



Short communication

An efficient method for synthesizing monofunctionalized derivatives of 1,1,3,3-tetramethyldisiloxane in ionic liquids as recoverable solvents for rhodium catalyst

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ABSTRACT

Functionalized siloxanes, as one of the most important classes of organosilicon compounds, are widely applied in industry. In our studies, we have investigated, the reaction between 1,1,3,3-tetramethyldisiloxane (TMDSO) and 1-octene, using the rhodium catalyst immobilized in six phosphonium-based ionic liquids differing in the structure of cation and anion. Studies have shown high potential for using ionic liquids to create biphasic system with reactants, where IL/catalyst phase can be separated and reused in subsequent reaction cycles allowing, in this way, for efficient and highly selective monofunctionalization of TMDSO with reuse of the same portion of catalyst up to 20 times in comparison to conventional homogenous reaction.

1. Introduction

Unsymmetrical organosilicon compounds generate a lot of attention, due to their potential application as for example liquid crystals [1,2], solid polymeric electrolytes [3], coupling agents [4] or monomers for UV induced polymerization [5,6]. They are also key reagents in synthesis of hyperbranched polymers [7,8] and dendrimers [9]. One of the most interesting examples of organosilicon compounds described in the literature is 1,1,3,3-tetramethyldisiloxane (TMDSO) due to its broad scope of applications in preparation of functionalizing agents of fluorinated polyethers [10], polysiloxane ingredients for heat conductible silicone compositions [11] and surfactants for production of skin-care cosmetics [12]. The conventional methods for obtaining unsymmetrical silicon based compounds involve condensation reactions and co-hydrolysis reactions of two silanols, chlorosilanes and alkoxy silanes [13]. However, in a view of the literature reports the hydrosilylation reaction seems to be the most convenient and most often used protocol for synthesis of new organosilicon derivatives [14].

Although, hydrosilylation reactions are widely investigated and performed in homogenous single-phase systems [14], there is still a large problem with later separation of the catalyst from the product after the reaction. In order to overcome this problem, some efforts are being made in investigating new methods for hydrosilylation reaction performed in heterogenous systems where catalyst is used on solid

support and thus not lost after the reaction [15,16,17]. Another approach investigated in recent years is by using ionic liquids to create biphasic reaction system with substrates, where the catalyst is dissolved in ionic liquid phase [18]. This way IL/catalyst phase can than be easily separated from reactants and products and reused in subsequent reaction cycles. Literature presents some examples of studies of using ILs, as solvents for platinum or rhodium catalysts, to perform catalytic hydrosilylation reactions in batch biphasic systems [19,20,21,22,23,24,25,26]. Moreover our group has recently presented investigation of series of ILs as an effective catalyst immobilizing phase for the formation of biphasic liquid/liquid system for reactions performed in continuous microreactor system. In performed reactions the catalyst could be easily separated and reused in subsequent reaction cycles without significant loss in the product yield and reaction selectivity, in comparison to results from reactions carried in batch system [27]. Our previous studies have shown that phosphonium cation-based ionic liquids are a very promising group of ionic liquids for performing such reactions [28]. Thus as a result, determining the effect of the catalyst and the type of ionic liquid on the reaction yield and selectivity permitted us to choose optimal catalytic system for easy separation of the product and high yield of the reaction in repeated catalytic cycles. Our group has also investigated selective functionalization of 1,1,3,3-tetramethyldisiloxane (TMDSO) with wide range of unsaturated organic and organosilicon compounds, *via* catalytic

