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Synthesis of new functional siloxane derivatives of limonene. Part I: Combination of hydrosilylation and hydrothiolation reactions☆

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ABSTRACT

This article discusses the synthesis of mono- and difunctional siloxane derivatives of limonene obtained by hydrosilylation followed by hydrothiolation. It has been shown that, because of the different reactivity of the double bonds present in the limonene molecule, selective addition to one of them can be performed, which opens the possibility of obtaining various siloxane derivatives of limonene that can be used as initial monomers in the synthesis of polymers.

1. Introduction

Terpenes are natural hydrocarbons with either cyclic or acyclic structures that are widely manufactured from essential oils of plants, fruits and resin of coniferous trees [1–3]. Pinene and limonene are the most common monoterpenes. The annual world production of these compounds exceeds 70,000 and 300,000 tons, respectively [4]. At present, the scientific community is challenged with the task of obtaining environmentally friendly polymers based on plant raw materials, terpenes in particular. β-pinene was one of the first monoterpenes in terms of polymer chemistry. It was selected as a precursor for the synthesis of homopolymers by the cationic polymerization method [5–7], as well as copolymers with styrene [8] and with N-substituted maleimides [9]. Due to the low activity of the double bond in the limonene ring (4-isoprenyl-1-methylcyclohexene), only low molecular weight homopolymers were previously obtained by the cationic polymerization [10]. In this case, free radical polymerization does not allow one to obtain high molecular weight polymers due to high rate of primary radical termination as well as degradative chain transfer processes [11,12]. In the case of copolymers of limonene with methyl methacrylate (MMA) [13], N-vinylpyrrolidone (NVP) [14], and vinyl acetate [15] also only low molecular weight products were obtained. A significant success in polymer chemistry was associated with the use of hydrosilylation [16–20] and thiol-ene reactions [21–25]. These reactions are also applicable in the chemistry of terpenes for the synthesis of both functional monomers and polymers. For example, the thiol-ene reaction was carried out in order to obtain various derivatives and polymers based thereon using limonene [26–29], myrcenol [30], geraniol [31] and other terpenes [32].

Various derivatives of terpenes were also obtained by the hydrosilylation reaction. As examples, hydrosilylation of pinene [33,34], carvone [35], ionone and similar compounds [36] can be given. Analysis of literature shows that only a few references to the hydrosilylation of limonene are available at the moment [37,38]. It was shown that limonene was hydrosilylated selectively at one propylene double bond [39]. However, no attempts were made to use terpenes with one or more double bonds as starting materials for the preparation of siloxane copolymers by means of hydrosilylation. Therefore, the aim of this work was, first, to demonstrate the possibility of carrying out the hydrosilylation reaction of terpenes with a double bond, for example, limonene, with hydride-containing siloxane compounds; second, by combining hydrosilylation and thiol-ene chemistry, to produce various functional derivatives for further use as the monomer base in the syntheses of siloxane-based copolymers based on limonene.

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2. Material and methods

Solvents were purified under standard conditions and freshly distilled prior to use. D-Limonene, 1,1,1,3,5,5,5-heptamethyltrisiloxane, hexanedithiol-1,6, benzophenone, thioacetic acid and lithium aluminum hydride were purchased from Sigma-Aldrich with purity not less than 95% and used as it is. The Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane) was purchased from ABCR GMbH and used as 2% solution in dry o-xylene. Gel Permeation Chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation, Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 500 Å was used. ^{1}H, ^{13}C, ^{29}Si Nuclear Magnetic Resonance (NMR) spectra and their nucleus correlations were recorded using a Bruker Avance II 300 spectrometer at 300, 75 and 60 MHz, respectively. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed in the positive ion mode (interface capillary voltage: 4500 V) or in the negative ion mode (3200 V), mass range from *m/z* 50 to *m/z* 3000. External or internal calibration was done using the ESI Tuning Mix, Agilent. A syringe injector was used for solutions in acetonitrile, methanol, or water (flow rate 3 μL/min). Dry nitrogen gas was used; the interface temperature was set to 180 °C.

2.1. 1,1,1,3,5,5,5-Heptamethyltrisiloxane (compound 1)

This compound was synthesized according method published us earlier [40]. Yield of HMS was 78% as colorless dense liquid. b.p. 140–141 °C. ^{1}H NMR (300 MHz, Chloroform-d) δ: 4.65 (s, 1H, Si<u>H</u>), 0.12 (s, 21H, SiC<u>H</u>$_3$).

