

Study of Karstedt's Catalyst for Hydrosilylation of a Wide Variety of Functionalized Alkenes with Triethoxysilane and Trimethoxysilane

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The hydrosilylation is one of the most important methods for the synthesis of organosilicon compounds. Karstedt's catalyst $[\text{Pt}_n(\text{H}_2\text{C}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_m]$ is a kind of platinum catalyst which is widely used in the hydrosilylation. In this paper, we studied the catalytic activity of Karstedt's catalyst for the hydrogenation of olefins and especially aminated alkenes with trimethoxysilane and triethoxysilane, and demonstrated the excellent performance in terms of the yield and selectivity.

Keywords Karstedt's catalyst, hydrosilylation, aminated alkenes, selectivity

Introduction

The hydrosilylation is the reaction of organosilicon compounds containing Si—H bond with unsaturated compounds. Silicon hydrogen addition reaction is one of the most widely studied and widely used reactions in organosilicon chemistry, and many silicon monomers containing functional groups have been synthesized via this reaction. Since Sommer *et al.* reported the hydrosilylation reaction in 1947,^[1] its reaction mechanism,^[2] catalytic system^[3] and application^[4] become hot topics of research work.

A lot of catalysts have been developed for the hydrosilylation.^[5] Since Speier found that chloroplatinic acid (H_2PtCl_6) was a selective and efficient homogeneous alkene hydrosilylation catalyst in 1957,^[6] transition metal catalysts on the basis of metals such as platinum,^[7] rhodium,^[8] copper^[9] and cobalt^[10] with high catalytic activity and selectivity have attracted much attention in theoretical and practical applications. At present, platinum catalyst is the most comprehensive and widely used catalyst in the study of hydrosilylation catalyst, due to the high catalytic activity and selectivity, and the high stability towards heat, oxygen and moisture.^[11]

In 1973, Karstedt reported that the platinum(0) and divinyltetramethyldisiloxane complex ($[\text{Pt}_n(\text{H}_2\text{C}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_m]$, as shown in Figure 1), termed as Karstedt's catalyst, was an effective catalyst for hydrosilylation.^[12] Karstedt's catalyst is a kind of homogeneous catalyst with high catalytic efficiency, wide application range and small amount, *etc.*, so it is

widely used at present. The discovery of the Karstedt's catalyst is a significant advance in the field of hydrosilylation catalyst research.

The hydrosilylation reactivity is usually affected using aminated alkenes, because the amino groups are involved in the reaction and produce undesired byproducts,^[13] and cause a kind of hydrolyzation of ethoxy-/methoxy-silane groups in the presence of trace water. Up to now, there are few reports on the hydrosilylation of aminated alkenes substrates.^[13,14] In this paper, we described the hydrosilylation reaction of different aminated alkenes with trimethoxysilane and triethoxysilane in the presence of the Karstedt's catalyst, and further extended the hydrosilylation reaction with a series of other functionalized alkenes substrates.

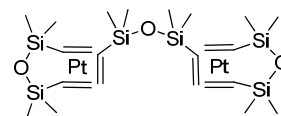


Figure 1 Structure of Karstedt's catalyst.

Experimental

The reaction was carried out by modifying the reported method.^[15] Into the mixture of a certain amount of alkene and equimolar amount of trimethoxysilane or triethoxysilane in a Schlenk tube was added platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst) (*i.e.*, 20 μmol per mol of silane).

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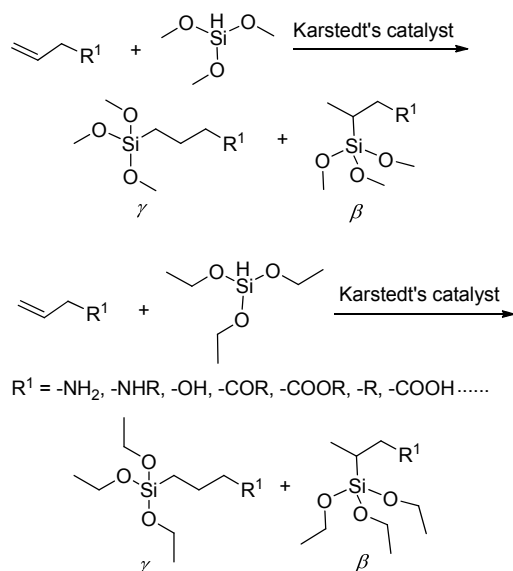
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Then the mixture was stirred under argon at 80 °C for 20 h (Scheme 1). After being cooled to room temperature, the crude was purified by vacuum distillation or by chromatography on a silica gel column to afford the desired product.

