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Vinylation of Silanes and Disiloxanes. Preparation of Hexavinyldisiloxane

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Abstract—Vinylation of silanes and disiloxanes has been studied. It has been shown that in the reactions of silanes with vinyl chloride and magnesium or sodium the sole product formed is tetravinylsilane. In the reactions of hexaethoxydisiloxane with vinyl chloride and magnesium, tetravinylsilane is the sole product formed. Hexavinyldisiloxane with yield up to 85% is formed in the reaction of hexaethoxydisiloxane with vinyl chloride and magnesium in the presence of copper(II) salts as alkylation catalyst.

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Hexavinyldisiloxane is a raw monomer for production of siloxane polymers with trivinylsilyl end groups, that are applied as components of coatings [1] or cold-setting compositions for dental use [2]. Two synthetic routes are known for preparation of hexavinyldisiloxanes: preparation of trivinylsilane $(CH_2=CH)_3SiX$ with X = Cl, OCH_3, OC_2H_5, $CH=CH_2$, C_6H_5, or H, and subsequent transformation into hexavinyldisiloxane; preparation of disiloxane with functional groups that may be easily substituted with vinyl ones, $X_3SiOSiX_3$ with X = Cl, OCH_3, or OC_2H_5.

Preparation of hexavinyldisiloxane via tetravinylsilane. Preparations of trivinylphenylsilane [3, 4], tetravinylsilane [3, 5, 6], and trivinylsilane [3, 7] have been described in the literature. All cited works, except for [5], describe separate preparation of vinylmagnesium chloride in tetrahydrofurane starting from metal magnesium and vinyl chloride, and subsequent alkylation of corresponding silanes. In the tetrahydrofurane medium the vinylmagnesium chloride is formed smoothly with 85–90% yield via the Grignard reaction. The solution thus obtained is used for chlorosilanes or alkoxysilanes alkylation.

$$Mg + CH_2=CHCl \rightarrow CH_2=CHMgCl,$$

$$\equiv Si–Cl + CH_2=CHMgCl \rightarrow \equiv Si–CH=CH_2 + MgCl_2.$$

However, attempts to prepare products of partial vinylation, trivinylchlorosilane or trivinylalkoxysilane, suitable for subsequent conversion into hexavinyldisiloxane, failed [6]. It is believed that the reaction cannot be stopped at the stage of partial vinylation due to decrease of vinylsilanes reactivity towards vinylmagnesium chloride in the following row: $(CH_2=CH)_3SiCl > (CH_2=CH)_2SiCl_2 > > (CH_2=CH)SiCl_3$.

In the case of tetraethoxysilane also the only product was tetravinylsilane. Similar situation was observed in silicon hydrides interaction with vinylmagnesium chloride: The substituents exchange occurs between atoms of silicon and magnesium.

$$\equiv Si–H + CH_2=CHMgCl \rightarrow \equiv Si–CH=CH_2 + MgHCl.$$

Thus, the method described is convenient for the preparation of tetravinylsilane and trivinylphenylsilane that are valuable monomers as well.

Besides the Grignard reagent, vinylmagnesium chloride, the application of the system sodium/vinyl chloride in diethyl ether is known for chlorosilanes and alkoxysilanes vinylation leading to tetravinylsilane formation in 65% yield [5].

$$SiCl_4 + 4CH_2=CHCl + 8Na \rightarrow (CH_2=CH)_4Si + 8NaCl.$$

The reaction proceeds via vinylsodium formation, which is an alkylation agent in the subsequent reaction with silane.

In this work, we studied the interaction of various silanes with vinyl chloride and sodium in order to obtain trivinylsilane with ethoxy or chlorine substituents, and to optimize the procedure of tetravinylsilane preparation.

Inhibitors effect on tetravinylsilane polymerization degree

Inhibitor	*T*, °C	Time, min	Polymer yield, %
Absent, in air	35	160	16
	65	160	36
Absent, under inert atmosphere	30	160	26
	60	160	40
Hydroquinone disilyl ether	30	150	13.5
Hydroquinone monomethyl ether	30	150	14
Hydroquinone	20	150	15
Phenothiazine	30	150	10
	90	150	22
Allylbenzene	30	150	11
	90	150	22
$CuCl_2 \cdot 2H_2O$	30	150	13
Chromium(III) acetylacetonate	30	150	5.5–6
Cobalt(II) acetylacetonate, dihydrate	90	160	17
Cobalt(III) acetylacetonate	90	160	4.4
Iron(III) acetylacetonate	65	170	3
Copper sulfide	70	170	9

