Hydrosilylation of Olefins with Monosilane in the Presence of Lithium Aluminum Hydride

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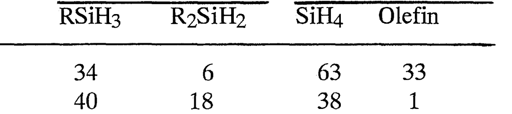
Hydrosilylation reactions of 1-hexene and ethylene with SiH_4 occurs in the presence of $LiAlH_4$ as a catalyst. Hexylsilane and dihexylsilane were produced from 1-hexene and SiH_4. Ethylsilane was produced from ethylene and SiH_4. The reaction mechanism involving SiH_4 and the alkyl anion, which is formed by the interaction between $LiAlH_4$ and the olefin, has been proposed.

The hydrosilylations of olefins with $HSiCl_3$, CH_3SiHCl_2 or $(CH_3)_3SiH$, which are easily obtainable by Rochow's direct process, have been extensively investigated using many transition metal complexes as catalysts.[1] But the reports concerning the hydrosilylations with H_2SiCl_2, $(CH_3)_2SiH_2$, $C_6H_5SiH_3$, SiH_4 or Si_2H_6, which have several Si-H bonds in the molecule, are few.[2] The pyrolytic reactions and photoreactions were carried out between SiH_4 or Si_2H_6 and ethylene or acetylene at an elevated temperature in the gas phase with very low yields and selectivities.[3] $RSiH_3$ and SiH_4 were alkylated in the presence of $NaAlR_4$ (R is a alkyl radical) at elevated temperature.[4] We have selectively obtained some silylated compounds ($RSiH_3$) by the hydrosilylation of olefins with SiH_4 in the presence of transition metal complexes as the catalysts, though the transition metal complexes have easily been deactivated by interaction with SiH_4.[5] Recently, Sakakura et al., have also found that $Cp^*{}_2NdCH(SiMe_3)_2$ catalyzes the hydrosilylations between SiH_4 and olefins.[6] In this paper, we report a new catalyst for the hydrosilylation of olefins with SiH_4 and discuss the reaction mechanism.

SiH_4 of 99.999% purity and ethylene of 99.9% purity were used. 1-Hexene was dried over molecular sieves and distilled prior to use. A solution of diethyl ether containing $LiAlH_4$ was refluxed and the undissolved substance was separated from the solution by filtration. The solution was then dried under reduced pressure at 70 °C, and white crystals of $LiAlH_4$ were obtained. Diethyl ether, benzene and pentane were dried over calcium hydride, phosphorous pentoxide and molecular sieves, respectively, and were distilled prior to use.

All experiments were performed in a 70 ml autoclave. The prescribed amount of 1-hexene, $LiAlH_4$ and solvent were charged into the autoclave (see Table 1). SiH_4 was then poured into the autoclave under pressure, and the reaction was carried out at 120 °C for 20 h at a pressure of about 30~40 kg/cm^2 abs. After the reaction, all gases in the autoclave were replaced with nitrogen and passed through a solution of lithium in ethanol. Unreacted SiH_4, which was converted into silicon tetraethoxide in the solution, was analyzed by GC. The liquid products (hexylsilane and dihexylsilane) were separated by distillation under reduced pressure, and assigned based on the GC-MS, infrared and ^1H NMR spectra. They were compared with the spectra of the compounds which were prepared by $LiAlH_4$ reduction of hexyltrichlorosilane and dihexyldichlorosilane.[5,7] The amounts of unreacted olefin and some liquid products were determind by GC using n-eicosan as an internal standard. Ethylene was poured into an autoclave under pressure like SiH_4. The gassy product (ethylsilane) was analyzed by GC-MS and infrared spectroscopy[8] and the amount of ethylsilane was determind by measuring the ethyltriethoxysilane in a solution of lithium in ethanol. $C_6H_5SiH_3$ and $(C_2H_5)_3SiH$ were also used instead of SiH_4.

The results are shown in Table 1. The reaction proceeded at 120 °C without a decrease in reactivity of $LiAlH_4$. Hexylsilane (**1**)[9] and dihexylsilane (**2**)[9] were obtained by the reaction of SiH_4 with 1-hexene, and ethylsilane (**3**)[9] was obtained from the reaction of SiH_4 and ethylene.



$$SiH_4 + CH_2{=}CH(CH_2)_3CH_3 \longrightarrow \underset{\mathbf{1}}{CH_3(CH_2)_5SiH_3} + \underset{\mathbf{2}}{[CH_3(CH_2)_5]_2SiH_2}$$

$$SiH_4 + CH_2{=}CH_2 \longrightarrow \underset{\mathbf{3}}{CH_3CH_2SiH_3}$$

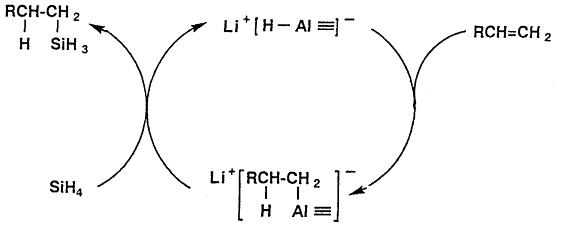
Scheme 1. The hydrosilylation of olefins with SiH_4.