2.2. Compound 2

To a stirring solution of 2.45 g (11.0 mmol) 1,1,1,3,5,5,5-heptamethyltrisiloxane (Compound **1**) in excess limonene in argon flow 0,1 vol % of Karstedt's catalyst was added and reaction mixture was stirred at 60 °C for 6 h. After the reaction was completed, excess of limonene was isolated in vacuum, toluene solution of crude product was passed through thin layer of silica and solvent was vaporized. The product was distilled in vacuum. Clean product was obtained as colorless liquid with b.p. = 99–101 °C (0.6 mbar). HRMS (ESI) *m/z*: calcd for $C_{17}H_{38}O_2Si$ $[M + H]^+$: 360.3227; found: 360.3252. Yield of the product was 93%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.3. Compound 3

To a stirring of 2.5 g (6.95 mmol) compound **2** in argon flow, 2.12 g (27.8 mmol) of thioacetic acid was added dropwise and reaction mixture was stirred for 40 min. After that, excess of thioacetic acid was evaporated in vacuum to afford 98% yield of the product as yellow sticky liquid. HRMS (ESI) *m/z*: calcd for $C_{19}H_{42}O_3SSi_3$ $[M + H]^+$: 435.2227; found: 435.2235. Calculated for $C_{19}H_{42}O_3SSi_3$: C 52.48%; H 9.74%; O 11.04%; S 7.37%; Si 19.38%. Found: C 51.84%; H 9.63%; S 6.53%; Si 18.85%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.4. Compound 4

This substance was synthesized according to [23] from 2.10 g (3.32 mmol) of Compound 3 and 0.28 g (7.30 mmol) $LiAlH_4$ in 50 ml dry diethyl ether. Clean product as yellowish odored liquid was obtained by vacuum distillation with 96% yield. HRMS (ESI) *m/z*: calcd for $C_{17}H_{40}O_2SSi_3$ $[M + Na]^+$: 415.2033; found: 415.2049. Calculated for $C_{17}H_{40}O_2SSi_3$: C 51.98%; H 10.26%; O 8.15%; S 8.16%; Si 21.45%. Found: C 51.65%; H 8.96%; S 7.44%; Si 19.28%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.5. Compound 5

To a stirred degassed mixture of 0.55 g (1.53 mmol) compound 2 and 0.06 g benzophenone, 1,2-ethanedithiol was added and reaction was illuminated with UV-lamp (365 nm, p = 15 W) during 4 h. Reaction completeness was estimated by NMR. Reaction mixture was dissolved in minimum volume of hexane and the product was reprecipitated by addition of excess of ethanol. Dry product was obtained as yellow sticky liquid with 86% yield. HRMS (ESI) *m/z*: calcd for $C_{36}H_{82}O_4S_2Si_6$ $[M + H]^+$: 867.4975; found: 867.4969. Calculated for $C_{36}H_{82}O_4S_2Si_6$: C 53.27%; H 10.18%; O 7.88%; S 7.90%; Si 20.76%. Found: C 52.85%; H 9.98%; S 6.54%; Si 19.37%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.6. Compound 6 (1,1,3,3,5,5-hexamethyltrisiloxane)

Synthesis of HMTS was performed according to [41] from 67.1 g (0.5 mol) of 1,1,3,3-tetramethyldisiloxane and 32.2 g (0.25 mol) of dichlorodimethylsilane. After distillation, yield of the product was 90%. B.p. = 128–130 °C. ^{1}H NMR (300 MHz, Chloroform-d) δ: 0.08 (s, 6H, Si–C<u>H</u>$_3$); 0.20 (d, J = 2.7 Hz, 12H, Si–C<u>H</u>$_3$); 4.71 (m, 2H, Si–<u>H</u>).

