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Preliminary communication

Hydrosilylation of olefins with monosilane catalyzed by transition metal complexes

Masayoshi Itoh *, Kenji Iwata, Ryo Takeuchi [1] and Mineo Kobayashi
Central Research Institute, Mitsui Toatsu Chemicals, Inc., 1190 Kasama-cho, Sakae-ku, Yokohama 247 (Japan)

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Abstract

Hydrosilylation of 1-hexene and 1,5-hexadiene with SiH_4 in the presence of transition metal or its compound as catalyst produced alkylated silanes.

The transition metal complex catalyzed hydrosilylation of olefin has been extensively studied. Various hydrosilanes such as $HSiCl_3$, CH_3SiHCl_2, H_2SiCl_2 or $C_6H_5SiH_3$ have been employed [1–8]. However, there are a few reports on the hydrosilylation with monosilane (SiH_4) [9–17]. The thermal or photochemical reactions of SiH_4 with ethylene or acetylene were reported. The yield of products was quite low. Recent development of polysilicon and amorphous silicon provides SiH_4 as a new raw material in organosilicon industry. Hydrosilylation using SiH_4 is a new route to trihydroorganosilanes. Thus, a more mild and selective reaction is desired. In this communication, we report the first example of transition metal complex catalyzed hydrosilylation of olefin with SiH_4.

All experiments were performed in an autoclave. At standard reaction conditions, 42 mmol of the olefin and a small amount of catalyst were charged into an autoclave. Then, 14 mmol of SiH_4 was poured in under pressure, and the reaction was carried out for 3 h at 80 °C at pressures of about 10 kg/cm^2 abs. The products were obtained by distillation under reduced pressure, and assigned by GC–MS, IR and ^1H NMR spectra. They were compared with the spectrums of the compounds which were prepared by $LiAlH_4$ reduction of hexyltrichlorosilane, dihexyldichlorosilane, 5-hexenyltrichlorosilane and dichlorosilacycloheptane [18–20]. Unreacted SiH_4 and the liquid sample were analyzed using gas chromatography.

The results are shown in Tables 1 and 2. Hexylsilane (I) and dihexylsilane (II) were obtained by the reaction of SiH_4 with 1-hexene, and 5-hexenylsilane (III) and

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[1] Present address: Department of Chemistry, Yokohama City University, Kanazawa-ku, Yokohama 236 (Japan).

Table 1

Hydrosilylation of 1-hexene with SiH_4

No	Catalyst [a]	Product yield (%) [b]			TN [d] (mol/mol cat.)
		I	II	Others [c]	
1	$Pt(PPh_3)_4$	37.4	4.7	1.5	139
2	$PtCl_2(PPh_3)_2$	16.6	1.6	0.6	45
3	Pt/C (Pt 5wt%)	9.4	3.7	0.7	43
4	Rh/C (Rh 5wt%)	24.2	2.2	0	93
5	$NiCl_2(PPh_3)_2$	1.0	0	0	3
6	$Pt(PPh_3)_4$ [e]	21.9	1.1	2.7	795

[a] About 0.04 mmol of catalyst was used. [b] Based on SiH_4. The mass balance of silicon, which was calculated by adding the amounts of the products and unreacted SiH_4, was in the range 70–90% in any experiment. [c] Other products detected by gas chromatography. [d] Turnover number, the ratio of the amount of the two main products versus used catalyst. [e] 50 mmol of SiH_4 and 0.02 mmol of catalyst were charged. Reation was carried out for 20 h at a pressure of 36 kg/cm^2 abs.

silacycloheptane (IV) were obtained from SiH_4 and 1,5-hexadiene in the presence of a catalyst. Intramolecular hydrosilylation of III gave IV. The resulting reaction was not altered using toluene or benzene as solvent.

In two olefins, the regioselectivity of this hydrosilylation was similar to that observed with $HSiCl_3$. Platinum complexes showed high catalytic activity. $Pt(PPh_3)_4$ was a better catalyst than Speier's one, which was a typical hydrosilylation catalyst.

