



SYNTHESIS OF HEXAMETHYLTRISILOXANEDIOL AND 1,1,3,3,5,5,7-HEPTAMETHYL-7-PHENYLCYCLOTETRASILOXANE ON ITS BASIS

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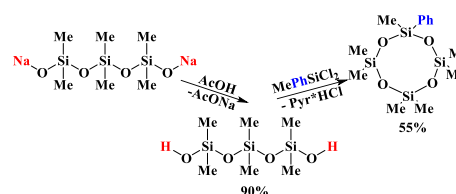
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Abstract

A method for the directed synthesis of hexamethyltrisiloxanediol and 1,1,3,3,5,5,7-heptomethyl-7-phenylcyclotetrasiloxane from sodium hexamethyltrisiloxanediolate in 90% and 55% yields, respectively, is suggested.

Key words: hexamethyldisiloxanediol, sodium hexamethyltrisiloxanediolate, mixed cycles.



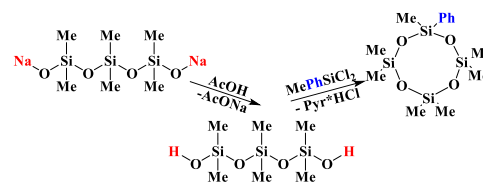
Introduction

Nowadays, cyclosiloxanes find extensive use as components for various purposes, for example, as a starting reagent for the production of siloxane homo- and copolymer-based rubbers and fluids [1], functional precursors for molecular design [2], cross-linking agents [3], fire retardants [4], as components of dry cleaning and detergent compositions [5], solvents for dyeing fabrics [6], and also in cosmetics [7].

Of particular interest is the synthesis of mixed cyclosiloxanes due to the ample opportunities of their application for the synthesis of oligo- and copolymers with a given set of properties and modification of the main polymer chain of polyorganosiloxanes. At present, the synthesis of mixed cyclosiloxanes is carried out either by the hydrolysis of the corresponding diorganodichlorosilanes and siloxanes, or by the heterofunctional condensation of hydroxy- and chlorine-containing precursors. These approaches are characterized by low selectivity and yields, and in the second case also by the complicated synthesis of the initial oligomers of a given length [8]. A recently developed method for obtaining mixed cyclosiloxanes [9] from sodium hexamethyltrisiloxanediolates affords unsymmetrical cyclosiloxanes in 40 to 80% yields depending on the reaction conditions, but the insolubility of sodium hexamethyltrisiloxanediolate in most organic solvents creates certain difficulties in the synthesis. The sensitivity to moisture and reaction temperature, heterogeneous nature of the process, or the use of high dilution (5 wt %) restrict its applicability. At the same time, the availability of simple and selective methods for the synthesis of the salt [10] and the possibility of obtaining it actually from waste products render further development of the directed synthesis of mixed cycles from this precursor highly promising.

Results and discussion

Taking into account the above-mentioned, the goal of this work was to study the possibility of the directed synthesis of hexamethyldisiloxanediol from sodium hexamethyltrisiloxanediolate and mixed cyclosiloxanes on its basis, for example, 1,1,3,3,5,5,7-heptomethyl-7-phenylcyclotetrasiloxane (Ph-D₄). The suggested synthetic route is depicted in Scheme 1.



Scheme 1. General scheme for the synthesis of mixed cyclotetrasiloxanes.

At the first stage, sodium hexamethyltrisiloxanediolate, preliminarily prepared by the published procedure [10], was neutralized with anhydrous acetic acid in dry methyl *tert*-butyl ether (MTBE) at -80 °C. The resulting product was washed to the neutral pH value, the solvent was evaporated, and the residue obtained was distilled under vacuum. The main fraction was collected at 110 °C/1 mm Hg and analyzed by ²⁹Si NMR spectroscopy (Fig. 1).

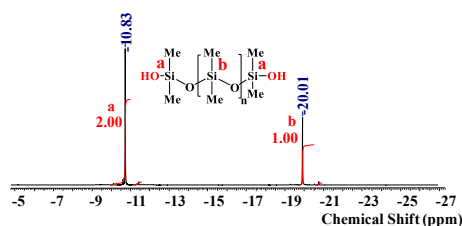


Figure 1. ²⁹Si NMR spectrum of hexamethyltrisiloxanediol.

To evaluate the product purity, a sample was blocked with chloro(dimethyl)vinylsilane followed by the analysis of the resulting silylated derivative by ^1H NMR spectroscopy and gas-liquid chromatography (GLC). The ratio of the integral intensities of the signals of the terminal (dimethyl)vinylsilyl group protons and those of the chain dimethylsilyl groups, determined from the ^1H NMR spectrum (Fig. 2), corresponded to the theoretical value: for every 6 vinyl protons, there were 12 methyl protons at the terminal silicon atoms and 18 methyl protons at the chain silicon atoms. According to the results of the GLC analysis, the purity of the product was 90% (Fig. 3a).