2.7. Compound 7

This compound was obtained similarly to compound **2** from 8.86 g (65.0 mmol) limonene and 6.16 g (29.5 mmol) compound **6**. Dry product was isolated by vacuum distillation, b.p. = 210–213 °C (2 mbar). Yield of the product was 96%. HRMS (ESI) *m/z*: calcd for $C_{26}H_{52}O_2Si_3$ $[M + K]^+$: 519.3083; found: 519.2907. Calculated for $C_{26}H_{52}O_2Si_3$: C 64.93%; H 10.90%; O 6.65%; Si 17.52%. Found: C 64.29%; H 9.83%; Si 16.94%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.8. Compound 8

This compound was obtained similarly to compound **3** from 1.79 g (3.72 mmol) compound **7** and 1.13 g (14.9 mmol) thioacetic acid. Yield of the product was 96%. HRMS (ESI) *m/z*: calcd for $C_{30}H_{60}O_4S_2Si_3$ $[M + H]^+$: 633.3308; found: 633.3314. Calculated for $C_{30}H_{60}O_4S_2Si_3$: C 56.91%; H 9.55%; O 10.11%; S 10.13%; Si 13.31%. Found: C 56.74%; H 9.31%; S 11.08%; Si 12.68%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

2.9. Compound 9

This compound was obtained similarly to compound 4 from 2.10 g (3.32 mmol) compound 6 and 0.28 g (7.30 mmol) $LiAlH_4$ in 30 ml of dry diethyl ether. The product was isolated from reaction mixture by extraction with diethyl ether (2 × 50 ml), washed with brine and water and dried over sodium sulfate. Solvent was evaporated and pure product as transparent liquid was obtained by vacuum distillation (b.p. 210 °C/0.1 mbar) with 87% yield. HRMS (ESI) *m/z*: calcd for $C_{26}H_{56}O_2S_2Si_3$ $[M + H]^+$: 549.3103; found: 549.3102. Calculated for $C_{26}H_{56}O_2S_2Si_3$: C 56.87%; H 10.28%; O 5.83%; S 11.68%; Si 15.34%. Found: C 55.91%; H 9.56%; S 12.05%; Si 14.87%. ^{1}H, ^{13}C and ^{29}Si NMR spectra are presented in SI section.

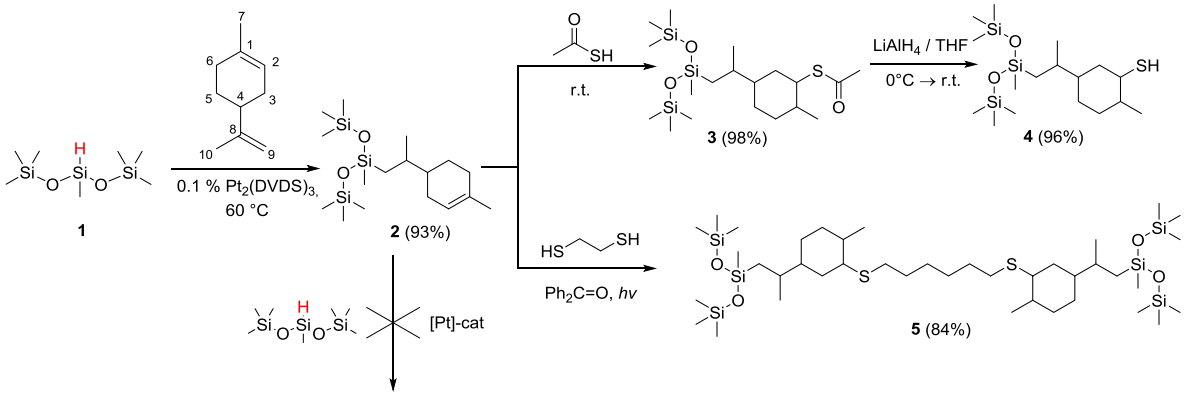

Fig. 1. Synthesis of monofunctional siloxane derivatives of limonene.

2.10. Polymer synthesis by thiol-ene polyaddition

Monomer **9** (2.00 g, 0.67 mmol), then benzophenone (photo-initiator) (0.02 g, 1.09 mmol) were placed into a single-necked round-bottomed flask, then hexanedithiol (0.10 g, 0.67 mmol) was added. The reaction was carried out with stirring under UV radiation (365 nm) for 10 h. The crude polymer product obtained was precipitated 3 times from toluene with a six-fold excess of ethanol. The resulting product was dried under vacuum at 0.5 mbar. Dry polymer was obtained as a transparent viscous yellowish liquid in 1.87 g (83%) yield.

The GPC curve and ^{1}H NMR spectrum are presented in SI section.

3. Results and discussion

1,1,1,3,5,5,5-Heptamethyltrisiloxane (HMS) (**1**) was selected as a model siloxane compound for hydrosilylation of limonene since it is an available and convenient model siloxane compound for hydrosilylation [42–44]. The reaction was carried out in excess limonene, using it as a solvent (Fig. 1). Hydrosilylation was carried out in the presence of Karstedt's catalyst at 60°C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. It was shown that hydrosilylation occurs regioselectively at the terminal double bond (C8–C9), while the cyclohexene double bond (C1–C2) remains unchanged.

