Synthesis of macrocyclic tris-cis-tris-trans-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane in carbonic acid solution

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ABSTRACT
The possibility to synthesize stereoregular tris-cis-tris-trans-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane (tris-cis-tris-trans-[PhSi(O)OH]12) in an inorganic liquid medium – aqueous carbonic acid solution was shown. The interaction of polyhedral phenylcoppersodiumsiloxane, [(C6H5Si(O)O]12(Cu2+)(Na+)4(L)m (L = BuOH, H2O), with carbonic acid can be considered as a new ‘green’ method to obtain functional organosiloxane macrocycles. In contrast to the known methods, no organic solvents were used during the reaction. The identification of the structure of the end compound was performed by means of NMR and Infrared spectroscopy as well as X-ray crystallography.

1. Introduction
Until recently, stereoregular siloxane macrocycles were not easily accessible compounds due to the difficulty to obtain such compounds with good yield caused by the peculiar character of their direct synthesis (1–5). As for the macrocyclic siloxanols they could not be synthesized by traditional reaction routes used in siloxane chemistry.

Successful efforts in synthesis of stereoregular organosiloxanols by means of different synthetic approaches (6–11) have attracted much attention because of high potential usage of these unique synthons in synthesis of well-defined siloxane structures.

Studies on the synthesis of polyhedral organometallasiloxanes and their subsequent controlled decomposition have led to the development of a relatively easy and reliable way to obtain stereoregular functional organocylosiloxane compounds (12–18). Metal ion-directed self-assembly pathways to form selectively polyhedral organometallasiloxane molecules with well-defined regular configurations were elaborated upon by means of hydrolytic condensation reaction of different trifunctional organoalkoxysilanes in the presence of ions of alkaline and transition metals. In accordance with this method, the desired polyhedral molecules contain only one type of a stereoregular cyclooligosiloxanolate fragment coordinated to a metal ion matrix. The cyclosiloxanolate fragment size depends on the metal ions used as well as the reaction conditions. According to this strategy, the metal ions serve both as templating
units and as structural elements. The subsequent reaction of the polyhedral organometallasiloxanes either with triorganylchlorosilanes or with dilute hydrochloric acid in organic solvents allows the metal ions to be removed effectively as metal chlorides and for cyclosiloxanes to be obtained (12–14,18).

By following this reaction scheme, macrocyclic siloxanols, [PhSi(O)OH]n, (n = 6, 12), were obtained for the first time (18). These siloxanols can be considered as unique model compounds as well as valuable building blocks for directed molecular design of organosiloxane polymers, namely polyorganosilsesquioxanes, with tailored properties (such as thermal stability or dielectric characteristics (19)). Furthermore, these macrocycles can be exploited as precursors for supramolecular organic–inorganic hybrid compounds.

However, current synthetic methods for the synthesis of the macrocyclic siloxanols are rather complicated. Hydrochloric acid not only destroys the structure of a metallasiloxane but serves also as a catalyst for possible condensation of silanol groups. Thereby the reaction has to be carried out in a mixture of organic solvents (a biphasic polar/organic system) at a sufficient low concentration of organometallasiloxane and the exact calculated amount of hydrochloric acid to be added. Indeed, even a slight deviation in the amount of the acid or some delay in the washing out of salt residues may lead to noticeable decreases in the yield of the desired siloxanol macrocycles.

A typical procedure (18) of this method includes, for example, usage of the diluted solution of phenylcopper-sodiumsiloxane in the mixture of toluene and ethanol, which is to be treated with the diluted solution of hydrochloric acid at 0°C. The product formed (e.g. tris-cis-tris-trans-[PhSi(O)OH]12 (18)) is to be washed and dried fast. Large amounts of organic solvents as well as a complicated cooling procedure are thus required for this method.

The aim of our present research is to develop an alternative method of synthesis of macrocyclic siloxanols in the framework of ‘green’ chemistry approach.

