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Cp_2TiPh_2-Catalyzed Dehydrogenative Coupling of Polyhydromonosilanes

Taichi NAKANO, Hidehisa NAKAMURA, and Yoichiro NAGAI
Department of Chemistry, Gunma University, Kiryu, Gunma 376

The Cp_2TiPh_2-catalyzed reaction of dihydrosilanes afforded dehydrogenative coupling products, disilanes and/or trisilanes. The reaction using phenylsilane produced hydride-terminated poly(phenylsilylene) polymers with $\overline{M}_n$=730 and $\overline{M}_w$=960, which exhibited the longest UV absorption maximum at 245 nm(ε, 5.7×10^4).

The syntheses of organopolysilanes involving straight chains,[1,2] cyclics,[3] ladders,[4] and cages[5] recently received much attention, because the polysilanes introduce newer valuable aspects into the area of silicon chemistry. In fact, the unique application of the polysilane polymers as silicon carbide ceramic materials, photoinitiators for radical polymerization of polymerizable olefins, photoresist materials, and semiconductors upon treatment with oxidizing agents such as SbF_5, AsF_5, or I_2 is associated with the great practical importance.[6] However, polysilanes are usually synthesized only by the conventional dehalogenative coupling of halosilanes with alkali metals or alkaline earth metals. Although the dehydrogenative coupling of hydrosilanes is considered to be a potential alternative, only a few reports along this line have been published on the reaction. For example, the dehydrogenative coupling of polyhydromonosilanes has been reported to occur in the presence of a transition metal complex such as $(PPh_3)_3RhCl$,[7] $(PPh_3)_2Pt(CH_2{=}CH_2)$,[8] Cp_2TiR_2(R=methyl or benzyl),[9] Cp_2ZrMe_2[10] and Cp_2ZrH_2.[10] We found that the dehydrogenative coupling of polyhydromonosilanes such as dihydrosilanes and phenylsilane took place in the presence of catalytic amounts of diphenyltitanocene(Eq. 1) and wish to report herein our preliminary results.

Typically, a mixture of diphenylsilane(5.5 g, 30 mmol) and diphenyltitanocene(0.199 g, 0.6 mmol) was heated at 110 ℃ for 24 h with stirring under argon.

GLC analysis of the resulting mixture disclosed that 66% of the hydrosilane was

$$n\ R^1R^2SiH_2 \xrightarrow{Cp_2TiPh_2} H\text{-}(Si(R^1)(R^2))_n\text{-}H \qquad (1)$$

$R^1=R^2=Ph$; $R^1=Me, R^2=Ph$; $R^1=Ph, R^2=H$.

consumed and 1,1,2,2-tetraphenyldisilane was produced in 72% yield based on the silane consumed. Identification of the disilane was performed by comparing its IR, ^1H NMR, and MS spectra with those of an authentic sample. On the other hand, the reaction of methylphenylsilane under similar conditions gave 1,2,3-trimethyl-1,2,3-triphenyltrisilane(32% yield) as well as 1,2-dimethyl-1,2-di-phenyldisilane(14% yield). In the same reaction in which cyclooctene was employed as an additive a better yield(88% yield) of the trisilane was realized. It should be noted that the yield of the trisilane is better than that given by the previously reported Rh(I) catalysis.[6] The results are summarized in Table 1. Alkenes employed as a hydrogen acceptor[11] were converted, in all cases, to alkanes in variable yields(50-90%) based on the alkene charged.

The dehydrogenative coupling of phenylsilane proceeded more rapidly than did the dihydrosilanes and resulted in the formation of polysilane polymers 1 with a bimodal molecular weight distribution in the range MW= 17300-340. $\overline{M}_n$ and $\overline{M}_w$ of the polymers 1 were evaluated to be 730 and 960, respectively.

