

Dehydrogenative Coupling between Hydrosilanes and Alkynes Catalyzed by Alkoxides, Alkylmetals, and Metalamides

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The selective dehydrogenative coupling reaction between phenylsilane and ethynylbenzene occurred in the presence of some homogeneous base catalysts such as alkoxides, alkyl compounds, and the amides of alkali metals or barium. The order of the catalytic activities was $\text{Ba}(\text{OR})_2 > \text{LiN}(\text{SiMe}_3)_2 \sim n\text{-BuLi} > \text{LiOEt}$. Barium alkoxide showed the highest activity and selectivity for the reaction, and gave the polymer poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] in the reaction of phenylsilane with *m*-diethynylbenzene. The correlation between the catalytic activities and the catalyst basicities was discussed, and a reaction mechanism involving both the metal acetylide and the metal hydride was proposed. © 1999 Academic Press

Key Words: dehydrogenative coupling; hydrosilane; alkyne; alkoxide; alkylmetal; metalamide; base catalyst.

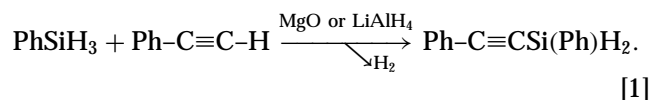
INTRODUCTION

There have been some reports on the dehydrogenative cross-coupling reactions of hydrosilanes with mono-substituted alkynes to produce alkynylsilanes. $\text{H}_2\text{PtCl}_6/\text{LiI}$, I (1–3), and $\text{IrH}_2(\text{SiEt}_3)(\text{COD})(\text{AsPh}_3)$, iridium catalysts formed by adding triarylsilanes or triarylphosphines to $[\text{Ir}(\text{OMe})(\text{diolefin})]_2$ (4), $[\text{IrH}(\text{H}_2\text{O})(bp)L_2]\text{SbF}_6$, or RhClL_3 ($L = \text{PPh}_3$, $bp = 7,8\text{-benzoquinolino}$), (5) have been used as catalysts. In these cases, the dehydrogenative cross-coupling reactions were found to accompany the significant hydrosilylation reactions to produce the corresponding alkenylsilanes. Calas and Bourgeois obtained alkynylsilane ($n\text{-Bu-C}\equiv\text{C-SiEt}_3$) from Et_3SiH and 1-hexyne using Na or NaH as the catalyst (6). Liu and Harrod reported that the CuCl/amine catalyst led to the highly selective dehydrogenative cross-coupling reactions of hydrosilanes with alkynes (7).

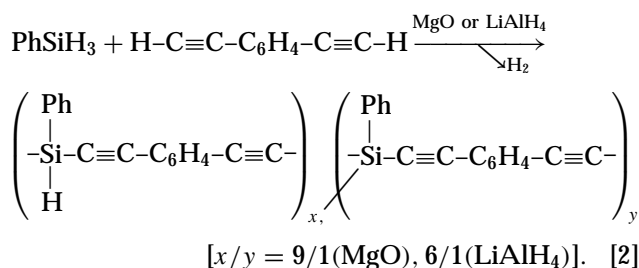
We have found that a solid base such as MgO catalyzes the selective dehydrogenative coupling reactions (8–10). Baba *et al.* have also recently reported KNH_2 loaded on Al_2O_3 , which is a solid base, and showed the catalytic activity for the

same reaction (11). Moreover, we have recently found that LiAlH_4 shows a much higher activity than MgO (12, 13). We have obtained a new highly heat- and burn-resistant thermosetting polymer, poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (abbreviated MSP) by applying the reaction to the polymerization (10, 13).

The dehydrogenative coupling reaction can be written as



The dehydrogenative coupling polymerization reaction can be written as



As MgO is easily separated by filtration from the reaction solution after the completion of the polymerization reaction, the polymer is very pure and stable in air. However, the catalytic activity of MgO is low, so a large amount of MgO is needed to obtain the product in high yield. We have been searching for a more active catalyst.

In this paper, we report some new catalysts for the above dehydrogenative coupling reaction and discuss their reaction mechanisms.

EXPERIMENTAL

Reaction Procedures

Phenylsilane, diphenylsilane, triphenylsilane, hexylsilane, and triethylsilane were used as the hydrosilanes. Ethynylbenzene (abbreviated EB), 1-octyne, and *m*-diethynylbenzene (abbreviated *m*-DEB) were used as the alkynes.

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These liquid reactants were dried over 3-Å molecular sieves prior to use. Metal compounds, including alkoxides, alkylmetals, and metalamides were used as the catalysts (see Table 1). Alkali and alkaline earth metal compounds were mainly used. The solvents diglyme, monoglyme, toluene, THF, dioxane, tetrahydropirane, diethoxyethane, and anisol were dried over 3-Å molecular sieves.

All experiments were carried out in a nitrogen atmosphere. The reactions were performed in a 100-ml glass flask under atmospheric pressure. The prescribed amount of hydrosilane, ethynyl compound, catalyst, and solvent were charged into the glass flask (see Tables 1, 3, and 6) and the reaction was carried out under homogeneous condition. After the reactions, the products were removed and analyzed as follows.

