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Cage-rearrangement of silsesquioxanes†

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Abstract—Deca- and dodeca-silsesquioxane cages were prepared by partial rearrangement of octa-silsesquioxanes, $R_8(SiO_{1.5})_8$ (**I**), to give species of the type $R_{10}(SiO_{1.5})_{10}$ (**II**) and D_{2d}-$R_{12}(SiO_{1.5})_{12}$ (**III**). This rearrangement is catalysed by sodium acetate, sodium cyanate, sodium sulfite, sodium hydroxide and potassium carbonate in acetone as solvent. The mixture of $[Cl\text{-}(CH_2)_3]_8(SiO_{1.5})_8$ (**Ic**), $[Cl\text{-}(CH_2)_3]_{10}(SiO_{1.5})_{10}$ (**IIc**) and D_{2d}-$[Cl\text{-}(CH_2)_3]_{12}$-$(SiO_{1.5})_{12}$ (**IIIc**) can be separated by NP-HPLC. The reaction was also studied in acetonitrile using sodium fluoride, sodium or potassium hexafluorosilicate and 18-crown-6 as catalysts. Simultaneous reaction of (**Ic**) and $[NCS\text{-}(CH_2)_3]_8(SiO_{1.5})_8$ (**If**) with sodium acetate in acetone leads to a mixture of octa-, deca- and dodeca-silsesquioxanes with a statistical distribution of the $Cl(CH_2)_3$- and $NCS(CH_2)_3$-side groups. The ^{29}Si NMR data of the synthesized silsesquioxanes have been collected. The shift data can be calculated following simple additivity rules. © 1997 Elsevier Science Ltd

Keywords: silsesquioxanes; rearrangement; catalysts; NMR; HPLC.

Functionalized polyhedral siloxanes, also called silsesquioxanes, present themselves as models for the investigation of surface modified silica gels. Of the many possible polyhedral cage sizes and configurations only a few types are actually known as shown in reviews by Voronkov and Lavrent'yev [1] and by Calzaferri [2]. The widest variety in cage structures is found for the hydridosilsesquioxanes $(HSiO_{1.5})_n$, where polyhedra with $n = 8,10,12,14,16$ and 18 vertices have been isolated [2,3]. A similar range of polyhedral siloxanes has been observed in aqueous solutions of silicates by ^{29}Si NMR [4]. The cubic cage is favored in the case of the organosilsesquioxanes (Fig. 1). Because of their use as models of silicates, an easy way for the preparation of other cage sizes is desirable.

RESULTS

Under the influence of some catalysts it was possible to rearrange octa-silsesquioxanes to the greater cages deca- and dodeca-silsesquioxanes (Fig. 1). To examine the effects of different silsesquioxanes, catalysts and solvents on the rearrangement several combinations of these parameters were studied. In acetone as a solvent, potassium carbonate (1), sodium hydroxide (2,5), sodium cyanate (3), sodium acetate (4) and sodium sulfite (6) proved to be effective as catalysts. There seems to be a correlation between the reactivity of the 3-X-propyl(octa-silsesquioxanes) to undergo the equilibrium reaction and the electronegativity of the substituent X [5]:

$$X = H < I < C_6F_5 < Br < Cl < NCS$$

The catalyst has to be adjusted to the silsesquioxane considered. A highly active catalyst can lead to ill-defined polymers. The catalytic activity follows the progression:

$$K_2CO_3 > NaOH(1.4\ 10^{-3}\ mol/l)$$
$$> NaOCN > CH_3COONa$$
$$\approx NaOH(1.4\ 10^{-4}\ mol/l) > Na_2SO_3$$

The concentrations of the different cage sizes in the product mixture depend mainly on the organic part of the silsesquioxane. The average distributions of the cage sizes are shown in Table 1 and a ^{29}Si NMR spectrum of a typical reaction product is shown in Fig. 2. The reaction is reversible. The rearrangement

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† Dedicated to Professor Alois Hass on the occasion of his 65th birthday.