It has been known that vinylsodium is formed in the hydrocarbon solvents with yields not exceeding 35% [9]. We demonstrated that the addition of the copper(II) complex salt Li_2CuCl_4 [10], which was normally used for alkylation of alkyl halides with organomagnesium and organolithium compounds [11, 12], increased the tetravinylsilane yield to 90%, and that of trivinylphenylsilane, up to 85%, according to gas-liquid chromatography data. The reaction was performed by dosing vinyl chloride into a mixture of granular sodium, hexane, silane, and copper salt. The reaction started upon addition of the very first vinyl chloride portion at 20°C, and was accompanied with significant self-heating and the formation of a substantial quantity of precipitate consisting of sodium ethylate (in the case of tetraethoxysilane) and sodium chloride. The reaction was monitored by the gas-liquid chromatography, and the vinyl chloride addition was stopped when there was no initial silane in the reaction mixture.

Studies of trichlorosilane vinylation revealed that the reaction did not start in the absence of the catalyst. When using copper(II) salt under inert atmosphere at 10–15°C, trivinylsilane was formed along with tetravinylsilane, in the ratio of tetravinylsilane/trivinylsilane equal to 4:1, however, with heating to even 20°C trivinylsilane completely decomposed to give tetravinylsilane. At higher reaction temperature, tetravinylsilane was formed exclusively.

We applied the alkylation catalyst, copper(II) salt Li_2CuCl_4, to the tetraethoxysilane or tetrachlorosilane reaction with vinyl chloride and magnesium (the Grignard reaction) in tetrahydrofurane, to obtain 85–90% of tetravinylsilane.

Thus, tetravinylsilane was formed with high yield from any chloro- or alkoxysilane in reaction with vinyl chloride and sodium or magnesium. It was not possible to obtain trivinylsilane bearing chlorine or alkoxy substituent via this reaction. However, upon tetravinylsilane distillation or later during its transformation into hexavinyldisiloxane, complications arose due to its polymerization. For instance, upon heating the reaction mixture up to 60°C the polymer was formed already in 0.5 h.

We investigated tetravinylsilane stability towards polymerization in the presence of various inhibitors, taken in the same amount, 1 mol % with respect to tetravinylsilane. The data obtained are collected in the table.

The data presented show that such common inhibitors as hydroquinone and its monomethyl ether, phenothiazine, or allylbenzene were not effective in inhibiting tetravinylsilane polymerization. Iron(III) and cobalt(III) acetylacetonates were, on the contrary, effective, allowing to isolate tetravinylsilane by vacuum distillation without noticeable loss.

In order to transform tetravinylsilane into hexavinyldisiloxane, one of the four vinyl group of the former should be eliminated. It is known [6] that polyvinylsilanes react with hydrogen chloride at several groups simultaneously. Tetravinylsilane gives the following product in the reaction with hydrogen chloride: trivinylchlorosilane (88%), divinyldichlorosilane (11%), and vinyltrichlorosilane (0.5%). Since the boiling points of these products are close the isolation of pure trivinylchlorosilane is impeded; thus, in the subsequent hydrolysis reaction, a mixture of polyvinylsiloxanes is obtained.

We prepared hexavinyldisiloxane by treating the tetravinylsilane solution with concentrated (16.5–17.5 mol l^{-1}) sulfuric acid.

$$(CH_2=CH)_4Si + H_2SO_4 \rightarrow (CH_2=CH)_3SiOSO_3H,$$

$$(CH_2=CH)_3SiOSO_3H + H_2O \rightarrow (CH_2=CH)_3SiOSi(CH_2=CH)_3.$$

The reaction was performed in hexane, at tetravinylsilane/H_2SO_4 ratio of 2:1, at 10–15°C. The subsequent hydrolysis of trivinylsulfosilane yielded 80% of hexavinyldisiloxane that was isolated by vacuum distillation.

Hexavinyldisiloxane preparation from hexaethoxydisiloxane. The most convenient route to prepare hexavinyldisiloxane is presumably starting from hexaethoxydisiloxane formed from tetraethoxysilane via hydrolytic condensation according to well known procedures [13, 14].

It is known [15] that vinylation of hexaethoxydisiloxane by vinylmagnesium chloride in tetrahydrofurane proceeds with hexavinyldisiloxane yield of 53%.

We studied the hexaethoxydisiloxane vinylation reaction in order to optimize the synthesis procedure and to increase the end product yield. Hexaethoxydisiloxane was isolated by vacuum distillation from ethylsilicate-40, the cheapest and accessible organosilicon raw material, in the 50% yield.

In the experiments targeted at the vinylation of hexaethoxydisiloxane with the sodium/vinyl chloride mixture, tetravinylsilane was obtained exclusively, due to breaking up of the siloxane bond by the forming sodium ethylate. Hexaethoxydisiloxane reacted with vinylmagnesium chloride in tetrahydrofurane with the end product yield of approximately 50%. The hexavinyldisiloxane yield was increased to 80% by using the alkylation catalyst, copper(II) salt, at the vinylation stage.