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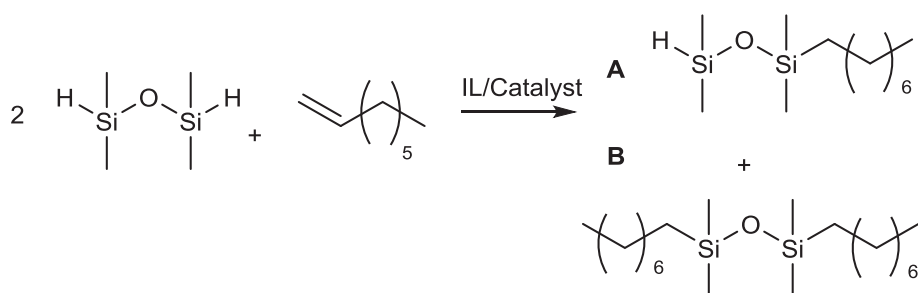


Fig. 1. Possible products (A. monofunctionalized, B. bifunctionalized TMDSO) in model reaction of 1,1,3,3-tetramethyldisiloxane and 1-octene.

hydrosilylation promoted by different rhodium and platinum complexes, with using both conventional solvents and solvent-free conditions. However, in order to obtain only desired monofunctional-substituted products, quite high amounts of the catalyst had to be used [4,29].

Combining the concept of monofunctionalization of TMDSO with concept of using ionic liquids as carrier for recoverable catalyst system, in this paper, we report studies concerning the selective and high-yield derivatization of TMDSO with 1-octene via hydrosilylation catalyzed by rhodium (I) and platinum (0) complexes immobilized in ionic liquids. After reaction completion, phases were separated and IL/catalyst phases were reused to perform subsequent reaction cycle.

2. Experimental

The hydrosilylation reaction was performed using 1,1,3,3-tetramethyldisiloxane (TMDSO) and 1-octene with Karstedt and di- μ -chlorobis[(1,2,5,6- η)-1,5-cyclooctadiene]dirhodium catalysts (Fig. 1). In all of performed experiments the molar ratio of substrates: TMDSO: 1-oct: catalyst was set to: 2:1:2 $\times 10^{-4}$. This molar ratio, in our previous studies, was found as most effective and selective system for hydrosilylation TMDSO by 1-octene (Table 1) [29]. Specific method for hydrosilylation reaction is described below:

To the glass tube the ionic liquid in amount of 20% of mass of substrates and [Rh] or [Pt] catalyst were added and then the system was stirred at r.t. for 5 min. After that time 7.4 mmol of TMDSO and 3.7 mmol of 1-octene were added to the reaction vessel. The mixture of substrates and ionic liquid/catalyst was stirred at the temperature of 50 °C. After 60 min, the reaction system was cooled to r.t. and ionic liquid/catalyst phase was separated from the reaction mixture. The ionic liquid/catalyst was then reused in the next reaction cycles (with added new portion of substrates). Each time the reaction selectivity and yield were examined by GCMS.

Ionic liquids [P₄₄₄₁₄][Cl], [P₆₆₆₁₄][DCA] and [P₄₄₄₁][MeSO₄] were purchased from Iolitech GmbH, Germany. Synthesis of [P₈₈₈₈][NTf₂], [P₄₄₄₁₄][NTf₂] and [P₆₆₆₁₄][NTf₂] was performed using generally accepted methods [30,31,32] from their halogen precursors. Karstedt

Table 1
Hydrosilylation of 1-octene by 1,1,3,3-tetramethyldisiloxane without use of ionic liquids.

Catalyst	TMDSO:1-octene: [Pt] or [Rh] [mol]	1-octene conversion [%]	Products distribution [%]	
			A	B
1.C1	1:1: 2 $\times 10^{-4}$	100	68.6	31.4
2.C1 [29]	1:1: 2 $\times 10^{-5}$	100	66.2	33.8
3.C1 [29]	2:1: 2 $\times 10^{-5}$	100	67.2	32.8
4.C2 ^a [29]	1:1: 2 $\times 10^{-4}$	100	88.7	11.3
5.C2 [29]	2:1: 2 $\times 10^{-4}$	100	100	0
6.C2 [29]	1:1: 2 $\times 10^{-4}$	100	88.6	11.4
7.C2	2:1: 2 $\times 10^{-5}$	98	98.4	1.6

C1 – Karstedt catalyst [Pt]; C2 – {[RhCl(COD)]₂}.