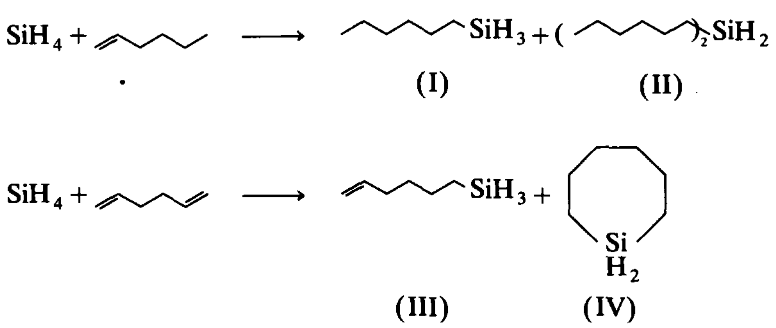
The reaction took place rapidly during the first 30 min, but the catalyst was immediately destroyed, as shown in Fig. 1. Complete conversion of SiH_4 was not achieved. Therefore, the turnover numbers of these reactions were low compared with those for $HSiCl_3$, which was completely transfered to the trichlorosilylated compound under the same reaction conditions. The catalyst would be reduced to

Table 2

Hydrosilylation of 1,5-hexadiene with SiH_4

No	Catalyst [a]	Product yield (%) [b]			TN [d] mol/mol cat.
		III	IV	Others [c]	
1	$Pt(PPh_3)_4$	16.0	15.3	6.3	20
2	$PtCl_2(PPh_3)_2$	19.1	10.5	3.3	19
3	$H_2PtCl_66H_2O$	3.6	3.6	1.5	4
4	H_2PtCl_6 [e]	10.2	17.0	–	15
5	Pt/C (Pt 5wt%)	12.6	9.3	7.5	15
6	Rh/C (Rh 5wt%)	11.1	2.5	3.1	9
7	$NiCl_2(PPh_3)_2$	3.9	0	5.7	3
8	$Co_2(CO)_8$	4.2	0	–	3
9	$Mn(acac)_2$	2.1	0	0.5	1
10	$MoO_2(acac)_2$	2.1	3.9	0.3	5
11	$W(CO)_6$	0.9	0.9	–	1
12	$VO(acac)_2$	4.5	0	–	3

[a] About 0.2 mmol of catalyst was used. [b] Based on SiH_4, The mass balance of silicon, which was calculated by adding the amounts of the products and unreacted SiH_4, was in the range 70–90% in any experiment. [c] Other products detected by gas chromatography. The main component was di-5-hexenylsilane. [d] Turnover number, the ratio of the amount of the two main product, versus used catalyst. [e] Pretreated with O_2, followed by CH_3SiHCl_2. Reaction was carried out at 110 ° C [8].



Scheme 1.

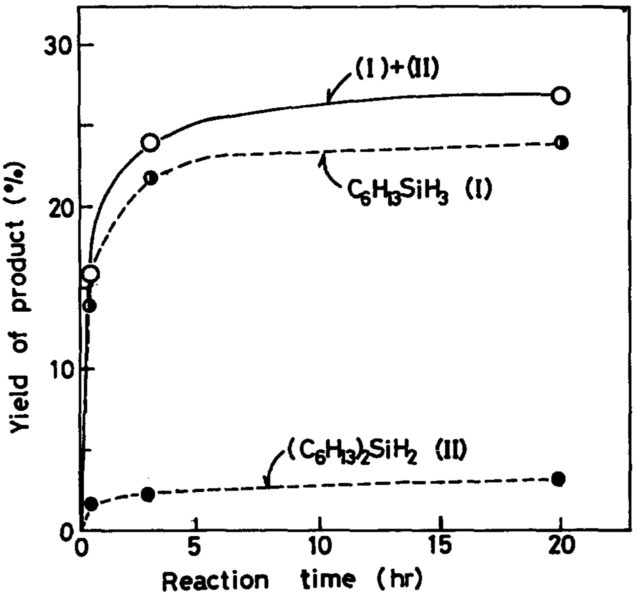


Fig. 1. Reaction of SiH_4 with 1-hexene. 0.02 mmol of $Pt(PPh_3)_4$ was used in every experiment.

the metal deposit, which has no catalytic activity, by the strong reducing ability of SiH_4. In fact, the catalyst did not show any catalytic activity after the treatment of catalyst by SiH_4. A similar poisoning effect of alkylhydrosilanes was observed during the hydrogenation of olefins under Pt and Rh catalyst [21].

Further studies on mechanism and synthetic application of hydrosilylation of SiH_4 are in progress. This report offers a new direct route for preparing alkylsilanes from SiH_4, and indicate an example for using SiH_4 as a new raw material in organosilicon chemistry.

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