Scheme 1 Hydrosilylation reactions of different functionalized alkenes with trimethoxysilane and triethoxysilane



Results and Discussion

The products of the hydrosilylation reaction of olefins with trimethoxysilane or triethoxysilane include γ -isomer (*anti*-Markovnikov isomer) and β -isomer (Markovnikov isomer), and they could be determined from ^1H NMR spectra. Based on the ^1H NMR data, it was found that the main product was γ -isomer and there was little β -isomer, this is due to steric effect of the reactants.^[16]

The yield and the selectivity were calculated on the basis of ^1H NMR spectrum using the Eq. 1:^[17]

$$P_x = P_{\text{std}} \times \frac{M_x}{M_{\text{std}}} \times \frac{N_{\text{std}}}{N_x} \times \frac{m_{\text{std}}}{m_x} \times \frac{A_x}{A_{\text{std}}} \times 100\% \quad (1)$$

where P_{std} is the purity ($\text{g} \cdot \text{g}^{-1}$) of the internal standard; A_x and A_{std} are the integral value of the signals belonging to the analyte and the internal standard, respectively; M_x and M_{std} are the relative molar mass (molecular weight, $\text{g} \cdot \text{mol}^{-1}$) of the analyte and internal standard ($M_{\text{std}} = 226.44 \text{ g} \cdot \text{mol}^{-1}$), respectively; N_x and N_{std} correspond to the number of spins of the analyte and the internal standard ($N_{\text{std}} = 2$), respectively; m_x and m_{std} are the weighted mass of the analyte and the internal standard, respectively. The purity P_x which stands for the yield was calculated for each isomer and the ratio of γ - to β -isomers was correspondingly determined. In the work, 2,4,6-trichloronitrobenzene was used as the internal standard from ^1H NMR spectrum with the ^1H chemical shift at δ 7.46 (t, 2H),^[18] the ^1H chemical shift

of Si-CH₂ at δ 0.45–0.65 (m, 2H) was chosen as the characteristic peak of γ -isomer, the ^1H chemical shift of Si-CH-CH₃ at δ 0.90–1.05 (m, 3H) was chosen as the characteristic peak of β -isomer.^[19]

As can be seen from Table 1, the yields of the hydrosilylation of the aminated alkenes with trimethoxysilane and triethoxysilane using Karstedt's catalyst were higher than 90%. The γ -isomer is often the desired product in the hydrosilylation of allyl derivatives.^[20] For the primary allylamine (Entry 1), the reaction yields with trimethoxysilane and triethoxysilane were more than 94%, and the ratio of γ -isomer/ β -isomer was 84/16. For the secondary allylamine (Entry 2), the yield of each hydrosilylation reaction was more than 93%, and the selectivity with the trimethoxysilane reagent was better than that with the triethoxysilane reagent. The ratios of γ -isomer/ β -isomer of the two groups were 83/17 and 78/22, respectively. For the tertiary allylamine (Entry 3), the yield of the hydrosilylation reaction of *N,N'*-dimethylallylamine with trimethoxysilane or triethoxysilane was about 95%, and the ratios of γ -isomer/ β -isomer of *N,N'*-dimethylallylamine with trimethoxysilane and triethoxysilane were 86/14 and 95/5, respectively. The hydrosilylation reaction of *N*-ethyl-2-methylallylamine (Entry 4) showed the highest yield of 97.1% and 98.2%, the ratios of γ -isomer/ β -isomer of *N*-ethyl-2-methylallylamine with trimethoxysilane and triethoxysilane were 81/19 and 77/23, respectively.