Reaction Products of Hydrosilanes with Ethynyl Compounds

After the completion of the reaction, the amounts of the reaction products and unreacted monomers were analyzed by GC (Shimadzu Co.; capillary column-CBPI-M25-025) using tetradecane as the internal standard. The liquid products were separated by distillation under reduced pressure, and assignments were made based on the GC-MS, IR, and ^1H , ^{13}C , and ^{29}Si NMR spectra (8, 12, 13).

Polymerization Reaction Products of Phenylsilane with *m*-DEB

The reaction products and unreacted monomers were analyzed by GC and gel permeation chromatography (GPC) (Shimadzu Co.; column-shodex KF-802 and 806L). The reacted solution was then added to 20 ml of toluene and 20 ml of 1 N HCl aq. in a vessel with stirring and separated into two layers [(I) and (II)]. The bottom layer (II) was added to 5 more ml of toluene and the toluene solution (III) layer was separated. The upper layer (I) was added above the toluene solution (III) and washed with water three times. The upper layer (I) was then dried over calcium sulfate and evacuated for 50 h at 60°C to give the liquid or solid polymer.

In a reaction (run 8 in Table 6), 30 ml of the reacted solution was separated and stirred with 0.5 g of a cation exchange resin (Mitsubishi Chemical Co., DIAION (RCP160M), particle size 0.39 mm, specific surface area 30 m² g⁻¹, average pore size 20–30 nm), which had been dried for 24 h at 110°C at room temperature. After the treatment, the resin was removed by filtration and the solution was evacuated for 50 h at 60°C.

IR, and ^1H , ^{13}C , and ^{29}Si NMR spectra were employed to determine the structure of the polymers (9, 13). Molecular weights were obtained by GPC with retention times calibrated against polystyrene samples.

Product Characterization

1 [Ph-C≡CSi(Ph)H₂], **2** [(Ph-C≡C)₂Si(Ph)H], **3** [Ph-CH=CHSi(Ph)H₂], **4** [Ph-CH(SiPhH₂)-CH₂Si(Ph)H₂], and **5** [PhC≡CSi(Ph) (CH=CH-Ph)H]: see references 9 and 12.

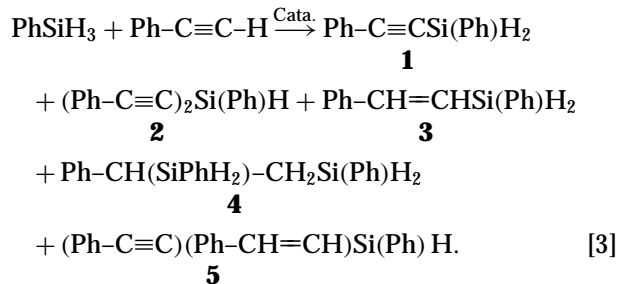
Ph-C≡CSi(Ph)₂H: [MS(*m/z*) (EI-mode) 284 ((M)⁺, base peak), 206, 181, 129, 105]. (Ph-C≡C)₂Si(Ph)₂: [MS(*m/z*) (EI-mode) 307 (base peak), 384 (M)⁺, 129, 205, 278]. Ph-C≡CSi(C₆H₁₃)H₂: [MS(*m/z*) (EI-mode) 131 (base peak), 105, 160, 84, 216(M)⁺]. (Ph-C≡C)₂Si(C₆H₁₃)H: [MS(*m/z*) (EI-mode) 231 (base peak), 129, 260, 274, 316(M)⁺]. C₆H₁₃-Ph-C≡CSi(Ph)H₂: [MS(*m/z*) (EI-mode) 81 (base peak), 105, 67, 146, 216(M)⁺]. (C₆H₁₃-Ph-C≡C)₂Si(Ph)H: [MS(*m/z*) (EI-mode) 81 (base peak), 67, 105, 95, 324(M)⁺]. Ph-CH(SiPhH₂)-CH(SiMe₃)[Si(Ph)H₂]: [MS(*m/z*) (EI-mode) 238 (base peak), 131, 73, 161, 207, 285, 390(M)⁺].

Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (run No. 8 in Table 6): IR (neat) ν (Si-H, C≡C) 2156, δ (Si-H) 796 cm⁻¹; ^1H NMR(CDCl₃/TMS) δ 3.09 (s, C≡CH), 4.74 (s, (Ph)SiH₂), 5.05 (s, (Ph)SiH), 7.1–8.0 (m, PhH); ^{13}C NMR(CDCl₃/CDCl₃) δ 78.3 (C≡CH), 82.4 (CCH), 86.6 (C≡C-C₆H₄-), 107.1 (C≡C-C₆H₄-), 123–136 (Ph); ^{29}Si NMR(CDCl₃/TMS) δ -59.4((Ph)SiH₂), -63.1((Ph)SiH), -69.1((Ph)Si).

