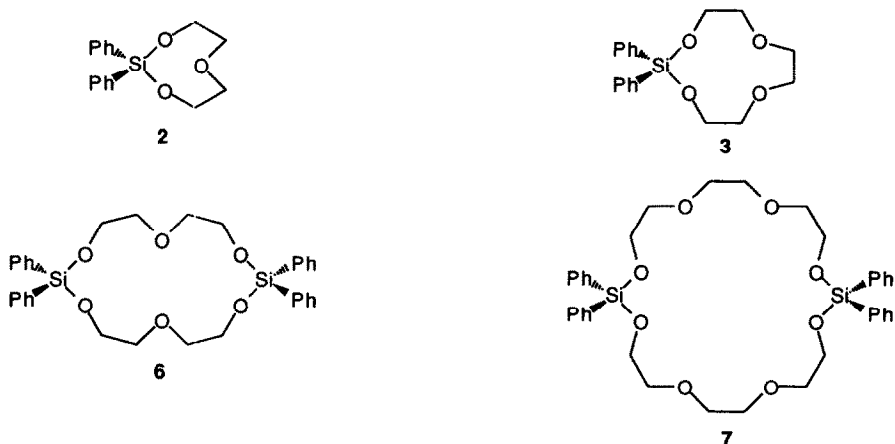
In such a strategy, the final step leading to the desired macrocycles would be the closing of an $\alpha,\omega$-diol chain by treatment with dichlorodiphenylsilane. The synthesis of the diol containing the $Ph_2Si$ group may be achieved, in recursive way, by the reaction of a monoprotected diol with dichlorodiphenylsilane followed by the deprotection of the alcohols. In principle, this type of strategy should avoid polymerisation reactions and furthermore it should reduce the formation of cyclic compounds containing only one silane group. Following our strategy, we prepared the monoprotected triethyleneglycol derivatives 9-12 (scheme 1). The reaction of compounds 9-12
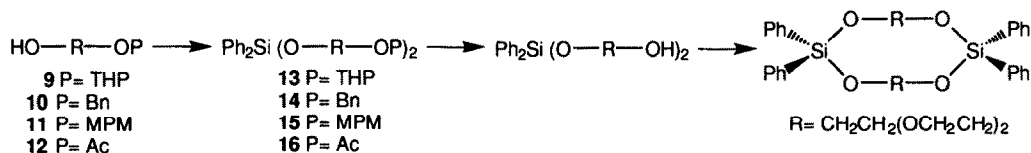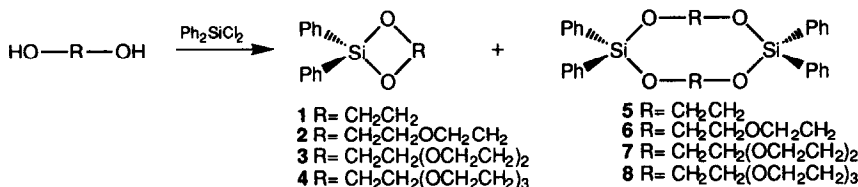


Scheme 1

with dichlorodiphenylsilane afforded the protected silane derivatives 13-16. Unfortunately, we were unable to remove the protective groups using a vast variety of described methods. Interestingly, while we were investigating the synthesis of acetoxy derivative 16 we noticed that, under certain conditions, the reaction of the monoacetoxytriethyleneglycol 12 with dichlorodiphenylsilane produced two other compounds which were identified to be the cyclic monosilane 3 (11,11'-diphenyl-1,4,7,10-tetraoxa-1-sila-cycloundecane, [11]$O_4Si$) and the desired macrocyclic disilane 7 ([22]$O_8Si_2$). Indeed, the treatment of the monoacetoxy protected triethyleneglycol 12 with one equivalent of NaH (55-65% dispersion, Fluka), in dry THF to generate the monoanion, followed by the subsequent reaction with dichlorodiphenylsilane afforded the monoprotected silane derivative 16 in only 10 % yield. The later could be further increased to 45 % by using MeLi as the base. Whereas in the above cited reactions no trace of cyclic compounds 3 and 7 was found, under the same conditions, the reaction in the presence of NaH (95 %, Aldrich)[7] afforded both the compound 3 and 7. This observation is not unprecedent since Sprung, while investigating the reaction of dichlorodimethylsilane and diethoxydimethylsilane with diols, reported in 1958 the formation of cyclic sila compounds.[3] This observation lead us to investigate the direct reaction of mono-, di-, tri-, and tetraethyleneglycol with dichlorodiphenylsilane (scheme 2). Although the reaction of diethyleneglycol and triethyleneglycol with dichlorodiphenylsilane both afforded the monosila compounds 2 and 3 as well as the disila derivatives 6 and 7, in the case of ethyleneglycol and tetraethyleneglycol, under the same conditions, no trace of compounds 1, 4, 5 or 8 was found. In order to optimise the yield, as a first parameter, the ratio of the diol, the base and the silane reagent was varied.