Table 1 Karstedt's catalyst for the hydrosilylation of different aminated alkenes with the trimethoxysilane and triethoxysilane reagents, respectively

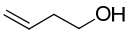
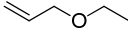
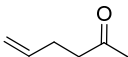
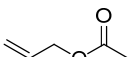
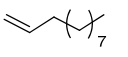
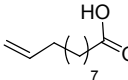
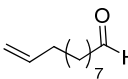
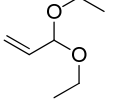
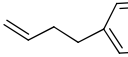
Entry	Alkene	Yield ^a /%	Ratio ^a (γ/β)	Yield ^b /%	Ratio ^b (γ/β)
1		94.3	84/16	94.2	84/16
2		93.2	83/17	91.9	78/22
3		95.6	86/14	94.8	95/5
4		97.1	81/19	98.2	77/23

The yield and the selectivity were calculated on the basis of ^1H NMR spectra. ^aHydrosilylation of olefins with trimethoxysilane. ^bHydrosilylation of olefins with triethoxysilane.

The catalytic effect of many catalysts on the hydrosilylation of aminated alkenes is not satisfactory, which may be attributed to poisoning of the catalyst by the amino function, which reduces the activity and selectivity of the catalysts. As indicated in Table 1, the hydrosilylation of these three aminated alkenes with Karstedt's catalyst showed higher selectivity and the ratio of γ -isomer/ β -isomer was not less than 3/1. It can be seen that Karstedt's catalyst has good yield and selectivity in catalytic hydrosilylation addition of aminated alkenes with trimethoxysilane and triethoxysilane.

Moreover, in order to obtain more information of the catalytic activity and selectivity of the Karstedt's catalyst, the hydrosilylation of various functionalized alkenes with trimethoxysilane and triethoxysilane using Karstedt's catalyst was tested under similar conditions. The results are summarized in Table 2.

Table 2 Karstedt's catalyst for the hydrosilylation of different functionalized alkenes with the trimethoxysilane and triethoxysilane reagents, respectively

Entry	Alkene	Yield ^a /%	Ratio ^a (γ/β)	Yield ^b /%	Ratio ^b (γ/β)
1		92.0	85/15	94.9	84/16
2		91.5	100/0	92.8	100/0
3		95.2	95/5	97.6	92/8
4		97.6	100/0	93.8	100/0
5		91.6	100/0	94.7	100/0
6		95.7	81/19	92.2	79/21
7		98.2	81/19	97.8	85/15
8		82.7	90/10	80.5	89/11
9		92.6	97/3	94.1	91/9

The yield and the selectivity were calculated on the basis of ¹H NMR spectrum. ^a Hydrosilylation of olefins with trimethoxysilane. ^b Hydrosilylation of olefins with triethoxysilane.

As indicated in Table 2, the hydrosilylations gave high yields (>80%) for all substrates attached with various functional groups (—OH, —OR, —COR, —COOR, —R, —COOH, —CHO, —C(OR)₂, —C₆H₅), and these reactions also showed a good selectivity with the γ -isomer/ β -isomer ratio of more than 79/21.

As shown in Table 2, catalytic hydrosilylation reactions of allyl ethyl ether (Entry 2), allyl acetate (Entry 4) and 1-undecene (Entry 5) with trimethoxysilane and triethoxysilane were carried out, and the corresponding hydrosilylation products were obtained in yield of more than 90%, and almost all of the products were γ -isomers. The highly regioselective result indicated that the Karstedt's catalyst has good selectivity for these functional groups of olefins.

Conclusions

In summary, we comprehensively studied the catalytic activity of Karstedt's catalyst for the hydrogenation of a variety of functionalized olefins and especially aminated alkenes with trimethoxysilane and triethoxysilane, demonstrating that the Karstedt's catalyst has the excellent performance for the hydrosilylation in terms of the yield and selectivity. Further studies are underway to expand the scope of the applications of the hydrosilylation reaction.

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