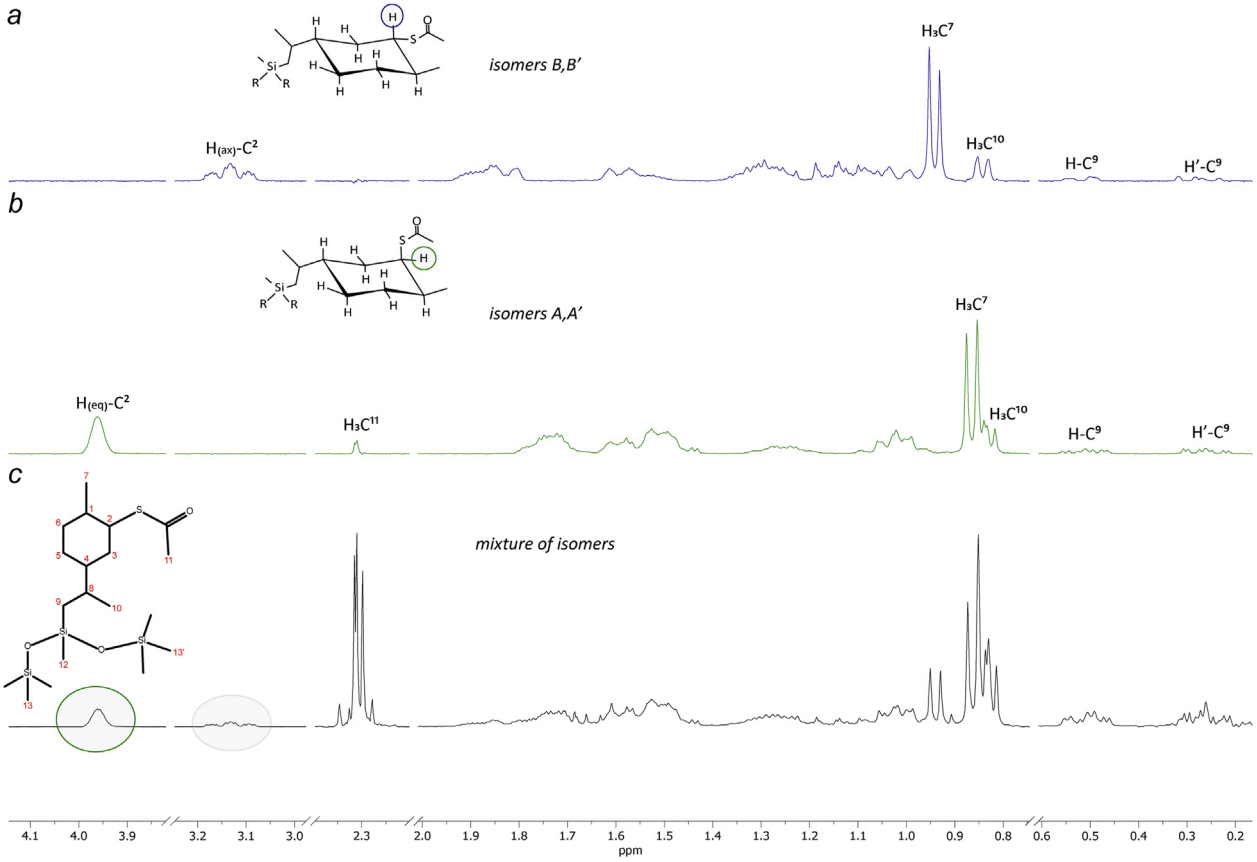

Fig. 2. A fragment of the ^{1}H NMR spectrum of a mixture of product 3 isomers (c) and signals of individual isomers isolated using the TOCSY sequence (a,b).