As expected, the 1/2/1 ratio was found to be the optimum. On the other hand, the nature of the base was systematically varied. Hydrides (MH, M = Li, Na, K), alcoholate (ROM, R = *tert*-butyl, M = Li, Na, K),



HO—R—OH $\xrightarrow{\text{Ph}_2\text{SiCl}_2}$

**1** R= CH$_2$CH$_2$
**2** R= CH$_2$CH$_2$OCH$_2$CH$_2$
**3** R= CH$_2$CH$_2$(OCH$_2$CH$_2$)$_2$
**4** R= CH$_2$CH$_2$(OCH$_2$CH$_2$)$_3$

**5** R= CH$_2$CH$_2$
**6** R= CH$_2$CH$_2$OCH$_2$CH$_2$
**7** R= CH$_2$CH$_2$(OCH$_2$CH$_2$)$_2$
**8** R= CH$_2$CH$_2$(OCH$_2$CH$_2$)$_3$

Scheme 2

**Table**: Yields (%) of compounds **2, 3, 6** and **7**.[8]

| Base | MH | | | *tert*-BuOM | | | RLi | | PhNMe$_2$ |
|---|---|---|---|---|---|---|---|---|---|
| | Li | Na | K | Li | Na | K | Me | Bu | |
| **2** | 14 | 9 | 32 | <1 | 23 | 23 | 2 | 5 | 31 |
| **3** | 8 | 8 | 8 | 32 | 24 | 19 | 26 | 30 | 1 |
| **6** | 2 | 9 | 7 | 28 | 19 | <1 | 24 | 16 | <1 |
| **7** | <1 | 4 | <1 | 5 | 7 | 5 | 6 | 6 | 2 |

alkyllithium (RM, R = Me, Bu, M = Li) and an amine (N,N'-dimethylaniline)[9] were used. The results are assembled in table. The yields observed in the presence of hydrides were rather erratic. This was probably due to the non homogeneous nature of the reaction mixture. In the case of alcoholates, some interesting results were obtained. Although without any selectivity, *tert*-BuONa gave with diethyleneglycol the highest total yield (42 %) of **2** and **6**. On the other hand, with triethyleneglycol **3** was formed in 24 % yield whereas **7** was present in only 7 % yield. Interestingly, *tert*-BuOLi produced with diethyleneglycol mainly the disilamacrocycle **6** in 28 % yield and only traces of **2**. Under the same conditions, with triethyleneglycol the major (32 %) compound was **3** and **7** was only present in 5 % yield. *tert*-BuOK gave with both di- and triethyleneglycol mainly the monosila compounds **2** (23 %) and **3** (19 %) with traces of **6** and only 5 % of **7**. Both MeLi and BuLi with diethyleneglycol gave **6** whereas with triethyleneglycol **3** was the major compound. In both cases, 4-6 % of **2** and **7** were produced. On the other hand, N,N'-dimethylaniline, a neutral base, produced only **2** in 31 % yield with diethyleneglycol whereas with triethyleneglycol both **3** and **7** were present in very poor yields (total yield of 3 %).

In summary: 1) whereas for all compounds **2, 3** and **6** highest yields of 32 %, 32 % and 28 % respectively were obtained, for the large macrocycle **7** the highest yield never exceeded 7 %. 2) Up to ca 40 % overall yields of cyclic compounds were observed with both the di- and triethyleneglycol, whereas with ethyleneglycol and tetraethyleneglycol no trace of **1, 4, 5** or **8** was observed. 3) Depending on the nature of the cation used, in the case of diethyleneglycol, either **2** or **6** could be exclusively produced. Whereas with Li$^+$ mainly **6** was obtained, with K$^+$ **2** was exclusively observed. 4) For the formation of **3**, the acceptable yield (25%) obtained in the presence of cations was substantially higher than the yield observed in the presence of the

neutral base PhNMe$_2$. 5) Comparing the results obtained with different bases composed of an anion and a cation with those observed with neutral base such as N,N'-dimethylaniline, indicated a metal template effect for the synthesis of **3** and **6**. For the compound **7**, probably due to its large cavity, no complexation of cations used could take place and thus no template effect could be observed. Indeed, the observed yields were low (5%) and rather invariable in the presence and in the absence of all cations used.

The $^1$H NMR spectra of the disila compounds **6** and **7** were both rather simple and showed two triplets for SiO*CH2* and SiOCH2*CH2* fragments and a singlet for O*CH2CH2*O protons.[8] Whereas for **2** and **3**, the signals corresponding to SiO*CH2* and SiOCH2*CH2*O fragments appeared as complicated multiplets indicating a rather rigid conformation in both cases. In order to ascertain the structure of these compounds, suitable monocrystals of **3** were grown. An X-Ray structure determination confirmed indeed the proposed structure.

The binding properties towards cations as well as the extraction abilities of compounds **2, 3, 6** and **7** are under current investigation. These compounds will be also studied in phase transfer catalysis.