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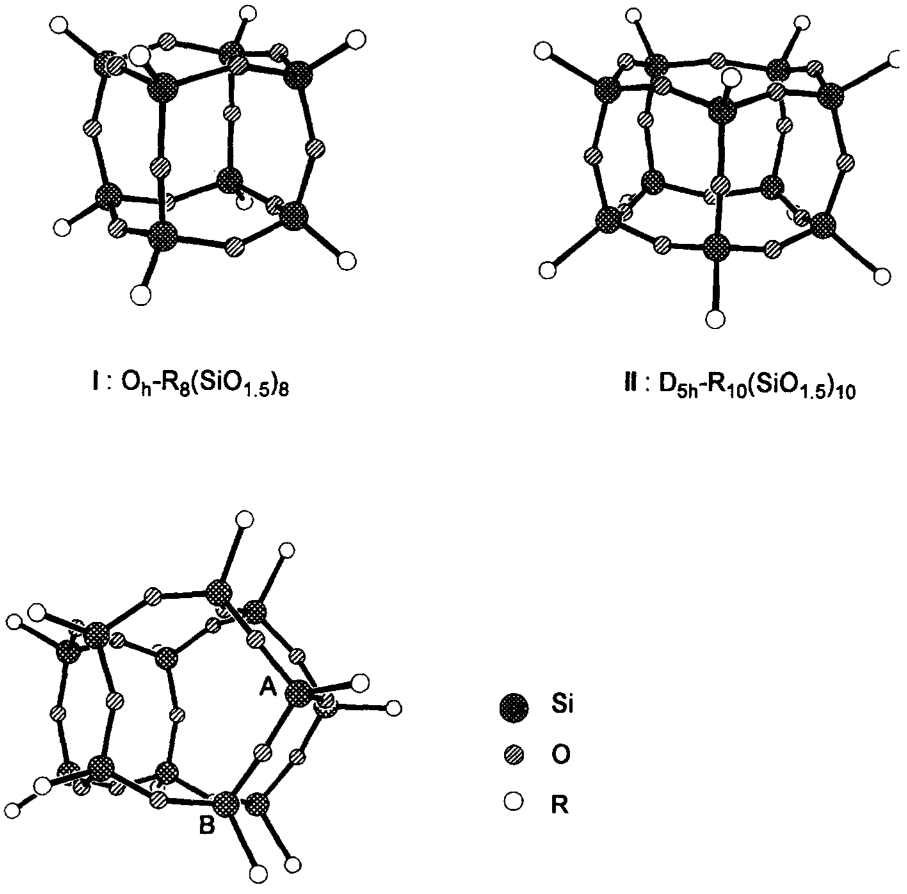

I : O_h-$R_8(SiO_{1.5})_8$

II : D_{5h}-$R_{10}(SiO_{1.5})_{10}$

III : D_{2d}-$R_{12}(SiO_{1.5})_{12}$

R =

a: C_2H_5-
b: C_3H_7-
c: ClC_3H_6-
d: BrC_3H_6-
e: IC_3H_6-
f: $NCSC_3H_6$-
g: $C_6F_5C_3H_6$-
h: C_4H_9-
i: C_5H_{11}-
j: C_7H_{15}-
k: C_8H_{17}-
l: C_9H_{19}-
m: $C_{10}H_{21}$-

Fig. 1. Structure diagrams for the octa- (I), deca- (II) and dodeca-silsesquioxanes (III).

of a deca-silsesquioxane (IIc) leads to the same distribution of cage sizes as starting from the octa-silsesquioxane. Other non-aqueous solvents such as diethylether, dichloromethane, dimethylsulfoxide and acetonitrile were also tested successfully as reaction media. The low solubility of the catalysts in these solvents requires a crown ether as a cocatalyst.