It is well known that aqueous carboxic acid solutions (formed when CO2 is being dissolved in H2O) are a peculiar medium with an acidity that can be tuned by varying the pressure and/or temperature. Moreover, with the increase in pressure the reaction equilibrium shifts toward the formation and dissociation of carboxic acid molecules (see Scheme 1) and therefore the pH of the medium decreases and can reach the value 2.8 at CO2 saturating pressures as high as 150–200 bar (20–22).

It seems that the transition toward usage of carbonic acid solution as a reaction medium for the synthesis of siloxane macrocycles should allow one to develop the method for preparing such compounds. As it was mentioned above, the main problem of the known approach is the necessity to suppress catalytic activity of acid as soon as silanol groups are formed to prevent its further condensation. In the new approach, neutralization of the carbonic acid proceeds spontaneously after decompression of the reactor. Moreover, such a synthetic route would not require usage of any organic solvents. As for the high CO2 pressure required, many established industrial chemical processes occur at high pressure (23–25). Besides, benefits of supercritical fluids such as CO2 as ‘green’ solvents have attracted significant additional attention toward high-pressure equipment in general. Therefore, during the last decades remarkable progress has been achieved in the field of development of facilities for high-pressure generation. As a result, new reliable and powerful pumps as well as convenient and sophisticated autoclaves have appeared, which are capable of providing chemical laboratories with high and controlled CO2 pressure for synthetic purposes (26,27).

Earlier we investigated the reaction of polyhedral phenylnickelsodiumsiloxane, \(([(C6H5Si(O)O)]6(Ni2+)x(Na+)4−(NaOH)2(C6H5Si(O)O−)6]^{xLx}_{(L = BuOH, H2O)}\) with carbonic acid in order to obtain cis-hexa[(phenyl) (hydroxy)]cyclohexasiloxane, cis-[PhSi(O)OH]16 (28). In this case our task was more complicated – the decomposition reaction of polyhedral phenylcopper-sodiumsiloxane in the carbonic acid solution with the purpose to obtain the macrocyclic siloxanol – tris-cis-tris-trans-[PhSi(O)OH]12 – a more unstable molecule requiring mild conditions in order to be isolated. Higher in twice number of silanol groups together with tris-cis-tris-trans structure of this compound made it much more sensitive to the intermolecular condensation reaction compared with the previous model. Indeed, success with treatment of such a complex model could convert this synthetic approach to a general method of neutralization of siloxanolates to siloxanols.

2. Results and discussion

The general scheme of the synthetic process is shown in Scheme 2.

The mixture of reaction products after the completion of the process and decompression became an aqueous suspension. The color of the dispersed phase is in the range from muddy blue to transparent blue depending on the reaction time. Separation of the suspended particles

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2H_2O + CO_2 ⇌ H_2CO_3 + H_2O ⇌ H^+ + HCO_3^-
\]

Scheme 1. The formation and subsequent dissociation of carboxic acid occurring when carbon dioxide is being dissolved in water.
was performed by filtration. To remove sodium bicarbonate formed in the system, the filtrate was washed with ∼100 mL of deionized water until the neutral reaction of wash water was detected (pH 7). The analysis of the obtained products was performed by infrared (IR) spectroscopy and X-ray crystallography. For comparison, the initial polyhedral phenylcoppersodiumsiloxane and the reference sample tris-cis-tris-trans-[PhSi(O)OH]₁₂ were also analyzed. In the IR spectra (Figure 1) one can see that when the reaction time of phenylcoppersodiumsiloxane (Figure 1, curve 1) with carbonic acid increases, the gradual replacement of the Cu–O–Si (1008 cm⁻¹) band with the Si–O–Si (1062 cm⁻¹) band takes place. It can be clearly seen from several experiments with increasing reaction times (Figure 1, curves 2, 3, 4, 5, and 6).

Scheme 2. The synthesis of tris-cis-tris-trans-[PhSi(O)OH]₁₂ in the carbonic acid solutions.