The synthetic process carried out in a one-pot mode is of practical importance: that is, the preparation of hexavinyldisiloxane by the reaction of hexaethoxydisiloxane with vinylmagnesium chloride, the latter being formed directly in the reaction mixture. To test this approach, vinyl chloride was dosed into the reaction mixture containing magnesium, copper(II) salt, and hexaethoxydisiloxane in tetrahydrofurane. If necessary, the reaction was activated with methods standard for the Grignard reaction (addition of iodine or methyl iodide). Vinylmagnesium chloride thus formed reacted with hexaethoxydisiloxane at once, and the mixture temperature increased to 40°C. After stopping the vinyl chloride addition, the mixture was boiled for approximately 2 h, then it was diluted with hexane, the organic layer was isolated and washed. Hexavinyldisiloxane was isolated by vacuum distillation.

EXPERIMENTAL

^{29}Si NMR spectra were recorded using Bruker Spectrospin AM-500 spectrometer, at 470.6 MHz with TMS as the internal reference, in $CDCl_3$.

The reaction mixtures and end products analysis, as well as reaction course monitoring, were performed by gas-liquid chromatography using the LKhM-8MD system, the column diameter 4 mm, column length 2 m, with 5% SE-30 on Chromatron-H stationary phase and helium as carrier gas..

Preparation of the alkylation catalyst Li_2CuCl_4. Lithium chloride (2.42 g, 0.057 mol) and copper(II) chloride (3.83 g, 0.028 mol), both dehydrated, were mixed and dissolved in 150 ml of anhydrous tetrahydrofurane. The catalyst concentration was 1.87×10^{-4} mol ml^{-1}.

General procedure of silanes vinylation with sodium/vinyl chloride in the presence of copper(II) salts. 70 g (3.0 mol) of sodium dispersed in 500 ml of hexane, 1.0 mol of the silane, and 26.5 ml of the catalyst solution were placed into a four-necked flask equipped with a mechanic stirrer, a cold-finger condenser, a thermometer, and a gas-inlet tube. The vinyl chloride dosing was started at room temperature, and the temperature was maintained below 25°C during the dosing by cooling with a bath of hexane with dry ice. The reaction started at 18–20°C. After the dosing of vinyl chloride had been completed, the mixture was heated up to 40°C and incubated at this temperature for 2 h. Subsequently, the mixture was cooled to room temperature, and the precipitate was filtered off. Tetravinylsilane was isolated by vacuum distillation, with addition of 1 mol % of cobalt(III) acetylacetonate.

Yield: 87% (130 ml) (from trichlorosilane); 90% (104 ml) (from tetraethoxysilane); 90% (119 ml) (from tetrachlorosilane); 85% (141 ml) (from phenyltrichlorosilane). bp 131–132°C, n_D^{25} 1.4615, d^{25} 0.793 g cm^{-3}. ^{29}Si NMR: δ_{Si} –28.00 ppm (δ_{Si} –28.50 ppm [16]).

Preparation of hexavinyldisiloxane from tetravinylsilane. A mixture of 20 ml of tetravinylsilane,

80 ml of hexane, and 40 ml of 92 mol % sulfuric acid was stirred at room temperature for 4 h. Then the reaction mixture was poured into water taken in such amount that the final sulfuric acid concentration was 10 mol %. The organic layer was separated, washed with water till the reaction of water phase was neutral. Hexane was evaporated, and 185 g of hexavinyldisiloxane was isolated by vacuum distillation. Yield 79%, bp 66–68°C (2 mm Hg) {115–116°C (20 mm Hg) [17]}. ^{29}Si NMR: δ_{Si} –22.0 ppm.

Preparation of hexavinyldisiloxane from hexaethoxydisiloxane. Sodium, 140 g (6.0 mol), dispersed in 1000 ml of hexane, 290 ml (1.0 mol) of hexaethoxydisiloxane, and 26.5 ml of the catalyst solution were placed into a four-neck flask equipped with a mechanical stirrer, a cold-finger condenser, a thermometer, and a gas-inlet tube. The vinyl chloride dosing was started at room temperature, the temperature was maintained below 25°C during the dosing by cooling with a bath of hexane with dry ice. The reaction started at 18–20°C. After the dosing of vinyl chloride had been completed, the mixture was heated to 40°C and incubated at this temperature for 2 h. Subsequently, the mixture was cooled to room temperature, and the precipitate was filtered out. Hexavinyldisiloxane, 187 g, was isolated by vacuum distillation. Yield was 80%.

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