In some cases, the products of the rearrangement can be separated by normal phase HPLC. A chromatogram of a semipreparative separation is depicted in Fig. 3. It can be shown that the simultaneous rearrangement of two differently substituted organo-octa-silsesquioxanes leads to a complete scrambling of the siloxane building units of the cages and results in complex mixtures (Fig. 4). The ^{29}Si chemical shift data of the newly formed cage sizes can be reduced to the chemical shifts δ_I of the corresponding octa-silsesquioxanes with the help of the following equations:

$$\delta_{II} = 1.028\delta_I$$

for the deca-silsesquioxanes and

Table 1. Results of cage rearrangements of octa-silsesquioxanes

Residue	**I** (%)	**II** (%)	**III**[a] (%)	catalyst[b]
Solvent = acetone				
a, C_2H_5-	41	55	4	1
b, C_3H_7-[c]	88	12		1,2
c, ClC_3H_6-[c]	23	60	17	3,4,5,6
d, BrC_3H_6-[c]	64	36		3,4,5
e, IC_3H_6-[c]	88	12		2,3
f, $NCSC_3H_6-$[c]	18	56	26	3,4,5,6
g, $C_6F_5C_3H_6-$[c]	51	49		3,4,5
h, C_4H_9-	82	18		1
i, $C_5H_{11}-$	90	10		1
j, $C_7H_{15}-$	96	4		1
k, $C_8H_{17}-$	85	15		1
l, $C_9H_{19}-$	92	8		1
m, $C_{10}H_{21}-$	93	7		1
Solvent = acetonitrile				
c, ClC_3H_6-[c]	28	61	11	7,8,9
d, BrC_3H_6-	93	7		9
e, IC_3H_6-	97	3		9
f, $NCSC_3H_6-$[c]	18	62	20	7,8,9
g, $C_6F_5C_3H_6-$[c]	48	52		7,8

[a] For silsesquioxane skeletons see Fig. 1.

[b] 1 = K_2CO_3, 2 = NaOH ($1.4\ 10^{-3}$ mol/l), 3 = NaOCN, 4 = CH_3COONa, 5 = NaOH ($1.4\ 10^{-4}$ mol/l), 6 = Na_2SO_3, 7 = Na_2SiF_6 + 18-crown-6, 8 = K_2SiF_6 + 18-crown-6, 9 = NaF + 18-crown-6.

[c] Averaged values.

$$\delta_{\mathrm{IIIA}} = 1.025\delta_{\mathrm{I}} \quad \delta_{\mathrm{IIIB}} = 1.064\delta_{\mathrm{I}}$$

for the two different positions A and B of the dodeca-silsesquioxane. These relations reflect the influence of ring strain on the chemical shift. In the octamer, the silicon atoms are part of three eight-membered rings, and in the decamer part of two eight- and one ten-membered ring. There are two different sites for the silicon atoms in a dodeca-silsesquioxane. In position A, the silicon atoms resemble that of the deca-silsesquioxane within two eight- and one ten-membered rings, but in position B the silicon is part of one eight- and two ten-membered rings. Ring strain leads to a downfield shift [6]. The exchange of an eight- for a ten-membered ring results in a shift of *ca* −2 ppm upfield because of the diminished strain. The ^{29}Si NMR chemical shift data of the compounds presented here are collected in Table 2. The ^1H and ^{13}C NMR data are as to be expected and do not offer new insights.

EXPERIMENTAL

Instrumentation

HPLC: Knauer, column: Merck Hibar RT 250-10 with Si 60 LiChrospher (5 μm), sample loop: 500 μl, mobile phase: hexane/chloroform (50/50 vol), flow rate 25 cm^3/min. ^{29}Si NMR: Bruker AMX300, 59.625 MHz, pulse angle 37°, 20 s recovery time, resolution 0.4 Hz/point. Chemical shifts are relative to $(CH_3)_4Si$ and positive shifts are shifts to higher frequencies.