^a Concentration of reagents in hexane - 50%.

catalyst (2.2% solution of Pt in xylene) was purchased from Sigma Aldrich. Di- μ -chlorobis[(1,2,5,6- η)-1,5-cyclooctadiene]dirhodium catalyst was synthesized using method described in the literature [33]. Conversion and selectivity of reaction were determined using NMR and GCMS analyses. The ¹H NMR and ¹³C NMR were recorded using Bruker Ultrashield 300 MHz spectrometer using a CDCl₃ as a solvent. The ²⁹Si NMR spectrum was recorded using Bruker Ascend 400 spectrometer. The mass spectra were obtained by GCMS analysis (Bruker MS320 Triple quad, equipped with a VF-5 Factor four capillary column (30 m) and a quadrupole detector). Viscosities values were measurement on a AR 2000ex (TA Instrument).

3. Results and discussion

The catalytic activity of systems composed of a rhodium or Karstedt catalyst immobilized in the ionic liquids used in hydrosilylation reaction of 1-octene with TMDSO (Fig. 1) was tested in presented work. The above systems were prepared with six ionic liquids: tributylmethylphosphonium methyl sulfate [P₄₄₄₁][MeSO₄], tributyltetradecylphosphonium bis(trifluoromethane)sulfonimide [P₄₄₄₁₄][NTf₂], trihexyltetradecylphosphonium bis(trifluoromethane)sulfonimide [P₆₆₆₁₄][NTf₂], trihexyltetradecylphosphonium chloride [P₆₆₆₁₄][Cl], trihexyltetradecylphosphonium dicyanamide [P₆₆₆₁₄][DCA], tetraoctylphosphonium bis(trifluoromethane)sulfonimide [P₈₈₈₈][NTf₂] (Fig. 2). The molar ratio of TMDSO:1-octene:catalyst was set to 2:1:2 $\times 10^{-4}$. In paper published before [29], we have reported effective conditions to perform selective functionalization of TMDSO in conventional organic solvents and in solvent-free conditions (Table 1) but without possibility to reuse catalyst from reaction mixture. As reported in cited article the selectivity of rhodium (I) catalyst (Table 1, C2) was higher in comparison to platinum Karstedt catalyst (Table 1, C1). Also, increase in the molar ratio of TMDSO to 1-octene from 1:1 to 2:1, had an significant impact on the products distribution, allowing to obtain product A with 100% selectivity (Table 1, 5.C2). Using conventional solvent like hexane did not affect product distribution in significant way allowing to obtain product A with 88.7% selectivity (Table 1, 4.C2). In addition, the reduction of the amount of catalyst from 2 $\times 10^{-4}$ (Table 1, 1.C1 and 5.C2) to 2 $\times 10^{-5}$ (Table 1, 2.C1 and 7.C2) did not have any observable effect on the selectivity of the reaction.

Thus, in presented work initial tests were also performed with lower catalyst concentration and different TMDSO:1-octene molar ratios using one selected ionic liquid – [P₄₄₄₁₄][NTf₂] to determine optimum conditions that will allow for high selectivity and conversion of 1-octene. Decreasing amount of catalyst (from 2 $\times 10^{-4}$) by ten times (molar ratio of substrates: TMDSO: 1-oct: catalyst: 2:1:2 $\times 10^{-5}$) and five times (molar ratio of substrates: TMDSO: 1-oct: catalyst: 2:1:4 $\times 10^{-5}$) had a negative effect on 1-octene conversion (22% and 48% respectively) and reaction selectivity (10% and 7% of product B respectively) already during the first reaction cycle. Experiment with adding 1-octene dropwise, using injection pump, to the mixture of TMDSO and ionic liquid/catalyst (molar ratio of substrates: TMDSO: 1-oct: catalyst: 1:1:2 $\times 10^{-4}$) also led to obtaining product with lower selectivity - 92%. Due to the fact that experiments mentioned above led to obtaining

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