Table 1. Hydrosilylations of olefins with hydrosilanes

Run No	Hydrosilane	mmol	Olefin	mmol	$LiAlH_4$ mmol	Solvent [a]	Product Yield / % [b] $RSiH_3$	Product Yield / % [b] R_2SiH_2	Recovery / % SiH_4	Recovery / % Olefin
1	SiH_4	100	1-hexene	89	4.5	none	34	6	63	33
2 [c]	SiH_4	100	1-hexene	91	4.5	none	40	18	38	1
3	SiH_4	84	1-hexene	46	2.2	diethyl ether		unreacted		
4	SiH_4	84	1-hexene	44	2.2	pentane	6	trace	83	76
5	SiH_4	84	1-hexene	47	2.2	benzene	22	1	72	49
6	SiH_4	56	ethylene	56	2.8	benzene	24	trace	74	-
7 [d]	$C_6H_5SiH_3$	50	1-hexene	48	2.6	none	61 [e]	4 [f]	18	3
8 [d]	$(C_2H_5)_3SiH$	50	1-hexene	50	2.5	none		unreacted		

[a] Twenty ml of the solvent was used in every experiment. [b] The percentage ratio of the product versus the charged silane compound.
[c] The reaction was carried out at 160 °C for 20 h. [d] The reaction was carried out at 150 °C for 20 h. [e] phenylhexylsilane [f] phenyldihexylsilane

The yields of the products indicate that the reactions are catalyzed by $LiAlH_4$. It is well known that the alkyl anion is formed by the interaction between $LiAlH_4$ and olefins (hydroalumination) above 110 °C.[10] SiH_4 may react with these anions to produce the silylated compounds, and $LiAlH_4$ would be regenerated. The mechanism of this reaction is shown in Scheme 2.



Scheme 2. A possible mechanism for the hydrosilylation of olefin with SiH_4.

When diethyl ether was used as a solvent in the reaction of SiH_4 with 1-hexene, no reaction occurred. This is due to the strong interaction between $LiAlH_4$ and diethyl ether, which inhibits the formation of the aluminate anion. Only hexylsilane (**1**) was obtained when pentane or benzene was used as the solvent. $NaAlH_4$ and $LiBH_4$ showed no catalytic activity. $C_6H_5SiH_3$, of which concentration in the reaction solution would be higher than that of SiH_4, also reacted and gave the alkylated compounds in the considerable yields. This suggests the hydrosilylation reactions using $LiAlH_4$ as a catalyst are applicable to other silane compounds. $(C_2H_5)_3SiH$ was not alkylated. This would be caused by the steric hindrance between the anionic intermediate (tetravalent aluminate anion) and $(C_2H_5)_3SiH$. $AlCl_3$ also catalyzed the hydrosilylation of olefins with hydrosilanes, and mechanism, which was accompanied by a trivalent aluminum compound as an intermediate, was proposed.[11] The hydrosilylations using $LiAlH_4$ and $AlCl_3$ would proceed via tetravalent aluminate compound and trivalent aluminum compound, respectively. Therefore, there would be large difference in the reactivities of the hydrosilanes (R_xSiH_{4-x}) between the two catalysts. We are going to have a further study about this problem.

Usually alkylsilanes are prepared by the reduction of the corresponding alkylchlorosilane using an expensive metal hydride.[12] This report offers a new direct route for preparing alkylsilanes, which have a reactive silyl group ($-SiH_3$) and are very useful materials.

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9 a) Hexylsilane(**1**) : 1H NMR($CDCl_3$/TMS) ; δ3.48 (t, 3H,J=3.9Hz, $Si\underline{H}_3$), 1.1~1.7 (m, 8H, $C\underline{H}_2$-$C\underline{H}_2$-$C\underline{H}_2$-$C\underline{H}_2$-CH_2-SiH_3), 0.6(m, 5H, $C\underline{H}_2$-SiH_3, $C\underline{H}_3$). IR (neat) ; ν(Si-H) 2150 cm-1, ν(C-H) 2850, 2920, 2952 cm-1, δ(SiH_3) 922 cm-1. MS(m/z), 116(M+); b) Dihexylsilane(**2**) : 1H NMR($CDCl_3$/TMS) ; δ3.64 (m, 2H, J=3.7Hz, $Si\underline{H}_2$), 1.1~1.7 (m, 16H, $C\underline{H}_2$-CH_2-$C\underline{H}_2$-$C\underline{H}_2$-CH_2-SiH_2), 0.5~1.1 (m, 10H, $C\underline{H}_2$-SiH_2, $C\underline{H}_3$). (neat) ; ν(Si-H) 2150 cm-1, ν(C-H) 2851, 2910, 2955 cm-1, δ(SiH_2) 942 cm-1. MS(m/z); 200(M+) ; c) Ethylsilane(**3**) : IR (neat); ν(Si-H) 2150 cm-1, ν(C-H) 2955 cm-1, δ(SiH_3) 938 cm-1. MS(m/z), 60(M+).

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