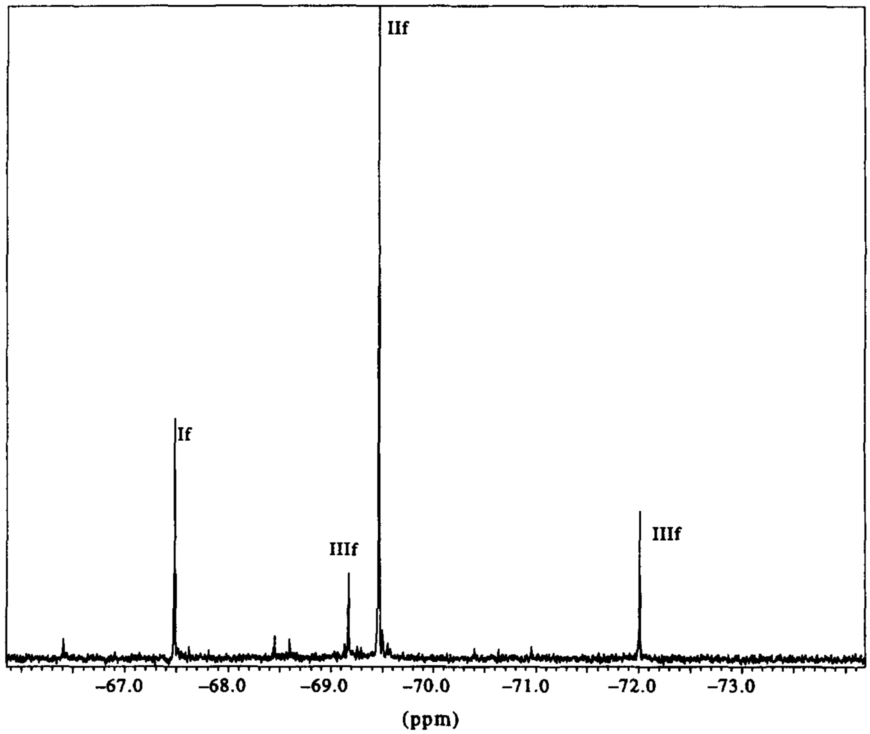

Fig. 2. ^{29}Si NMR spectrum of a reaction mixture of $(NCSC_3H_6)_8(SiO_{1.5})_8$ (**If**) in acetone with sodium sulfite as catalyst. For the abbreviations see Table 1.

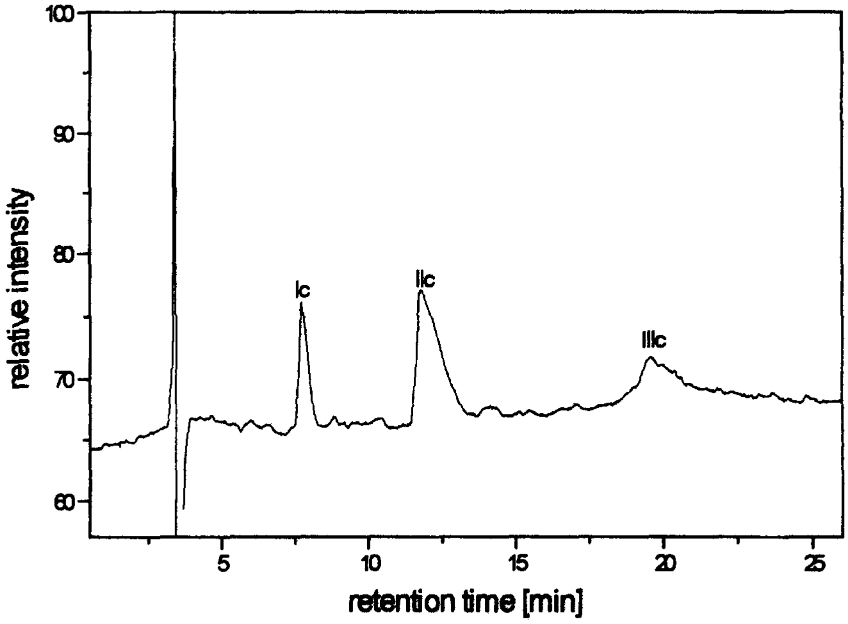

Fig. 3. NP-HPLC chromatogram of the separation of $(ClC_3H_6)_n(SiO_{1.5})_n$ with n = 8,10,12. For the abbreviations see Table 1.