RESULTS AND DISCUSSION

Reactions of Hydrosilanes with Ethynyl Compounds

The results of the reaction of phenylsilane with EB in the presence of some alkoxides, alkylmetals, and alkylamides are shown in Table 1. The catalytic activities depended on the types of metals and substitutions of the catalysts. The dehydrogenated products (**1**, **2**) were produced with a very small amount of the hydrosilylated products (**3**, **4**, and **5**) in the presence of the alkali metals, barium, and lanthanum compounds, which have strong basicities:



Products having higher molecular weight than those of products (**4**, **5**) were detected by using GPC. Almost no products were observed by GPC except for runs 9, 12, and 19 in Table 1. Barium 2-ethylhexoxide (Ba [OCH₂CH(C₂H₅)(CH₂)₃CH₃], abbreviated Ba(OC₈H₁₇)₂),

TABLE 1
Reactions of Phenylsilane with Ethynylbenzene (EB) in the Presence of Alkoxide, Alkylmetals, and Alkylamides^a

Run No.	PhSiH ₃ (mmol)	EB (mmol)	Catalyst	(mmol)	Conversion (%)		Product yield (%) ^b				
					PhSiH ₃	EB	1	2	3	4	5
1	53.7	52.5	LiOEt	0.26	46.2	43.5	34.3	6.2	0	0	0.5
2	51.3	52.6	LiO- <i>i</i> -Pr	0.34	57.9	75.8	47.4	14.6	0	0	0.2
3 ^c	50.8	51.9	NaOEt	0.31	62.0	85.4	46.1	17.8	0	0	0.1
4 ^d	49.5	51.1	KOEt	0.33	9.9	6.5	5.9	0.1	0	0	0
5	51.2	51.4	Ba(OMe) ₂	0.27	73.9	98.4	48.8	24.7	0	0	0
6	50.6	51.8	Ba(O- <i>i</i> -Pr) ₂	0.29	74.8	99.3	53.2	29.5	0	0	0
7	49.4	51.4	Ba(O- <i>t</i> -Bu) ₂	0.27	73.4	97.5	51.3	29.7	0	0	0
8	50.5	54.2	Ba(OC ₂ H ₄ OMe) ₂	0.28	75.8	99.6	53.1	29.8	0	0	0
9	51.3	49.8	Ba(OC ₈ H ₁₇) ₂ ^e	0.26	93.6	99.8	1.1	0	0	0.1	0.1
					(89.1)	99.8	3.7	0.4	0	0	0) ^f
10 ^g	50.6	50.2	Ba(OC ₈ H ₁₇) ₂	0.29	72.1	98.7	40.8	19.2	0	0	0
11 ^{g,h}	50.2	49.1	Ba(OC ₈ H ₁₇) ₂	0.31	66.3	74.4	72.8	5.7	0	0	0
12 ⁱ	49.9	50.3	Cu(OEt) ₂	0.27	42.7	95.1	0.9	0.4	20.2	0.5	1.4
13	51.1	52.1	La(O- <i>i</i> -Pr) ₃	0.27	51.9	50.9	35.4	5.6	0.6	0	0.6
14	53.5	51.5	<i>n</i> -BuLi	0.32	55.9	66.8	40.3	7.3	0.4	0	0.1
15	51.6	51.2	PhLi	0.34	51.3	62.5	45.3	10.2	0	0	0.5
16	49.5	50.9	Bu ₂ Mg	0.35	8.8	3.3	5.7	0	0.8	0	0
17	48.9	50.2	(C≡CPh) ₂ Ba	0.22	74.6	98.9	54.0	30.4	0	0	0
18	49.8	50.6	LiN(SiMe ₃) ₂	0.31	52.7	69.6	42.7	13.1	0	0	0
19	50.1	50.3	NaN(SiMe ₃) ₂	0.37	83.5	99.1	8.2	1.4	0.4	0.9	1.4
					(68.4)	93.9	39.5	20.0	0.3	0.3	1.2) ^j
20	51.8	53.9	KN(SiMe ₃) ₂	0.28	28.5	30.8	25.3	3.5	0	0	0
21 ^k	4.9	11.1	MgO	25	94.0	74.7	23.3	48.4 ^l	0	0	0
22 ^m	52.8	53.4	LiAlH ₄	2.7	52.8	56.4	41.9	9.2	1.0	1.0	0

^a Approx. 10 ml of diglyme was used as the solvent in each experiment and the reaction was carried out for 8 h at 80°C.

^b The mole percent ratio of the product vs. the charged PhSiH₃. [1, Ph-C≡CSi(Ph)H₂; 2, (Ph-C≡C)₂Si(Ph)H; 3, Ph-CH=CHSi(Ph)H₂; 4, Ph-CH(SiPhH₂)-CH₂Si(Ph)H₂; 5, Ph-C≡CSi(Ph)(CH=CH-Ph)H.]

^c 10 ml of diglyme and 1 ml of THF were used as the solvents.

^d 10 ml of diglyme and 1 ml of Et₂O were used as the solvents.

^e Barium 2-ethylhexoide.

^f The data at a 4 h reaction time.