Figure 1. IR spectra of the samples: (1) the initial phenylcoppersodiumsiloxane; (2), (3) and (4) reaction products after 1, 3 and 6 h, respectively, of the reaction with carbonic acid and subsequent washing with water; (5) the product obtained after 6 h of the reaction in carbonic acid, subsequent washing with water and the removal of copper basic carbonate with dilute acetic acid; and (6) reference tris-cis-tris-trans-[PhSi(O)OH]₁₂ sample, obtained accordingly to the previously described method (10).

Figure 2. Powder X-ray diffraction patterns of the samples: (1) the initial phenylcoppersodiumsiloxane; (2), (3), (4), (5) and (6) reaction products after 1, 2, 3, 5 and 6 h, respectively, of the reaction in carbonic acid solutions and subsequent washing with water, (7) the product obtained after 6 h of the reaction in carbonic acid, subsequently washed with water and treated with a diluted acetic acid in order to remove copper basic carbonate; and (8) reference tris-cis-tris-trans-[PhSi(O)OH]₁₂ sample, obtained accordingly to the previously described method (10).
1, curves 2–4). The increase in the intensity in the area of 4000–3000 cm\(^{-1}\) occurs also, which corresponds to the OH stretching vibrations. This observation suggests the increase in the amount of OH groups in the compound being formed. The accumulation of \(\text{Cu(HCO}_3\text{)}_2\) in the system was observed simultaneously (the bands in the range of 1500–1425 cm\(^{-1}\)).

The same process was confirmed by the X-ray diffraction analysis data (see Figure 2). When carbonic acid

Figure 3. \(^1\text{H NMR and }^{29}\text{Si NMR spectra of the product obtained after the reaction of polyhedral phenylcoppersodisiloxane in carbonic acid solution for 6 h, washing with water and removal of copper basic carbonate.}
reacted with phenylcoppersodiumsiloxane (curve 1) the latter decomposed and the tris-cis-tris-trans-[PhSi(O)OH]_{12} phase was formed. The intensity of the lines of the initial substrate decreases and the intensity of the lines of the tris-cis-tris-trans-[PhSi(O)OH]_{12} increased with the increase in the reaction time in the carboxic acid solutions. When the reaction was performed during 1–2 h (curves 2, 3), the purity of the product obtained was yet poor, but for longer reaction times (curves 4, 5) the fraction of crystalline impurities drastically decreased.

Only the reaction of destruction of metallasiloxane occurred and the presence of carboxic acid did not promote condensation of silanol groups of the cyclic siloxaneol being formed (see Figure 3). This fact allows us to consider the developed method as a very promising selective synthetic route to produce stereoregular macrocyclic cyclosiloxanes.

Comparing IR spectroscopy and X-ray diffraction data, one can notice that the duration of the process influences the completeness of the reaction. In the experiments where the reaction time is in the range of 1–5 h some amounts of the initial phenylcoppersodiumsiloxane could still be detected in the reaction products. Only when the reaction was carried out for 6 h the completed pure product was obtained after washing and drying. The product contained only tris-cis-tris-trans-[PhSi(O)OH]_{12} and copper basic carbonate (Figure 1, curve 4 and Figure 2, curve 6). The copper basic carbonate, which is not soluble in water, precipitated together with the cyclic siloxane. In order to remove the copper basic carbonate from the product completely, the precipitate was washed with small amounts of dilute acetic acid, and the traces of acetic acid was neutralized with aqueous solution of sodium bicarbonate. The end product was dried in a desiccator with a dehydrating agent. The IR spectrum of the obtained product (Figure 1, curve 5) perfectly matches the spectrum of the reference tris-cis-tris-trans-[PhSi(O)OH]_{12} sample (Figure 1, curve 6) obtained according to the method described earlier (10). Nevertheless, the X-ray diffraction pattern of the product after the separation of the reaction mixture (Figure 2, curve 7; Table 1) does not match completely to the curve for the reference tris-cis-tris-trans-[PhSi(O)OH]_{12} (Figure 2, curve 8; Table 1), which was obtained using the method described earlier (18).

The powder patterns look similar to each other; however, the differences in the peak positions are observed (Table 1). Thus, when phenylcoppersodiumsiloxane is treated with carboxic acid a new polymorph of the product forms.

