

Communication

Microwave-assisted synthesis of cyclopentyltrisilanol ($c\text{-C}_5\text{H}_9$)₇Si₇O₉(OH)₃

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Abstract

Microwave-assisted synthesis of cyclopentyltrisilanol by the hydrolytic condensation of the cyclopentyltrichlorosilane in aqueous acetone has been successfully performed. The reaction under microwave irradiation is considerably shorter in time in comparison to the traditional procedure and may be utilized for preparation of Si-containing building blocks for nanocomposite materials.

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1. Introduction

Incompletely condensed polyhedral oligosilsesquioxanes (the so-called trisilanols) which have general formula $R_7T_7(OH)_3$ (where R – organic substituents) are versatile precursors to a wide range of hybrid inorganic–organic nanomaterials [1]. They can generally be obtained in two ways:

- by the hydrolytic condensation of cyclopentyl-, cyclohexyl- or cycloheptyltrichlorosilane [2,3],
- by the controlled cleavage of completely condensed polyhedral oligosilsesquioxanes (POSS) in the presence of strong acids or bases [4–8].

Corner-capping of incompletely condensed POSS trisilanols is an efficient method for preparing POSS reagents in which only one corner is functionalized with a graftable or polymerizable group [9]. Corner-capping of the POSS trisilanol can be carried out using a variety of trichlorosilane $RSiX_3$ coupling agents. In addition to corner-capping reactions with $RSiX_3$, trisilanols react with a wide range of

main-group, transition-metal, and lanthanide elements to afford fully condensed metal-silsesquioxanes [10,11].

POSS reagents are unique in both their chemical composition and physical nature. The rigid, thermally stable silicon–oxygen framework contains an oxygen to silicon ratio of 3/2, which is intermediate between that for siloxanes and silica. Unfortunately, the preparation of these trisilanols requires inconvenient time-consuming synthesis before synthetically useful quantities can be obtained (3 days for cyclopentyltrichlorosilane and 2 months for cyclohexyltrichlorosilane). A useful solution could be application of microwave irradiation – this technique proves to be excellent in cases where traditional heating has low efficiency because of poor heat transmission, and hence local overheating is a main inconvenience. When molecules with permanent dipole are submitted to an oscillating electric field the orientation changes at each alternation. The strong agitation, provided by the reorientation of molecules, in phase with the electrical field excitation, causes an intense internal heating. Main advantages of microwave heating derive from the almost immediate “in core” heating of materials, in an homogeneous and selective manner, especially those with poor heat conduction properties [12]. Microwave heating has attracted the attention of investigators in that it makes it possible to shorten significantly the length of reactions, to increase their selectivity, and to

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increase the product yields, which is particularly important in the case of high-temperature processes that take a long time [13].

In case of cyclopentyltrisilanol's synthesis microwave effect can be explained by interaction of water and acetone molecules with microwave irradiation and generation of heat. The heating occurs via two mechanisms – dipolar polarization and conduction. The water and acetone dipoles are induced to move by interaction with the electric (rather than magnetic) field component of the microwave irradiation. When a dipole tries to re-orientate itself with respect to an alternating electric field, it loses energy (in the form of heat) by molecular friction. This leads to local superheating which results in increased reaction rate and higher yield than in classic synthesis of cyclopentyltrisilanol.

In this communication, we report on the synthesis of cyclopentylsilanetriol under microwave irradiation. Our procedure is based on the “classical” process described by Feher et al. [3] and consists of the hydrolytic condensation reaction of cyclopentyltrichlorosilane (CpSiCl₃) in refluxing aqueous acetone, for which microwave field was applied. To the best of our knowledge, this is the first work examining the microwave-assisted assembly of the –Si–O– core.

2. Experimental

2.1. Materials

Cyclopentyltrichlorosilane (97% grade) was purchased from ABCR GmbH & Co. KG, Karlsruhe, Germany. Acetone was of analytically pure grade and was obtained from POCH S.A., Gliwice, Poland. Both solvent and reagent were used without further purification.

2.2. Instruments and measurements

The reactions were conducted in a Milestone Start Labstation multimode microwave reactor with a maximum power output of 1000 W, equipped with a magnetic stirrer.

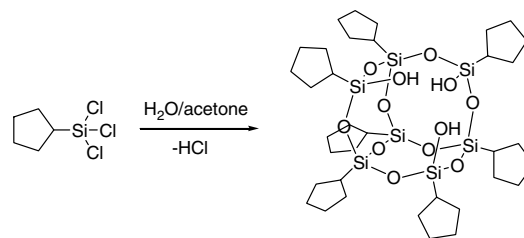
For the measurement of the IR spectrum, the powdered samples were mixed with KBr and pressed onto disk. The IR spectrum was measured by means of a Bio-Rad FTS 165 spectrometer.

¹³C NMR and ¹H NMR spectra were measured on a Varian Mercury-VX NMR spectrometer (¹³C, 75 MHz, ¹H, 300 MHz). Elemental analyses were performed using a Perkin–Elmer 2400 elemental analyzer.

2.3. Synthesis procedure of (c-C₅H₉)₇Si₇O₉(OH)₃

The general procedure is presented in Scheme 1.