^g The reaction was carried out at 40°C.

^h 10 ml of toluene was used as the solvent.

ⁱ (Ph-CH=CH)₂Si(Ph)H was also produced. [MS (*m/z*) (EI mode) 209 (base peak), 130, 105, 312 (M⁺), 183.]

^j The data at a 2 h reaction time.

^k 10 ml of benzene was used as the solvent and the reaction was at 80°C for 4 h.

^l (Ph-C≡C)₃SiPh was also produced (yield 5.5%).

^m The reaction was carried out for 20 h at 120°C (Ref. 13).

showed the highest activity. The activity of Ba(O-*i*-Pr)₂ was about 100 times that of LiAlH₄ and about 4000 times that of MgO (see Table 2).

On the other hand, the compounds of the elements belonging to Groups 2 (alkaline earth metals, excluding barium), 4, 12, and 13 of the periodic table such as Mg(OEt)₂, *n*-Bu₂Mg, *n*-BuMgCl, Ca(OEt)₂, Sr(O-*i*-Pr)₂, Zr(O-*i*-Pr)₄, Ti(OEt)₄, Et₂Zn, Al(OEt)₃, and Ga(OEt)₃, which have higher ionization potential energies than alkali metals, showed almost no catalytic activity. Cu(OEt)₂ showed a higher catalytic activity against hydrosilylation than dehydrogenation (run no. 12 in Table 1).

Figure 1 shows the changes in the conversions of the reactants and the yields of the main products with time when

TABLE 2

Relative Catalytic Activities vs the Dehydrogenative Reaction of Phenylsilane with EB^a

Catalyst activity ^b	Ba(O- <i>i</i> -Pr) ₂	LiN(SiMe ₃) ₂	<i>n</i> -BuLi	LiOEt	LiAlH ₄	MgO
1	4000	600	470	310	40	1
2	630	140	530	240	40	1

^a The reaction was carried out for 4 h at 80°C in diglyme (Table 1).

^b Relative catalytic activity calculated from the conversion of EB and the catalyst amount. 1, Per unit catalyst mole; 2, per unit catalyst gram.

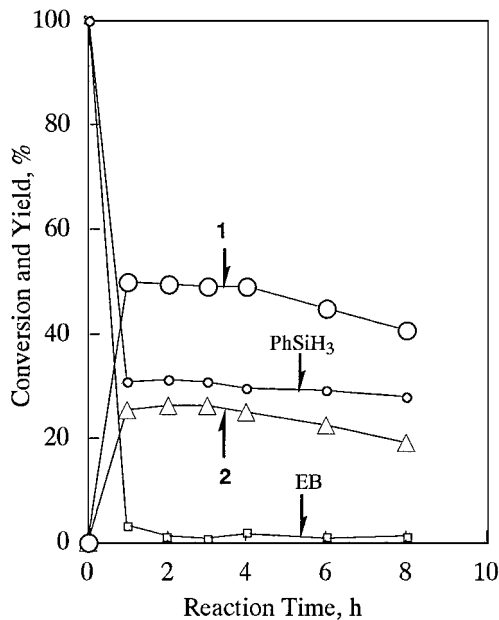


FIG. 1. Reaction of phenylsilane with EB in the presence of Ba(OC₈H₁₇)₂ (run 10 in Table 1). [**1**, Ph-C≡CSi(Ph)₂; **2**, (Ph-C≡C)₂Si(Ph)H.]

Ba(OC₈H₁₇)₂ was used as the catalyst. The dehydrogenative reaction rapidly occurred even at 40°C, and PhSiH₃ and EB decreased to produce **1** and **2** (run 10 in Table 1).

During the experiments of runs 9 and 19 in Table 1, very few products could be detected by GC, though almost all the

reactants were converted. Some compounds with a molecular weight of 400–500 were detected by GPC. Products **1** and **2** would be produced during an early stage of the reaction, and when all the EB was consumed, the hydrosilylation reactions of **1** and **2** and phenylsilane would proceed to produce the high-molecular-weight compounds. This presumption could be supported by the facts that products **1** and **2** were the main ones for the low conversions of the reactants (runs 10, 11, and 19 in Table 1), and the hydrosilylation reaction occurred between Ph-C≡CSiMe₃ and PhSiH₃ in the presence of Ba(OC₈H₁₇)₂ (run 7 in Table 3).