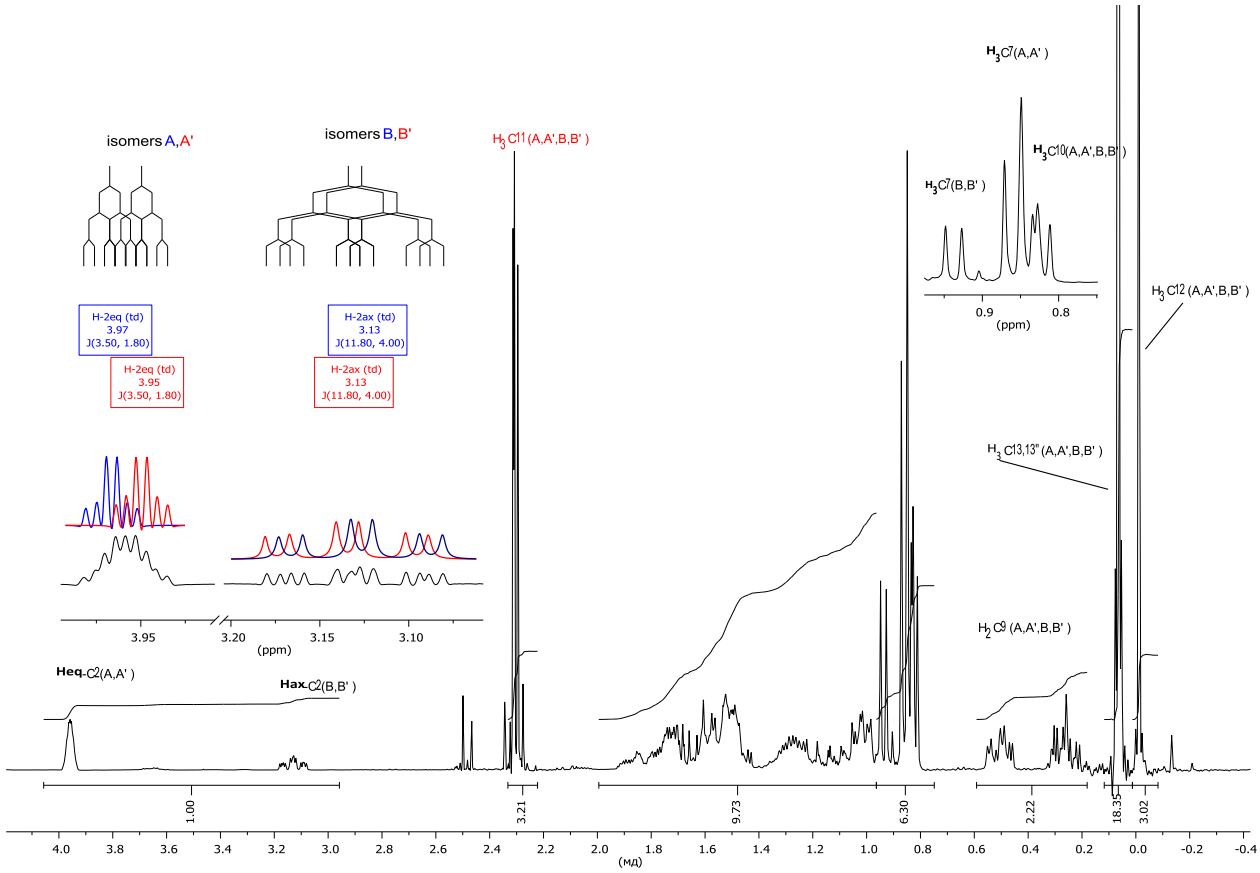

Fig. 3. ^{1}H NMR spectrum of Compound **3**.

This selectivity is obviously associated with the low activity of the cyclohexene double bond in the reaction. After the reaction was completed, the excess of unreacted limonene can be evaporated and recycled, which is an essential factor in production processes. Compound **2** as a transparent liquid can be easily distilled in a vacuum. It consists of a mixture of regioisomers.

In order to estimate the prospects of further functionalization of limonene derivative **2**, we decided to try thiol-ene addition to the cyclohexene double bond. The thiol-ene addition with excess thioacetic acid occurred spontaneously with a slight exothermic effect. Complete conversion was reached after 40 min of stirring. This fact is explained by the formation of a more reactive thioacetoxy radical from thioacetic acid. This accelerates the thiol-ene addition in this case and does not require additional activation. After the reaction was completed, the excess thioacetic acid was distilled off under reduced pressure.