\(^{1}H\) and \(^{29}Si\) NMR-spectroscopy data confirm that as a result of the experiment macroyclic dodeca[(phenyl)(hydroxyl)]cyclohexasiloxane with tris-cis-tris-trans configuration (Figure 3) was obtained. In the \(^{1}H\) spectrum two types of resonances in the ratio 2:1 corresponding to phenyl and hydroxyl protons were observed indicating the tris-cis-tris-trans configuration. The \(^{29}Si\) NMR spectrum also proves such a configuration with two silicon signals corresponding to the different silicon atoms in the structure of the cycle.

Earlier we have shown that the reaction of polyhedral phenylnickel.sodiumsiloxane with carboxic acid proceeded for 10 min to give cis-hexa[(phenyl)(hydroxyl)]cyclohexasiloxane, cis-[PhSi(O)OH]_{6} (28). In this case, the more complicated structure of phenylcoppersodiumsiloxane requires more time for its reaction with carboxic acid in order to obtain tris-cis-tris-trans-[PhSi(O)OH]_{12}. But it is very important that a significant increase in treatment time showed a very selective action of carboxic acid compared with HCl traditionally used for the neutralization. Carboxic acid cleaves Si–O–M bonds but does not catalyze condensation of OH-groups.

### Table 1. The most intensity peak positions of two tris-cis-tris-trans-[PhSi(O)OH]_{12} polymorphs.

| Reference tris-cis-tris-trans-[PhSi(O)OH]_{12} sample | 2θ,° | 6.99 | 13.16 | 14.05 | – | 21.12 | 23.52 | 24.58 |
| Sample 7 | 2θ,° | 7.17 | 13.52 | 14.39 | 18.05 | 21.66 | 23.48 | 24.51 |

3. Experimental

All solvents were purified before use according to the well-known procedures (29). n-Butanol was distilled. Acetic acid was distilled. Water was distilled. NaOH and CuCl\(_{2}\) were purchased from Aldrich.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker ‘Tensor 37’. The samples were prepared by pressing KBr pellets.

X-ray diffraction study was performed using an X-ray powder diffractometer Bruker D8 Advance equipped with variable slits, a Ni filter, and a position-sensitive detector LynxEye. The study was performed in an X-ray reflection mode (Bragg-Brentano geometry), with the rotation of the sample. The experimental data were collected using the Bruker DIFFRACplus package (30), the analysis of powder patterns was performed with EVA program (31).

NMR spectra were registered on a BrukerAvance™ 600 spectrometer. The chemical shift of acetone (\(δ = 2.05\) ppm) was used as a reference for \(^{1}H\) NMR. Chemical shifts for \(^{1}H\) were indirectly correlated with
tetramethylsilane (TMS) through the signals of the solvent. Chemical shifts for $^{29}\text{Si}$ were correlated with TMS as an external reference standard.

High-resolution mass spectra (HRMS) were measured using a Bruker microTOF II instrument with electrospray ionization (ESI) (Germany).

Molecular weights ($M_p$) were determined relatively to polystyrene standards by gel permeation chromatography (GPC) (high-pressure pump STAYER 2 (Aquilon, Russia), Smartline RI 2300 refractive index detector (KNAUER, Germany), JETSTREAM 2 PLUS thermostat (KNAUER, Germany)). Conditions: 40°C (±0.1°C), eluent – THF (1.0 mL/min), Phenogel columns (Phenomenex, USA) 300 × 7.8 mm with 5 µm particles (pore size 500 Å).

Experiments on transformations of phenylcoppersodiumsiloxane in carbonic acid solution were performed using an experimental setup, which is shown in Figure 4. This setup consisted of a high-pressure generator with an automatic control module produced by SITEC (Switzerland), a tank with CO$_2$ and a stainless steel high-pressure vessel (reactor) with a total inner volume of about 20 ml. The reactor was charged with the initial reagent, water, and a magnetic stirrer. All the experiments were performed at room temperature. In the experiments high-purity CO$_2$ (>99.997%, Linde Gas Rus, Russia) was used. Before each experiment water was freshly prepared on a Millipore Milli-Q Synthesis setup.