Mechanism of Dehydrogenative Coupling Reaction

In Table 4 and Fig. 2, the correlation between the first ionization potentials (abbreviated IP) of the metals of the alkoxides and their catalytic activities is shown. Alkoxides with a low IP, which are strong bases, have high catalytic activities, except for KOEt. The facts that the strong basic catalysts showed higher catalytic activities and the hydrogen of the ethynyl compound is acidic suggest that the reaction would proceed via an ionic intermediate. Bis(2-phenylethynyl)barium [(C≡CPh)₂Ba] showed a high catalytic activity and selectivity like the other barium compounds (run 17 in Table 1). Therefore, we presumed that the reaction would proceed involving a metal acetylide as an intermediate as shown in Fig. 3. The metal alkoxide would be converted into a metal hydride by the reaction with the hydrosilane as reported in the literature (Eq. (a) in Fig. 3) (15). Moreover, it is well known that an alkyl metal and

TABLE 3
Reactions of Hydrosilanes with Alkynes in the Presence of Ba(OC₈H₁₇)₂^a

Run No.	Hydrosilane	mmol	Alkyne	mmol	Ba(OC ₈ H ₁₇) ₂ (mmol)	Conversion (%)		Product yield (%) ^b		
						Hydrosilane	Alkyne	a	b	c
1 ^c	PhSiH ₃	50.6	EB	50.2	0.29	72.1	98.7	40.8 ^d	19.2 ^e	0
2	Ph ₂ SiH ₂	49.9	EB	52.2	0.25	76.8	99.1	57.9 ^f	31.3 ^g	0
3	Ph ₃ SiH	47.0	EB	50.6	0.25	0	4.4	0	—	0
4	C ₆ H ₁₃ SiH ₃	48.6	EB	51.0	0.26	81.4	99.3	58.7 ^h	31.7 ⁱ	0
5	Et ₃ SiH	49.9	EB	50.8	0.27	9.1	1.7	0	—	0
6	PhSiH ₃	49.9	C ₆ H ₁₃ -C≡CH	51.0	0.26	78.9	99.2	39.0 ^j	23.1 ^k	0
7	PhSiH ₃	51.0	Ph-C≡CSiMe ₃	50.0	0.24	25.3	7.3	0	0	7.3 ^l

^a Approx. 10 ml of diglyme was used as the solvent in each experiment and the reaction was carried out for 8 h at 80°C.

^b The mole percent ratio of the product vs the charged PhSiH₃. [**a**, **b**, dehydrogenation reaction products, **c**, hydrosilylation reaction products.]

^c The reaction was carried out at 40°C.

^d **1**, Ph-C≡CSi(Ph)₂.

^e **2**, (Ph-C≡C)₂Si(Ph)H.

^f Ph-C≡CSi(Ph)₂H.

^g (Ph-C≡C)₂Si(Ph)₂.

^h Ph-C≡CSi(C₆H₁₃)₂.

ⁱ (Ph-C≡C)₂Si(C₆H₁₃)H.

^j C₆H₁₃-Ph-C≡CSi(Ph)₂.

^k (C₆H₁₃-Ph-C≡C)₂Si(Ph)H.

^l Ph-CH(SiPhH₂)-CH(SiMe₃)[Si(Ph)H₂], Ph₂SiH₂ (yield 3.9%), and SiH₄ (yield 3.0%) were also produced.

TABLE 4

Correlation between the First Ionization Potential (IP) and the Catalytic Activities of the Alkoxide during the Dehydrogenative Reaction of Phenylsilane with EB

Run No.	Catalyst	Metal	IP (eV)	Conversion (%)		Yield (%)	
				PhSiH ₃	EB	1	2
1	KOEt	K	4.341	9.9	6.5	5.9	0.1
2	NaOEt	Na	5.139	62.0	85.4	46.1	17.8
3	Ba(O- <i>i</i> -Pr) ₂	Ba	5.212	74.8	99.3	53.2	29.5
4	LiOEt	Li	5.392	46.2	43.5	34.3	6.2
5	LiO- <i>i</i> -Pr	Li	5.392	57.9	75.8	47.4	14.6
6	La(O- <i>i</i> -Pr) ₃	La	5.577	51.9	50.9	35.4	5.6
7	Sr(O- <i>i</i> -Pr) ₂	Sr	5.695	3.8	0.1	0.1	0
8	Al(OEt) ₃	Al	5.986	7.0	2.1	0	0
9	Ga(OEt) ₃	Ga	5.999	3.7	0	0	0
10	Ca(OEt) ₂	Ca	6.113	0	0	0	0
11	Mg(OEt) ₂	Mg	7.646	2.2	3.4	0	0

^a The reaction was carried out for 8 h at 80°C in diglyme (runs 1–4, 5; see Table 1).

^b 1, Ph-C≡CSi(Ph)H₂; 2, (Ph-C≡C)₂Si(Ph)H.

metalamide react with ethynyl compounds to produce the metal acetylide at -78°C (Eqs. (b) and (c) in Fig. 3) (16, 17). The metal hydride or metal acetylide would then react with an ethynyl compound or hydrosilane, respectively, as shown in Eq. (d) in Fig. 3. From the results of the energy diagrams obtained by an *ab initio* calculation method using the 6-31G** basis set for the two elementary processes of the above mechanism as shown in Fig. 4, the endothermic elementary process (I) would be the rate-determining step.