A detailed study of the isomeric composition of the products was not our goal, but NMR spectroscopy makes it possible to obtain rather important information about it even without isolating each of the isomers. Hydrosilylation of limonene forms an asymmetric center at C8, which leads to a mixture of two diastereomers (1: 1). It can be seen in NMR spectra as duplication of the number of signals for some atoms. An NMR spectroscopic study of compound **3** synthesized confirmed that two new asymmetric centers at C1 and C2 appeared in the hydrothiolation product, which resulted in the formation of two additional diastereomers. This was confirmed by the TOCSY sequence (Fig. 2). In fact, the original ^{1}H NMR spectrum of Product **3** (Fig. 2c) contains proton signals at the C2 atom from two predominant diastereomers with an axial [isomer A (3.97 and 3.95 ppm (td, $^{3}J = 3.5$, 1.8 Hz, H–C2$_{eq}$, ~70%)] (Fig. 2b) and

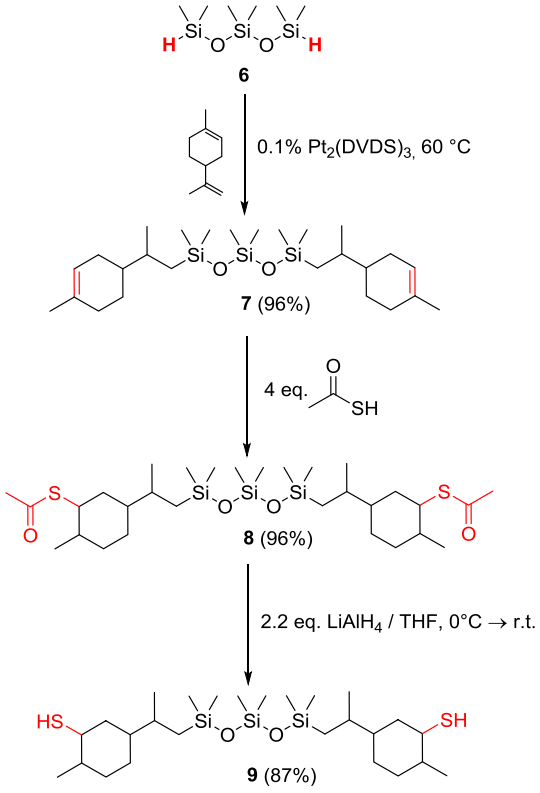

Fig. 4. Synthesis of difunctional siloxane derivatives of limonene.

equatorial [isomer B (3.13 and 3.12 ppm (td, $^{3}J = 11.8$, 4.0 Hz, H–C2$_{ax}$, ~30%)] (Fig. 2a) positions of the thioacetoxy groups in the cyclohexyl moiety of limonene (see Fig. 3).

The spin-spin coupling constants of the H–C2 proton in isomer B unambiguously indicate the axial position of the proton at C1 ($J_{ax\text{-}ax} = 11.8$ Hz). It is obvious that the bulky substituent at C4 in the cyclohexyl moiety of any possible isomer occupies a predominantly equatorial position and appear to be a "conformational anchor". Hence, isomer B has the configuration of the substituents shown in Fig. 2 (4r, 1t, 2c). In isomer A, the spin-spin coupling constants of the proton at C2 unambiguously indicate its equatorial position; however, the conformational position of the methyl group at Cl is not so obvious as in the case of isomer B because of the close values of the $^{3}J_{eq\text{-}eq}$ and $^{3}J_{eq\text{-}ax}$ spin-spin coupling constants.

Therefore, to determine the conformational position of the methyl group at C7, we used the value of its chemical shift (19.6 ppm) in the ^{13}C NMR spectrum of isomer A, which was very close to the chemical shift of the equatorial methyl group at C7 in isomer B (20.2 ppm), hence it is also equatorial. The configuration of substituents in isomer A is shown in Fig. 2b.

Thus, it has been shown that the hydrotiolation reaction occurs non-stereoselectively in this case, and the configuration of the substituents at the cyclohexyl moiety is determined by the reaction mechanism and the steric factors.

The synthesis of thiol **4** from derivative **3** was based on the procedure for acetoxythio group reduction with lithium aluminum hydride under mild conditions [45].

The main problem in this case lies in the stability of the siloxane bond in the presence of such a strong reducing agent as $LiAlH_4$, as well as the strongly basic medium during the isolation of the product from the reaction mixture. However, an adjustment of the reduction conditions allowed us to obtain the desired product, whose ^{1}H and ^{29}Si NMR spectra were in total agreement with the assumed structure.