Distilled water (11 ml, 0.611 mol) was dropped stepwise and with stirring to a solution of CpSiCl₃ (2 g, 9.8 mmol) and acetone (40 ml, 0.540 mol) in a 100 ml round-bottom flask equipped with a magnetic stirrer. The reaction mixture was then refluxed in a microwave reactor at 62 °C and a 50 W output power for the specified reaction time



Scheme 1. Synthesis route of cyclopentylsilanetriol.

(Table 1) was applied. The resulting crude product was collected on a Schott funnel and washed with acetone. In order to remove any remaining resinous material product was suspended in acetone (15 ml) and stirred for 2 h. After filtration the product was dried at 40 °C in a vacuum oven overnight to provide a white powder.

Cyclopentylsilanetriol was also synthesized by “classical” Feher method for comparison with our microwave synthesis results (Table 1).

3. Results and discussion

The effect of reaction time on the yield of trisilanol was investigated by performing the reaction at 62 °C for 10, 12, 15, 20 and 30 h, followed by rapid cooling to room temperature. The results are collected in Table 1 and show that yield of the condensation reaction increased with an increase of the reaction time, although different yield profiles for microwave and classical method occur (Fig. 1).

Table 1
Results of the synthesis under microwave and classical heating

Reaction time [h]	Microwave heating		Classic heating	
	Yield [mg]	Yield [%]	Yield [mg]	Yield [%]
10	2.0	0.16	0.0	0.00
12	5.0	0.41	–	–
15	30.0	2.44	–	–
20	173.5	14.11	7.0	0.57
30	200.0	16.26	180.0	14.63

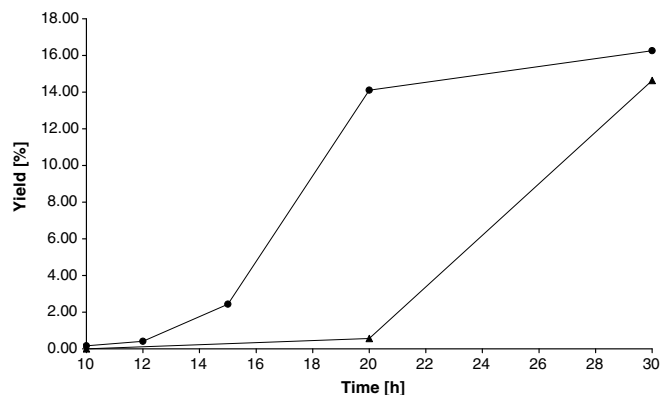


Fig. 1. Yield of the silanetriol vs. reaction time for synthesis in microwave conditions ● and for “classic” heating (▲).

In the microwave process useful quantities of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ can be obtained already after 20 h of reaction, whereby classical process requires more than 10 h longer reaction time to arrive at that yield. The same (or very similar) yield after 30 h of classical and MW-supported synthesis is, as we think, due to the fact that after that time reaction reaches equilibrium state due to fact that at these reaction conditions hydrogen chloride, which is a side-product of the hydrolytic condensation of cyclopentyltrichlorosilane, cannot be fully removed from the reaction environment. This kind of explanation can be applied to explain the existence of a plateau after 20 h in the MW-supported synthesis.

A plateau after 20 h in the MW-supported synthesis is probably also a result of changed composition of the reaction mixture which is not able to absorb microwave irradiation to that extent as it was possible during the first 20 h of the process.

Elem. Anal. for $\text{C}_{35}\text{H}_{66}\text{O}_{12}\text{Si}_7$ theoretical (found for “classic”) [found for microwave]: 48.02 (46.88) [46.41], 7.60 (7.36) [7.28].

NMR data show that compounds obtained in “classic” and microwave synthesis are cyclopentyltrisilanol. Both compounds exhibited three resonances (δ 23.78, 23.18, 22.63 for “classic” synthesis and δ 24.14, 23.54, 22.99 for microwave synthesis) with relative integrated intensities of 3:3:1 in the methine region of the ^{13}C NMR spectrum.

It can be observed that ^1H NMR spectra of trisilanols, obtained both in “classic” and microwave conditions, are identical and exhibited several characteristic resonances δ 8.72 (–OH); 1.26 (–CH–); 1.96, 1.67, 1.56 (–CH₂–) for “classic” synthesis and δ 8.72 (–OH); 1.25 (–CH–); 1.96, 1.70, 1.55 (–CH₂–) for microwave synthesis.

FT-IR spectra of both silanetriols are virtually the same and exhibits four characteristic bands: ν OH – 3206 cm^{-1} ;

ν_{as} CH₂ – 2953 cm^{-1} ; ν_{s} CH₂ – 2868 cm^{-1} ; ν_{as} Si–O–Si – 1106 cm^{-1} .

4. Conclusions

Microwave-assisted synthesis of cyclopentylsilanetriol by the hydrolytic condensation of the cyclopentyltrichlorosilane in aqueous acetone is considerably shorter in time in comparison to the traditional procedure. Further corner-capping of cyclopentylsilanetriol leads to efficient method for preparing POSS reagents in which one corner is functionalized with a graftable or polymerizable group. Such compounds are currently considered as important building blocks for advanced nanocomposite materials.

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