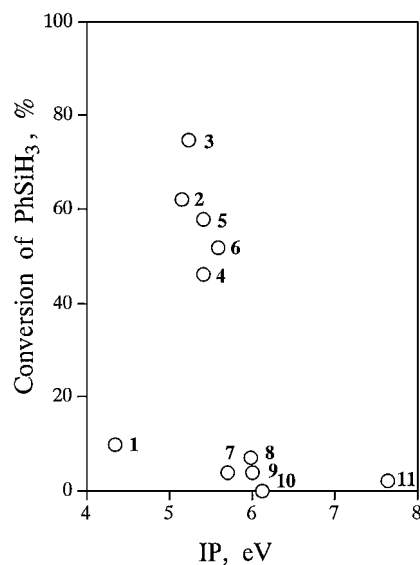


FIG. 2. Correlation between the first ionization potential (IP) and the catalytic activities of the alkoxide during the dehydrogenative reaction of phenylsilane with EB. 1, KOEt; 2, NaOEt; 3, Ba(O*i*Pr)₂; 4, LiOEt; 5, LiO-*i*-Pr; 6, La(O*i*Pr)₃; 7, Sr(O*i*Pr)₂; 8, Al(OEt)₃; 9, Ga(OEt)₃; 10, Ca(OEt)₂; 11, Mg(OEt)₂.

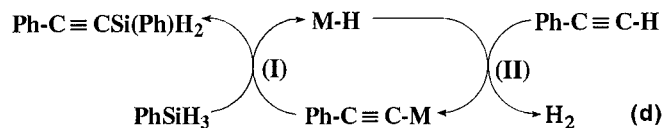
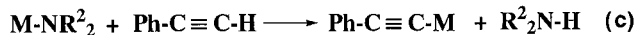
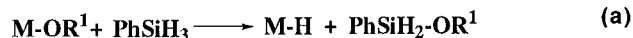


FIG. 3. Postulated mechanism of the dehydrogenative coupling reaction of hydrosilane with alkyne.

The reason for the low catalytic activity of KOEt is not obvious, but we think it is probably caused by the low solubility of potassium hydride in the organic solvent. Ethers such as diglyme and monoglyme were better solvents for the reaction than toluene (runs 10 and 11 in Table 1). The polarity of the ethers would be advantageous for the formation of the ionic intermediate. The activities of Ph₃SiH and Et₃SiH were low, as shown in Table 3, which would be caused by the steric hindrances.

In Table 5 and Fig. 5, the correlation between the catalytic activities of the lithium compounds and *p*K_as of their conjugate acids is shown. The catalytic activities of *n*-BuLi, PhLi, LiN(SiMe₃)₂, and LiOEt were much higher than those of LiOPh and LiOCOPh, which showed almost no catalytic activity. This would be caused by the low basicity of PhO⁻ and PhCOO⁻. Probably, *n*-BuLi, PhLi and LiN(SiMe₃)₂ would form the acetylide by the reaction with EB (*p*K_a = 21), and LiOEt would form the hydride by the reaction with PhSiH₃. On the other hand, LiOPh and LiOCOPh would not give the metal hydride by the reaction with an PhSiH₃.

It is well known that the R₃Si-H bond can be activated by transition metal complexes, and many reactions concerning hydrosilanes have been studied. We have shown that ionic (basic) compounds such as alkoxides, alkylmetals, and metalamides containing alkali metals or barium can activate the Si-H bond.

Polymerization Reactions of Phenylsilane with *m*-DEB

Barium alkoxide showed a much higher activity than MgO or LiAlH₄ as shown above. Therefore, we studied the polymerization reaction using Ba(OC₈H₁₇)₂ as a catalyst (see Table 6). The dehydrogenative coupling polymerization reaction occurred and the solid polymer poly[(phenylsililene)ethynylene-1,3-phenylenethynylene] was obtained. Figure 6 shows the changes in the conversions of the monomers and the yield and molecular weight of the polymer. The monomers rapidly decreased and the oligomer including the adduct of two monomers were produced during an early stage of the reaction. The molecular

TABLE 5

Correlation between the Catalytic Activities of Lithium Compounds and pK_a of their Conjugate Acids of the Catalysts during the Dehydrogenative Reaction of Phenylsilane with EB^a

Run No.	Catalyst	Conjugate acid	pK_a of conjugate acid	Conversion (%)		Yield (%) ^b	
				PhSiH ₃	EB	1	2
1	<i>n</i> -BuLi	<i>n</i> -Bu-H	50	55.9	66.8	40.3	7.3
2	PhLi	Ph-H	43	51.3	62.5	45.3	10.2
3	LiN(SiMe ₃) ₂	H-N(SiMe ₃) ₂	35	52.7	69.6	42.7	13.1
4	LiOEt	EtO-H	17	46.2	43.5	34.3	6.2
5	CpNa	Cp-H	15–18	11.7	6.6	8.8	0.3
6	LiOPh	PhO-H	10	2.4	0.0	0	0
7	LiOCOPh	PhCOO-H	4	6.0	4.2	0	0

^a The reaction was carried out for 8 h at 80 °C in diglyme (runs 1–3; see Table 1).

^b 1, Ph-C≡CSi(Ph)H₂; 2, (Ph-C≡C)₂Si(Ph)H.