Table 1. Cp_2TiPh_2-catalyzed Dehydrogenative Coupling of Dihydrosilanes[a]

Run	Silane	Hydrogen acceptor	Conv.[b] %	Products(Yield/%)[c]
1.	Ph_2SiH_2	neat	66	$(Ph_2SiH)_2$(72), Ph_3SiH(3)
2.	Ph_2SiH_2	decene-1	83	$(Ph_2SiH)_2$(66), Ph_3SiH(3)
3.	Ph_2SiH_2,	cyclooctene	66	$(Ph_2SiH)_2$(72), Ph_3SiH(5)
4.	$MePhSiH_2$	neat	68	$(MePhSiH)_2$(14), $H(MePhSi)_3H$(32)
5.	$MePhSiH_2$	decene-1	69	$(MePhSiH)_2$(15), $H(MePhSi)_3H$(23)
6.	$MePhSiH_2$	cyclooctene	80	$(MePhSiH)_2$(7), $H(MePhSi)_3H$(88)

a) A mixture of a dihydrosilane(30 mmol), Cp_2TiPh_2(0.6 mmol), and an alkene (10 mmol) was stirred at 110 °C for 24 h under argon.
b) Conversion of the silane.
c) Yields were determined by GLC and based on the silane consumed. The correction for thermal conductivity was made.

The polymers 1 exhibited IR characteristic absorption bands at 2090 cm^{-1}(ν_{Si-H}) and 910 cm^{-1}(δ_{Si-H} arising from secondary Si-H bonds).[12] The intensity of δ_{Si-H} was 0.47 relative to that of ν_{Si-H}. In view of the report by Harrod et al.[12] the spectrum suggests that the polymers 1 are hydride-terminated poly(phenylsilylene) polymers and the mean degree of polymerization is near 8.[12] The much higher reactivities of secondary Si-H bonds of hydrosilanes in comparison with that of tertiary Si-H bonds[13] in the Cp_2TiPh_2-catalyzed reaction supports well the polymers-backbone to be poly(phenylsilylene) structure. ^1H NMR measurement of the polymers 1 in acetone-d_6 showed a broad massif in the Si-H region(δ 5.7-4.0 ppm) whose integral was 1/3.9 with respect to the phenyl protons(δ 8.8-6.77 ppm) of the polymers 1. Consequently, the polysilane polymers 1 may be assigned to hydride-terminated poly(phenylsilylene) polymers and the mean degree of polymerization was evaluated by ^1H NMR and GPC analyses to be about 7. The polymers 1 (pale yellow and brittle glass with mp 63-77 °C dec.) are soluble in such solvents as benzene, toluene, and tetrahydrofuran. The longest UV absorption maximum of 1 in cyclohexane was observed at 245 nm (ε, 5.7×10^4)[14] which is shorter wavelength than that(λ_{max}: ≈270 nm, ε, ≈40000) of hydride-terminated poly(phenylsilylene) polymers 1'.[9] The results consist with that the mean degree of polymerization of the polymers 1 is bit smaller[2] than that of the polymers 1'. However, it is of great interest to note that the maximum degree of polymerization reached up to near 160. The same reactions in the presence of decene-1 and cyclooctene as a hydrogen acceptor are summarized in

Table 2. Average Molecular Weights (relative to polystyrene standards) of Poly(phenylsilylene) Polymers Prepared[a]

Run	Hydrogen acceptor	Polymer	Yield/wt%[e]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	n[f]
1.[b]	neat	pale yellow[c]	83(60)	730	960	1.3	160
2.	decene-1	brown[d]	99(71)	620	700	1.1	30
3.	cyclooctene	pale yellow[c]	(40)	620	780	1.3	40

a) A mixture of phenylsilane(30 mmol), Cp_2TiPh_2(0.6 mmol), and an alkene(10 mmol) was stirred at 110 °C for 24 h under argon.
b) Conditions; 110 °C, 1 h.
c) Glass. d) Viscous liquid.[15]
e) Crude yields. In pharentheses are shown isolated yields.
f) Highest degree of polymerization.

Table 2.

In conclusion, Cp_2TiPh_2 was found to activate efficiently a Si-H bond of dihydrosilanes and phenylsilane under the conditions at higher temperatures than the decomposition temperatures(70-90 °C) of the diphenyltitanocene to bring about the dehydrogenative coupling giving disilanes (and/or trisilanes) and hydride-terminated poly(phenylsilylene) polymers 1, respectively, although Harrod et al. recently reported that Cp_2TiPh_2 had not reacted with polyhydrosilanes at all.[9)]

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13) The dehydrogenative coupling of triethylsilane under similar conditions gave hexaethyldisilane only in 0.6% yield.
14) Molecular extinction coefficient was calculated based on the $\overline{M}_n$=730.
15) It was found by IR and ^1H NMR analyses that a terminal silicon atom in a polymer molecule links with one decyl group at the most.

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