In order to estimate the possibility of copolymer synthesis based on siloxane derivatives of limonene by the thiol-ene polyaddition reaction, we decided first to choose the reaction conditions using compound **2** as the model and hexanedithiol-1,6 as the dithiol derivative. The thiol-addition of hexanedithiol-1,6 to compound **2** was carried out with a 100% conversion of the reactants upon irradiation with UV light with a wavelength of 365 nm in the presence of benzophenone for 90 min. Compound **5** was isolated individually by vacuum distillation with yield 84%. This reaction can be considered as a model for the synthesis of polymers by thiol-ene polyaddition.

Based on the results obtained with the model monofunctional siloxane derivatives, we decided to study the possibility of synthesizing difunctional derivatives as the starting monomers for

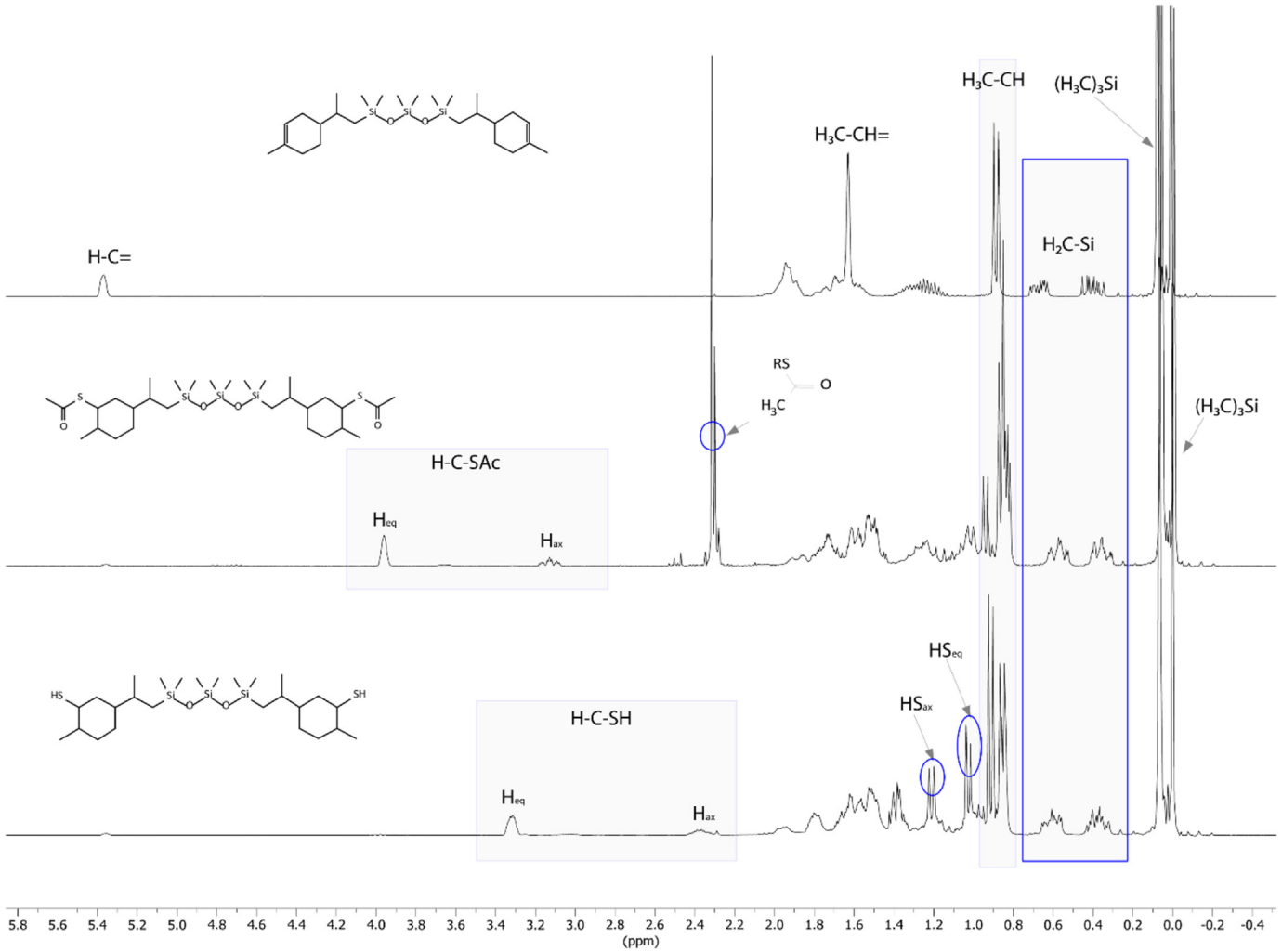

Fig. 5. Fragments of the ^{1}H NMR spectrum of compound 7, 8 and 9.