TABLE 6

Polymerization Reactions between Phenylsilane and *m*-DEB in the Presence of Ba(OC₈H₁₇)₂^a

Run No.	PhSiH ₃ (mmol)	<i>m</i> -DEB (mmol)	Ba(OC ₈ H ₁₇) ₂ (mmol)	Solvent ^a	Temp. (°C)	Conversion (%)		Polymer ^{b,d} yield (%)	Adduct ^c yield (%)	Molecular weight ^d		
						PhSiH ₃	<i>m</i> -DEB			Mw	Mn	Mw/Mn
1	39	43	0.40	Diglyme	80	91	95	88	5	5,560	1320	4.2
2	41	41	0.40	Monoglyme	80	82	89	78	11	1,380	750	1.8
3	40	42	0.41	Toluene	80	67	55	30	38	410	370	1.1
4	40	42	0.20	THF	67	78	73	61	21	650	490	1.3
5 ^e	41	42	0.21	Toluene	60	66	66	75	7	690	530	1.3
				Diglyme		(83)	88	85	5	1,760	850	2.1) ^f
6 ^e	41	42	0.22	Toluene	80	91	96	87	7	2,230	920	2.4
				Diglyme		(91)	100	102	3	20,100	2040	9.9) ^f
7	41	43	0.20	Monoglyme	75	92	100	93	3	21,880	2110	10.4
8 ^g	523	516	2.60	Monoglyme	75	93	100	93	3	12,470	1720	7.3

^a 30 ml of the solvent was used in each experiment and the reaction was carried out for 8 h.

^b The mole percent ratio of the weight of the polymer versus the total weight of the charged two monomers.

^c The reaction product of PhSiH₃ with *m*-DEB [HC≡C-Ph-C≡CSi(Ph)H₂].

^d The adduct was excluded.

^e 30 ml of toluene and 4 ml of diglyme were used as solvents.

^f The data at 20 h reaction time.

^g 375 ml of monoglyme was used.

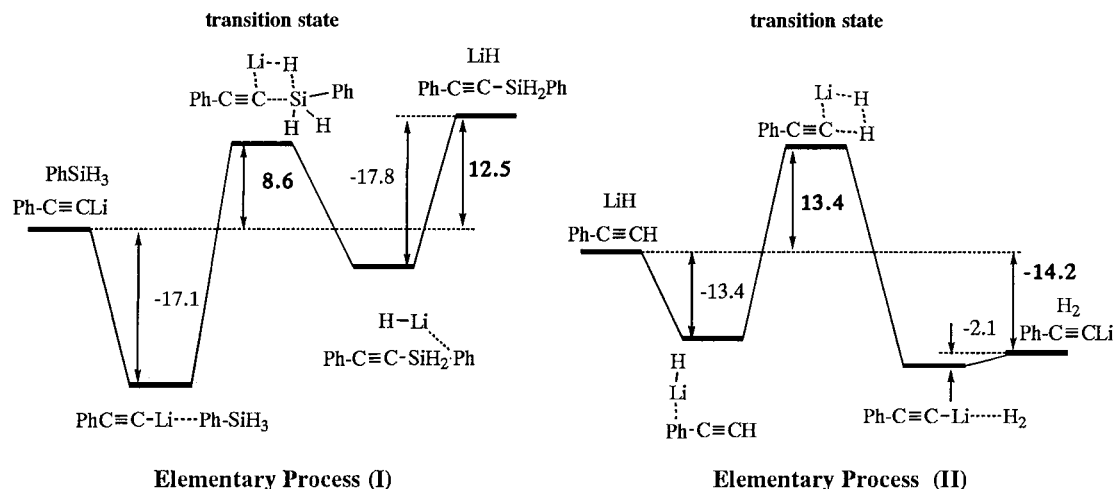


FIG. 4. Energy diagrams of elementary processes of the mechanism shown in Fig. 3.

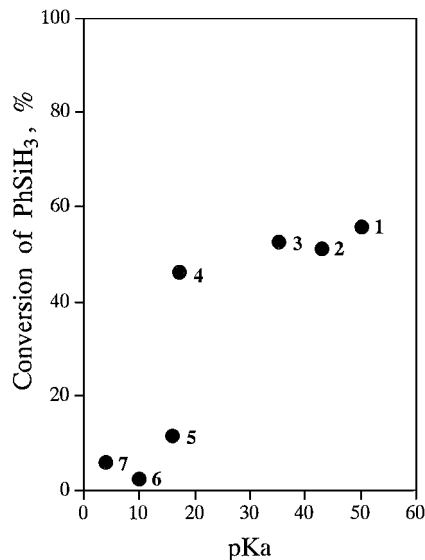


FIG. 5. Correlation between the catalytic activities of lithium compounds and pK_a of their conjugate acids of the catalysts during the dehydrogenative reaction of phenylsilane with EB. 1, *n*-BuLi; 2, PhLi; 3, LiN(SiMe₃)₂; 4, LiOEt; 5, CpNa; 6, LiOPh; 7, LiOCOPh.

weight of the polymer gradually increased when the monomers were consumed. The solvents of diglyme and monoglyme gave a polymer with a high molecular weight, but THF and toluene gave a polymer with a low molecular weight. No polymer could be obtained in dioxane, tetrahydropyran, diethoxyethane, and anisole.

