



NEW METHOD FOR THE SYNTHESIS OF 1,3-DIALLYL-1,1,3,3-TETRAMETHYLDISILOXANE

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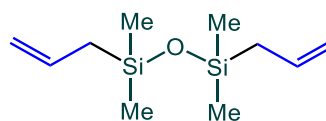
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Abstract

A new method for the synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane is proposed that includes several steps: the synthesis of dicellosolvoxy(dimethyl)silane by the transesterification reaction followed by obtaining allyl(cellosolvoxy)dimethylsilane from it under the action of the Grignard reagent and its condensation. The resulting product was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy as well as gas-liquid chromatography. The yield of the product was more than 90%, its purity was 99%.

Key words: hydrosilylation, allyls, allylsiloxanes, allylsilanes, siloxanes.



Introduction

Allylsilanes are extensively used in many fields, for example, as building blocks in organic and organoelement synthesis [1–3], in cross-coupling reactions [4, 5], polymer chemistry [6], and materials science [7]. However, the choice of starting allylsilanes is rather limited and is mainly represented by allylchlorosilanes or allylhydrosilanes, while the corresponding allyl(alcoxy)dimethylsilanes are much less represented on the market and, therefore, are most often synthesized in laboratories.

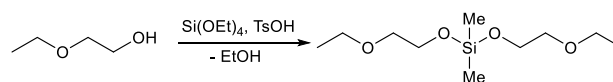
In turn, hydrolyzable chlorosilanes, alkoxydimethylsilanes, and disiloxanes are starting reagents for the production of silanols and sodium salts [8], different MQ, MQT and other resins [9], as well as polysiloxanes with terminal functional groups [10].

Herein, we present a new simple synthetic approach to 1,3-diallyl-1,1,3,3-tetramethyldisiloxane, which includes several steps: the synthesis of (dicellosolvoxy)dimethylsilane by the transesterification reaction followed by obtaining allyl(cellosolvoxy)dimethylsilane from it under the action of the Grignard reagent and its condensation.

Results and discussion

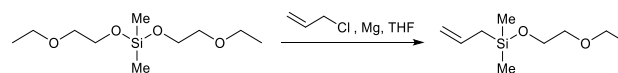
The synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane was carried out in several stages. The first one was the production of dicellosolvoxy(dimethyl)silane by the transesterification of diethoxy(dimethyl)silane and ethyl cellosolve in the presence of *para*-toluenesulfonic acid (Scheme 1).

The purity of the resulting product was determined by gas-liquid chromatography (GLC) (97%) (see the Electronic supplementary information (ESI)). Its yield was 90%.



Scheme 1. Synthesis of dicellosolvoxy(dimethyl)silane.

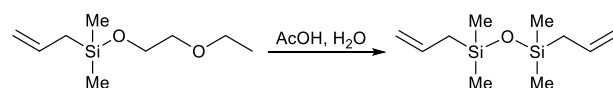
At the second step, allyl(cellosolvoxy)dimethylsilane was obtained by the reaction with the allylic Grignard reagent (Scheme 2). The reaction occurred in the presence of metallic magnesium and allyl chloride; the solvent was tetrahydrofuran.



Scheme 2. Synthesis of allyl(cellosolvoxy)dimethylsilane.

The purity of the resulting product was established by GLC (97%) (see the ESI). Its yield after distillation composed 74%.

The third stage was the production of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane by the hydrolytic condensation of allyl(cellosolvoxy)dimethyl silane (Scheme 3). The molar ratio of the reagent, acetic acid, and water was 1:5:2.5, respectively. The reaction mixture was stirred at room temperature for 8 h. The purity and structure of the product were confirmed by ¹H (Fig. 1), ¹³C, and ²⁹Si NMR spectroscopy, as well as GLC (see the ESI). The purity of the resulting compound was 99%, and its yield was 91%.



Scheme 3. Synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane.