The polyhedral phenylcoppersodiumsiloxane and reference sample of tris-cis-tris-trans-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane were obtained by the previously described methods ($^{15,18}$). In the experiment described below crystals of phenylcoppersodiumsiloxane were used right after the filtration on the SCHOTT glass filter.

3.1. Experiment 1. Monitoring of the reaction of phenylcoppersodiumsiloxane with carbonic acid solution

The high-pressure reactor with a magnetic stirrer was charged with 2 g (0.0007 mol) of phenylcoppersodiumsiloxane of the following formula: $\{[C_6H_5Si(O)O]^{-12}$ (Cu$^{2+}$)$_4$(Na$^{-}$)$_4$(C$_4$H$_9$OH)$_{10}$(H$_2$O)$_3$ and 10 ml of freshly prepared Milli-Q water. The reactor was tightened and liquid CO$_2$ was injected inside the reactor. Further, the pressure was increased up to 150 bar at room temperature ($\approx$23°C). Under these conditions the pH of the water phase in the lower part of the reactor reached the values around 2.8, while the upper part of the reactor was occupied with liquid CO$_2$ ($\rho \approx 0.9$ g/cm$^3$).

Depending on the experiment the reaction was performed during 1, 2, 3, 5 or 6 h with continual stirring. The reaction was finished by a rather slow decompression: the total removal of CO$_2$ took around 2–3 min. After that the obtained mixture was filtered on a SCHOTT filtering funnel with an additional paper filter and washed with ~100 mL of deionized water till the neutral reaction of wash water (pH 7). Then the filtrate was air-dried. As a result 1.36, 1.30, 1.26, 1.22 and 1.20 g of the product (with a color from muddy to light blue) were obtained depending on the reaction time.

The products obtained were investigated by IR spectroscopy and X-ray crystallography.

3.2. Experiment 2. Synthesis of tris-cis-tris-trans-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane

The experiment was performed similar to Experiment 1. The reaction was stirred for 6 h to achieve complete interaction of initial compounds. The only difference was that the product obtained after filtration was additionally washed with a 10% solution of acetic acid to remove Cu(HCO$_3$)$_2$ insoluble in water and then the residual acetic acid was neutralized with sodium bicarbonate. The white solid product obtained was washed with distilled water and then dried over CaCl$_2$. About 0.95 g of white crystalline powder with a yield of 81.9% was obtained from 2 g (0.0007 mol) of phenylcoppersodiumsiloxane.

Found %: C, 52.65; H, 4.42; Si, 20.21. Calculated for $[C_6H_5Si(O)OH]^{12}; C 72H72Si12O24$ molecular mass 1658.37, %: C, 52.14; H, 4.38; Si, 20.32.

$^1$H NMR (δ (ppm), acetone-d$_6$): 7.70 (d, 2H, o-Ph, cis-cis-Ph), 7.57 (d, 2H, o-Ph, cis-trans-Ph), 7.34 (m, 1H, p-Ph), 7.15 (m, 2H, m-Ph), 6.85 (s, 1H, cis-trans-OH), 6.80 (s, 1H, cis-cis-OH) $^{29}$Si NMR (δ (ppm), acetone-d$_6$): $−70.99$ (cis-trans), $−71.01$ (cis-cis).

HRMS (ESI) $m/z$ calcd. for C$_{72}$H$_{72}$O$_{24}$Si$_{12}$ [(M+Na)$^{+}$]: 1679.1537, found 1679.1528.

GPC: retention time 6.47 min.

4. Conclusions

Chemical approach to the synthesis of macrocyclic stereo-regular tris-cis-tris-trans-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane...
cyclooctadecasiloxane was performed following the ‘green’ chemistry paradigm. This approach allowed not only to simplify synthetic procedure, but also to exclude use of organic solvents. The complex model used as the target compound in this process and the results obtained earlier (28) showed promising prospects of the method used and proposed its prospects in many other siloxanolate–silanols transformations.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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