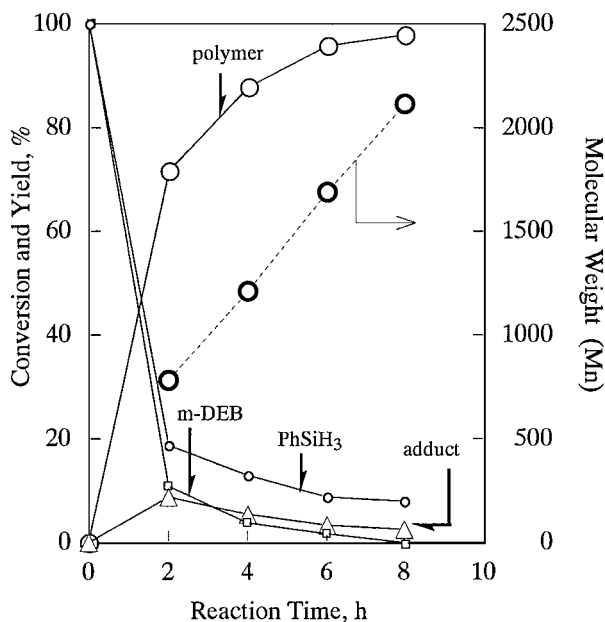


FIG. 6. Polymerization reaction of phenylsilane with *m*-DEB in the presence of Ba(OC₈H₁₇)₂ (run 7 in Table 6). Adduct: the reaction product of PhSiH₃ with *m*-DEB (HC≡C-Ph-C≡CSi(Ph)H₂).

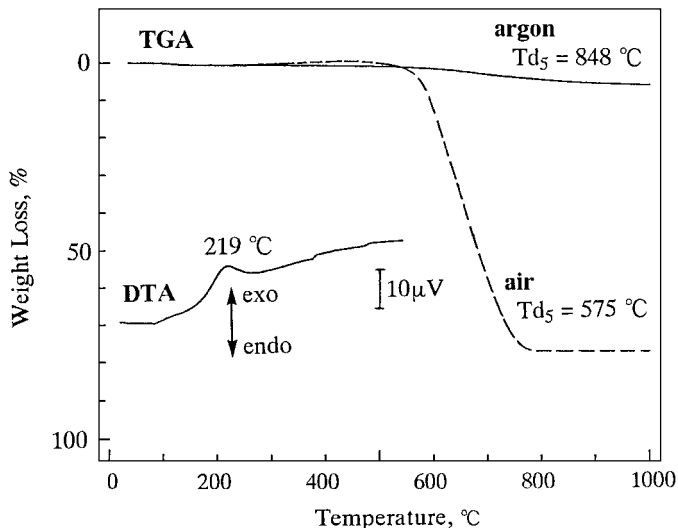


FIG. 7. TGA-DTA traces of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] prepared using Ba(OC₈H₁₇)₂ under argon and air.

The spectral data (IR and ¹H, ¹³C, and ²⁹Si NMR) of the polymer were very similar to those of the polymers obtained using MgO or LiAlH₄ as the catalyst, though the value of x/y in formula (2) was 7/4 (run 8 in Table 6), which was determined from the ²⁹Si NMR spectrum. The thermal properties were measured using TGA-DTA (Fig. 7). The Td_5 (temperature of 5% weight loss) in argon was 848°C [$Td_5 = 860^\circ\text{C}$ (MgO), 760°C (LiAlH₄)]. The polymer showed a high heat and burn resistance, similar to the polymer obtained using MgO (9, 14) or LiAlH₄ (13) as the catalyst.

The Si-H bond in the polymer is easily hydrolyzed in the presence of moisture to form a siloxane (Si-O) bond in the air when the polymer was contaminated with basic compound; therefore the catalyst residues must be removed thoroughly from the polymer. The reacted solution, which contained 2980 ppm of barium versus the polymer, was treated with the cation exchange resin, and almost all the barium compounds were removed from the reacted solution (less than 0.5 ppm). These results would enable the economical preparation process of MSP.

CONCLUSION

Alkoxides, alkyl compounds, or amides of alkali metals and barium, such as LiOR, NaOR, La(OR)₃, RLi, R₂Ba, LiN(SiMe₃)₂, NaN(SiMe₃)₂, and KN(SiMe₃)₂, showed high catalytic activity and selectivity vs the dehydrogenative coupling reaction between hydrosilanes and ethynyl compounds. Barium alkoxide showed the highest activity and selectivity for the reaction and gave the polymer poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] in the reaction of phenylsilane with *m*-diethynylbenzene. The residue of barium catalyst was easily

removed from the polymer by using the cation exchange resin.

The first ionization potential of the metal in an alkoxide and the pK_a of the conjugate acid in a lithium compound had good correlations with the catalytic activity. A reaction mechanism involving both the metal acetylide and metal hydride was proposed.

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