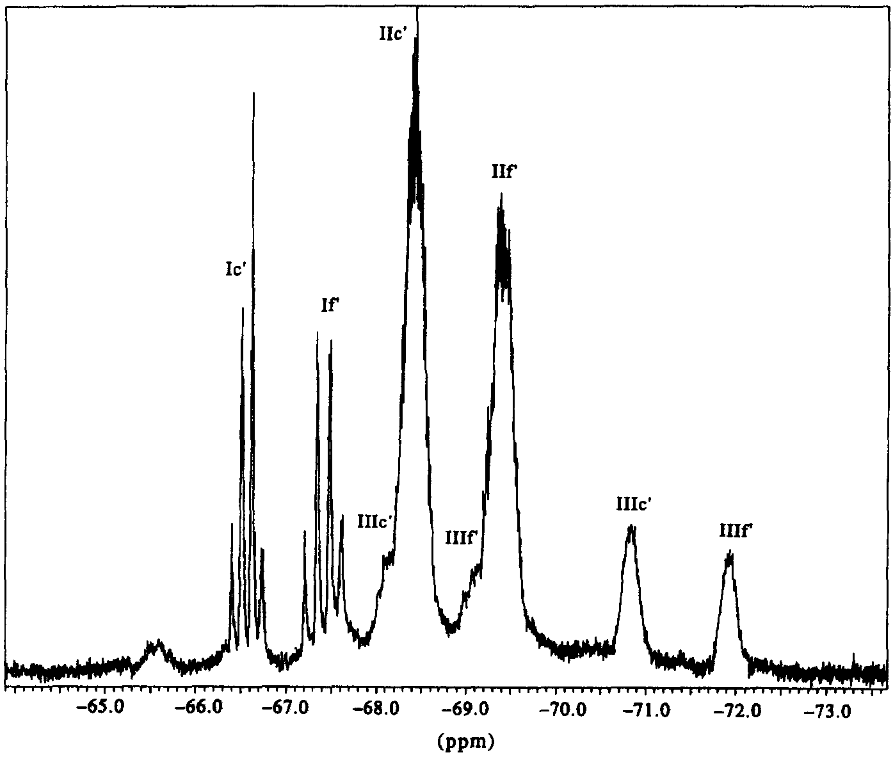

Fig. 4. ^{29}Si NMR spectrum of an equilibrium mixture of **Ic** and **If**. The roman numerals designate the cage sizes. (**I**: octa- **II**: deca-, **III**: dodecasilsesquioxane), the letters c and f, the side groups ClC_3H_6- and $NCSC_3H_6$-, respectively.

Table 2. ^{29}Si NMR chemical shift data [ppm] of some organosilsesquioxanes

Residue	I	II	III[a]	
			A	B
a, C_2H_5-	−65.71	−67.56	−67.53	−69.79
b, C_3H_7-	−67.22	−69.16		
c, ClC_3H_6-	−67.08	−68.97	−68.73	−71.37
d, BrC_3H_6-	−67.41	−69.31		
e, IC_3H_6-	−67.93	−69.85		
f, $NCSC_3H_6-$	−67.58	−69.56	−69.27	−72.07
g, $C_6F_5C_3H_6-$	−67.21	−69.11		
H, C_4H_9-	−66.81	−68.61		
i, $C_5H_{11}-$	−66.69	−68.61		
j, $C_7H_{15}-$	−66.63	−68.56		
k, $C_8H_{17}-$	−66.74	−68.68		
l, $C_9H_{19}-$	−66.69	−68.62		
m, $C_{10}H_{21}-$	−66.62	−68.55		

[a] For silsesquioxane skeletons see Fig. 1.

Materials

The functionalized silsesquioxanes are already described in ref. [7].

Basic procedure 1. 0.48 mmol of the silsesquioxane was refluxed with 18.3 mmol of a catalyst in 70 cm^3 of dry acetone for 24 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2. The CH_2Cl_2 was distilled off, the residue dissolved in $CDCl_3$ and characterized by ^{29}Si NMR spectroscopy.

Basic procedure 2. 0.48 mmol of the silsesquioxane, 18.3 mmol of the catalyst and 100 mg of 18-crown-6 were refluxed in 70 cm^3 of dry acetonitrile for 1 d. The product was then treated as in procedure 1.

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