### References and notes

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7. To a suspension of NaH (2 eq. , 95 % Aldrich) in dry THF (4 ml) a solution of HO-(CH$_2$CH$_2$O)$_n$-H, n= 1, 2, 3, 4 (1 eq.) in dry THF (10 ml) was added at 0°C. The mixture was stirred for 1 h. at r. t. before it was cooled to 0°C. A solution of dichlorodiphenylsilane (1 eq.) in dry THF (30 ml) was added. The mixture was stirred at r. t. for 12 h. before H$_2$O (20 ml) and ether (40 ml) were added. The aqueous layer was separated and further extracted with ether (15 ml). The organic layers were combined, dried over MgSO$_4$ and evaporated to dryness. The residue thus obtained was purified by chromatography (SiO$_2$, Hexane/AcOEt: 50/50) affording the mono- and di-cyclic silane derivatives.

8. **2 and 6**: NaH (0.48g, 18.8 mmol), diethyleneglycol (1g, 6.7 mmol), Ph$_2$SiCl$_2$ (1.4 ml, 6.7 mmol). **2**: r$_f$= 0.6 (SiO$_2$, Hexane/AcOEt: 50/50), M.p. 71 °C; $^1$H NMR (200 MHz, CDCl$_3$, 25 °C): δ= 3.75-3.82 (m, 4H, SiOCH$_2$*CH2*O), 4.00-4.08 (m, 4H, SiO*CH2*CH$_2$O), 7.35-7.45 (m, 6H, arom.), 7.69-7.75 (m, 4H, arom.). $^{13}$C NMR (50.32 MHz, CDCl$_3$, 25 °C): δ= 63.7, 72.1, 128.0, 130.2, 130.7, 134.9. Mass (*m/z*) 209 (M-Ph)$^+$. **6**: r$_f$= 0.7 (SiO$_2$, Hexane/AcOEt: 50/50), M.p. 90 °C; $^1$H NMR (CDCl$_3$): δ= 3.74 (t, 4.9Hz, 8H, SiOCH$_2$*CH2*O), 3.96 (t, 4.9Hz, 8H, SiO*CH2*CH$_2$O), 7.30-7.40 (m, 12H, arom.), 7.70-7.75 (m, 8H, arom.). $^{13}$C NMR (CDCl$_3$): δ= 63.1, 72.5, 127.9, 130.3, 133.0, 135.1. Mass (*m/z*) 495 (M-Ph)$^+$. **3 and 7**: NaH (0.34g, 13.3 mmol), triethyleneglycol (1g, 6.7 mmol), Ph$_2$SiCl$_2$ (1.4 ml, 6.7 mmol). **3**: r$_f$= 0.5 (SiO$_2$, Hexane/AcOEt: 50/50), M.p. 88 °C; $^1$H NMR (CDCl$_3$): δ= 3.64 (s, 4H, O*CH2CH2*O), 3.70-3.75 (m, 4H, SiOCH$_2$*CH2*O), 3.90-3.95 (m, 4H, SiO*CH2*CH$_2$O), 7.35-7.45 (m, 6H, arom.), 7.60-7.70 (m, 4H, arom.). $^{13}$C NMR (CD$_3$COCD$_3$): δ= 63.8, 71.4, 73.2, 128.6, 130.9, 134.4, 135.7. $^{29}$Si NMR (59.53 MHz, CDCl$_3$, 25 °C): δ= -32.2 (s). Mass (*m/z*) 253 (M-Ph)$^+$. **7**: r$_f$= 0.6 (SiO$_2$, Hexane/AcOEt: 50/50), M.p. 102 °C; $^1$H NMR (CD$_3$COCD$_3$): δ= 3.57 (s, 8H, O*CH2CH2*O), 3. 64 (t, 4.9Hz, 8H, SiOCH$_2$*CH2*O), 3.96 (t, 4.9Hz, 8H, SiO*CH2*CH$_2$O), 7.35-7.45 (m, 12H, arom.), 7.60-7.70 (m, 8H, arom.). $^{13}$C NMR (CDCl$_3$): δ= 62.8, 70.9, 72.4, 127.9, 130.3, 132.9, 135.0. $^{29}$Si NMR (CDCl$_3$): δ= -18.7 (s). Mass (*m/z*) 583 (M-Ph)$^+$.

9. To a solution of triethyleneglycol (1g, 6.7 mmol) and N,N-dimethylaniline (1.61g, 13.3 mmol) in dry ether (20 ml) a solution of Ph$_2$SiCl$_2$ (1.40 ml, 6.7 mmol) in dry ether (10 ml) was added dropwise at 25 °C. The reaction mixture was refluxed for 9h. before it was cooled to r. t. . H$_2$O (15 ml) was added at 0 °C and the layers separated. The aqueous phase was extracted with ether (2x15 ml). The organic layers were combined, dried over MgSO$_4$ and the solvent removed. The desired compounds were obtained after chromatography (SiO$_2$, Hexane/AcOEt: 50/50)