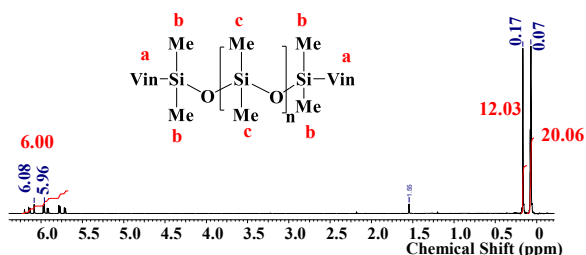


Figure 2. ^1H NMR spectrum of hexamethyltrisiloxanediol blocked with chloro(dimethyl)vinylsilane.

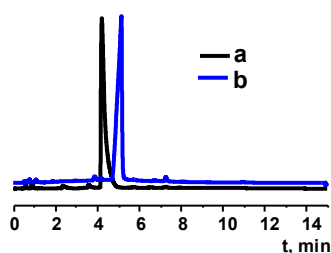


Figure 3. GLC curve of hexamethyltrisiloxanediol blocked with chloro(dimethyl)vinylsilane (a) and Ph-D₄ (b).

Thus, the neutralization of sodium hexamethyltrisiloxanediolate furnished hexamethyltrisiloxanediol in 90% yield.

Then it was reacted with dichloro(methyl)phenylsilane (10% excess) in the presence of pyridine as a hydrogen chloride acceptor (Scheme 1) in MTBE (30 wt %) at $-30\text{ }^\circ\text{C}$. The reaction mixture was washed until the neutral pH value, the solvent was evaporated, and the target product was isolated by vacuum distillation. The main fraction with a purity of 94% (Fig. 3b) was collected at $80\text{ }^\circ\text{C}/1\text{ mmHg}$. The ^1H and ^{29}Si NMR spectra of the product corresponded to the structure of target Ph-D₄ [9]. A comparison of the yields of target Ph-D₄ shows good prospects of the suggested approach: 55% vs. 40% in the case of the synthesis of the cyclic derivative from sodium hexamethyltrisiloxanediolate under heterogeneous conditions.

Experimental section

General procedure for the synthesis of hexamethyltrisiloxanediol. A flask was charged with acetic acid (71.08 g, 1.1846 mol) and MTBE (1200 mL). After cooling the system with liquid nitrogen to $-50\text{ }^\circ\text{C}$, sodium hexamethyltrisiloxanediolate (100 g, 0.3521 mol) was added under an argon atmosphere. After the reaction mixture reached room temperature, the resulting product was washed with water

to remove pyridine hydrochloride and sodium chloride until the neutral pH value. The resulting solution was dried over anhydrous sodium sulfate, after which MTBE was evaporated on a rotary evaporator. The product was isolated by vacuum distillation. The main fraction was collected at $110\text{ }^\circ\text{C}/1\text{ mmHg}$. The yield of hexamethyltrisiloxanediol was 85.5%. GLC: $\text{HOME}_2\text{Si}[\text{OSiMe}_2]_3\text{-OH}$ 96%, $\text{HOME}_2\text{Si}[\text{OSiMe}_2]_5\text{-OH}$ 4%. ^{29}Si NMR (CDCl_3): δ 20.01 s (1Si, $\text{OSi}(\text{CH}_3)_2$), 10.83 s (2Si, $\text{O}_{0.5}\text{SiMe}_2(\text{OH})$) ppm.

General procedure for the synthesis of Ph-D₄. A flask was charged with MTBE (33.33 g), pyridine (4.16 g, 0.0526 mol), and chloro(methyl)phenylsilane (10.05 g, 0.0526 mol). After cooling the system with liquid nitrogen to $-50\text{ }^\circ\text{C}$, a 30% solution of siloxanediol (10 g, 0.0438 mol) in MTBE was added under an argon atmosphere. When the reaction mixture reached room temperature, the resulting product was washed with water until the neutral pH value to remove sodium chloride. The resulting solution was dried over anhydrous sodium sulfate. Then MTBE was evaporated on a rotary evaporator. The product was isolated by vacuum distillation. The target fraction was collected at $140\text{ }^\circ\text{C}/1\text{ mmHg}$. The mass of the target fraction was 6.9 g (yield: 55%). GLC: Ph-D₄ 97%.

Conclusions

Hence, the potential of the directed synthesis of hexamethyltrisiloxanediol from sodium hexamethyltrisiloxanediolate and the mixed cycle Ph-D₄ on its basis was demonstrated.

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