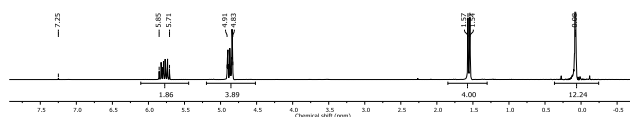


Figure 1. ^1H NMR spectrum of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane.

Experimental section

General remarks

The reagents purchased from commercial sources were used directly without further drying and purification. THF was dried by refluxing over calcium hydride for 3–5 h followed by distillation under argon and stored over 3 Å molecular sieves for 3 days.

Analysis and general methodology

The ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (300 MHz for ^1H ; 77.5 MHz for ^{13}C ; 59.6 MHz for ^{29}Si).

Syntheses

Synthesis of dicellosolvoxy(dimethyl)silane.

Diethoxy(dimethyl)silane (334 g, 2.3305 mol), ethyl cellosolve (838.9 mL, 9.322 mol), and *para*-toluenesulfonic acid (1 g) were loaded into a single-neck round-bottom flask equipped with a distillation bridge. The reaction mixture was stirred and simultaneously ethanol was distilled off to shift the reaction equilibrium. The reaction was carried out until ethanol was completely distilled off. The product was isolated by distillation.

^1H NMR (300 MHz, CDCl_3): δ 3.80 (m, 2H, Si-O- CH_2), 3.43–3.46 (m, 4H, CH_2 -O), 1.17 (m, 2H, CH_3 - CH_2), 0.12 (m, 3H, Si- CH_3) ppm.

Synthesis of allyl(cellosolvoxy)dimethylsilane. Metallic magnesium (20.6 g, 0.858 mol) was added to a two-necked flask. In a separate flask, dicellosolvoxy(dimethyl)silane (91.23 g, 0.613 mol), allyl chloride (75 mL, 0.919 mol), and THF (832.7 mL) were mixed. The resulting mixture was added dropwise to magnesium through a dropping funnel under an argon atmosphere. The product was isolated in several steps. First, THF was distilled off from the reaction mixture. Then hexane was added to the mixture, and the resulting precipitate was filtered off on a glass filter. The target product was isolated by distillation under reduced pressure.

^1H NMR (300 MHz, CDCl_3): δ 5.87–5.71 (m, 1H, CH-allyl), 4.90–4.82 (m, 2H, CH_2 -allyl), 3.80 (m, 2H, Si-O- CH_2), 3.43–3.46 (m, 4H, CH_2 -O), 1.58–1.56 (m, 2H, Si- CH_2), 1.17 (m, 2H, CH_3 - CH_2), 0.12 (m, 3H, Si- CH_3) ppm.

Synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane. Allyl(cellosolvoxy)dimethylsilane (120 g, 0.6377 mol), acetic acid (182 mL, 3.1883 mol), and water (29 mL, 1.5942 mol) were loaded into a single-neck round-bottom flask. The reaction mixture was stirred at room temperature for 8 h. The target product was washed with a toluene/water system. The organic layer was separated, dried over anhydrous Na_2SO_4 , and evaporated to dryness to give the product as a colorless transparent liquid. Yield: 109 g (91%).

^1H NMR (300 MHz, CDCl_3): δ 5.85–5.71 (m, 1H, CH-allyl), 4.91–4.83 (m, 2H, CH_2 -allyl), 1.57–1.54 (m, 2H, Si- CH_2), 0.08 (m, 3H, Si- CH_3) ppm.

Conclusions

Hence, the new method for the synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane was presented that can be carried out in several steps, including the synthesis of dicellosolvoxy(dimethyl)silane by the transesterification reaction followed by obtaining allyl(cellosolvoxy)dimethylsilane from it under the action of the Grignard reagent and its condensation. The yield of the product was more than 90%, while its purity was 99%. The resulting compound can be used as a monomer for the production of allyl-containing siloxanes, which, in turn, are used to obtain cross-linked silicones by the hydrosilylation reaction.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the GLC curves and NMR spectra of the compounds obtained. For ESI, see DOI: 10.32931/io2415a.

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