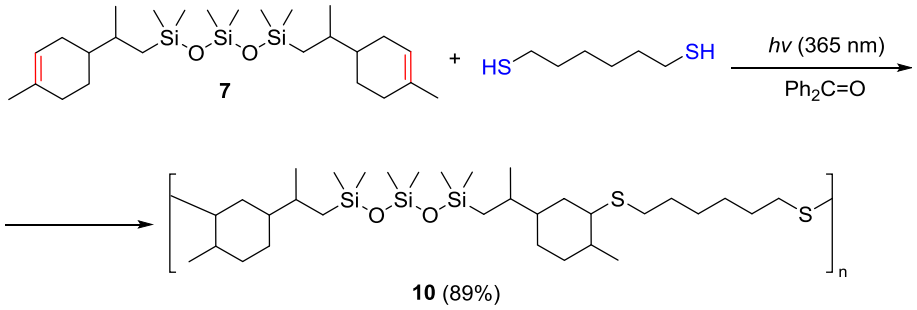

Fig. 6. Synthesis of polymer **10** by thiol-ene polyaddition from compound 9 and hexanedithiol-1,6.

further polymerization. The hydrosilylation reaction was carried out similarly to that described above, but instead of heptamethyltrisiloxane **1**, the difunctional 1,1,3,3,5,5-hexamethyltrisiloxane **6** was used (Fig. 4).

As a result, the product of double addition of limonene to hexamethyltrisiloxane **6** was obtained in 96% yield. From the point of view of polymer chemistry, this symmetrical compound is interesting for two reasons: on the one hand, cyclohexene double bonds can be functionalized further, and thereby an AA-type monomer for further polymerization can be obtained. On the other hand, derivative **7** itself can act as such type a monomer of this type, for example, in the case of thiol-ene polyaddition. We decided to demonstrate the possibility of further functionalization of derivative **7** by a synthesis of dithiol **9**, which can be subsequently used as a monomer in thiol-ene polyaddition. For this purpose, we used the scheme described earlier for the preparation of compound **4**: based on the starting difunctional compound **7**, bis(acetylthio) derivative **8** was first obtained by thiol-ene addition with 2 eq. thioacetic acid, and was then reduced with excess lithium aluminum hydride at 0 °C. The desired dithiol **9** was isolated from the reaction mixture with a purity of more than 95% according to NMR data and was used further without purification.

The ^{1}H NMR spectra of the compounds **7**, **8** and **9** synthesized are shown in Fig. 5. It can be seen from these data that the main characteristic signals are identical to those of the monofunctional derivative obtained previously, which proves the absence of impurities and confirms the expected structures.

To demonstrate the possibility of synthesizing polymers by the reaction of thiol-ene polyaddition, difunctional derivative **7** and hexanedithiol-1,6 were chosen. The reaction was carried out without a solvent under conditions similar to the preparation of derivative **5** (Fig. 6).

The conversion of the initial monomers during the reaction was determined by the disappearance of the characteristic signals at $\delta = 5.45$ ppm corresponding to the proton of the double bond in cyclohexene moieties of the original compound **7**. The polymer **10** obtained was a viscous transparent liquid. The molecular mass characteristics of the polymeric product obtained after purification were studied by GPC using polystyrene standards. The average molecular masses were $M_n = 5340$, $M_w = 8460$ with a polydispersity index PDI = 1.58.

4. Conclusion

Thus, in this paper, we have shown that limonene is selectively hydrosilylated with hydride-containing siloxane derivatives at the C1–C2 double bond. Using the suggested approach, derivatives of limonene and 1,1,1,3,5,5,5-heptamethyltrisiloxane, as well as limonene and 1,1,3,3,5,5-hexamethyltrisiloxane, were obtained for the first time. It was found that the cyclohexene double bond (C8–C9) in these derivatives was readily involved in thiol-ene addition reactions. This fact was used to obtain functional thiol derivatives. The content of regioisomers in the addition product obtained was confirmed by various NMR spectroscopy methods. Based on the product of limonene double addition to 1,1,1,3,5,5,5-heptamethyltrisiloxane and 1,6-hexanedithiol, a polymer was obtained under the conditions selected earlier and its molecular weight characteristics were measured. Thus, it has been shown that the compounds synthesized are suitable for the preparation of copolymers by the thiol-ene polyaddition reaction.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.11.004.

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