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Notes

Dehydrogenative Coupling Reactions between a Monosubstituted Alkyne and Monosilane in the Presence of Lithium Aluminum Hydride

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Summary: A selective dehydrogenative coupling reaction occurs in the presence of $LiAlH_4$ *as a catalyst between 1-hexyne and* SiH_4 *to give hexynylsilane and dihexynylsilane. A reaction mechanism involving* SiH_4 *and the alkynylaluminate anion, formed by the interaction between* $LiAlH_4$ *and the alkyne, is proposed.*

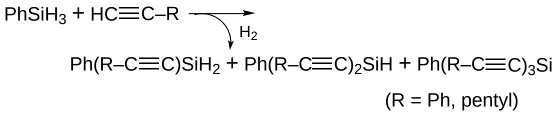
Introduction

The hydrosilylation of alkenes and alkynes with $HSiCl_3$ or $MeSiHCl_2$, which are easily obtainable by Rochow's direct process, have been investigated extensively using transition metal complexes as catalysts.[1] However, reports concerning such reactions with H_2SiCl_2, Me_2SiH_2, $PhSiH_3$, SiH_4, or Si_2H_6, which have several Si−H bonds in the molecule, are few in number.[2] Pyrolytic reactions and photoreactions have been carried out between SiH_4 or Si_2H_6 and ethylene or acetylene at elevated temperatures in the gas phase with very low product yields.[3] Recently, we and others have selectively obtained some silylated compounds ($RSiH_3$, R_2SiH_2) by the hydrosilylation of alkenes with SiH_4 in the presence of transition metal complexes,[4,5] $NaAlR_4$ (R = alkyl)[6] and $LiAlH_4$,[7] as catalysts.

$$SiH_4 + n\text{-}BuCH{=}CH_2 \rightarrow n\text{-}BuCH_2{-}CH_2SiH_3 + (n\text{-}BuCH_2{-}CH_2)_2SiH_2$$

$$SiH_4 + CH_2{=}CH_2 \rightarrow CH_3CH_2SiH_3$$

There have been few reports on the dehydrogenative coupling reactions of monosubstituted alkynes with hydrosilanes that produce alkynylsilanes. H_2PtCl_6/LiI, I_2,[8] and $IrH_2(SiEt_3)(COD)(AsPh_3)$ formed by adding triarylarsines or triarylphosphines to $[Ir(OMe)(diolefin)]_2$, $[IrH(H_2O)(bp)L_2]SbF_6$, $RhClL_3$ (L = PPh_3, bp = 7,8-benzoquinolinato),[9] have been used as catalysts. In these cases, the dehydrogenative coupling reaction was found to accompany the hydrosilylation reaction, which produced the corresponding alkenylsilanes. Calas et al. obtained alkynylsilane (n-Bu−C≡C−$SiEt_3$) by reaction of 1-hexyne and Et_3SiH using Na or NaH as the catalyst.[10] Liu and Harrod have reported that a CuCl/amine catalyst led to a highly selective dehydrogenative coupling reaction of alkynes with hydrosilanes.[11] We have recently found that a solid base such as MgO catalyzes selective dehydrogenative coupling reactions.[12]



(R = Ph, pentyl)

MgO can be easily separated by filtration from the reaction solution. The catalytic activity of MgO is low,

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Table 1. Reactions of Alkynes with Hydrosilanes

					product yield, %[b]			
run no.	hydrosilane (mmol)	alkyne (mmol)	$\mathrm{LiAlH_4}$ (mmol)	solvent[a]	**1**	**2**	**3**	**4** and **5**
1	$\mathrm{SiH_4}$ (100)	1-hexyne (89)	4.5	none	5	1	2	4
2	$\mathrm{SiH_4}$ (84)	1-hexyne (44)	2.2	diethyl ether	7	trace	0	0
3	$\mathrm{SiH_4}$ (100)	1-hexyne (91)	4.5	THF	24	7	0	0
4	$\mathrm{SiH_4}$ (84)	1-hexyne (46)	2.2	diglyme	20	5	0	0
					6	**7**	**8**	**9** and **10**
5	$\mathrm{PhSiH_3}$ (52)	ethynylbenzene (53)	2.7	diglyme	42	9	1	trace

[a] Twenty milliliters (run no. 2−5) and 10 mL (run no. 6) of the solvent was used in the experiments. [b] The percent ratio of the product versus the charged $\mathrm{SiH_4}$. (**1**, n-$\mathrm{BuC{\equiv}CSiH_3}$; **2**, ($n$-$\mathrm{BuC{\equiv}C)_2SiH_2}$; **3**, n-$\mathrm{BuCH{=}CHSiH_3}$; **4**, (n-$\mathrm{BuCH{=}CH)_2SiH_2}$, **5**, (n-$\mathrm{BuC{\equiv}C)Si(CH{=}CH}$-n-$\mathrm{Bu)H_2}$; **6**, $\mathrm{PhC{\equiv}CSi(Ph)H_2}$; **7**, $\mathrm{(PhC{\equiv}C)_2Si(Ph)H}$; **8**, $\mathrm{PhCH{=}CHSi(Ph)H_2}$; **9**, $\mathrm{PhCH[Si(Ph)H_2]{-}CH_2Si(Ph)H_2}$; **10**, $\mathrm{PhC{\equiv}CSi(Ph)(CH{=}CH{-}Ph)H}$).

so a large amount of MgO is needed to obtain the product in high yield. We have been searching for a more active catalyst for the dehydrogenative coupling reaction. Milder and more selective reactions are desired.

The recent development of polysilicon and amorphous silicon provides $\mathrm{SiH_4}$ as a new raw material in the organosilicon industry. Therefore, any reaction using $\mathrm{SiH_4}$ represents a new route to organosilicon hydrides ($\mathrm{RSiH_3}$, $\mathrm{R_2SiH_2}$, $\mathrm{R_3SiH}$). We report here a new catalyst for the dehydrogenative coupling reactions between monosubstituted alkynes and $\mathrm{SiH_4}$ that produce alkynylsilanes and discuss the reaction mechanism.

Experimental Section

Reaction Procedures. $\mathrm{SiH_4}$ of 99.999% purity was used. 1-Hexyne was dried over molecular sieves (3 Å) and distilled prior to use. A solution of diethyl ether containing $\mathrm{LiAlH_4}$ was refluxed, and the insoluble material was separated from the solution by filtration. The solution was then evaporated under reduced pressure at 70 °C, and white crystals of $\mathrm{LiAlH_4}$ were obtained. Diethyl ether and THF were dried over $\mathrm{LiAlH_4}$, and diglyme was dried over sodium metal. They were also distilled prior to use.

All experiments were performed in a 70 mL autoclave. The desired amount of 1-hexyne, $\mathrm{LiAlH_4}$, and solvent were charged into the autoclave (see Table 1). $\mathrm{SiH_4}$ was then introduced into the autoclave under pressure, and the reaction was carried out for 20 h at 120 °C at a pressure of about 30−40 kg/cm^2 abs. After completion of the reaction, all gases in the autoclave were replaced with nitrogen and passed through a solution of lithium in ethanol. Unreacted $\mathrm{SiH_4}$, which was converted into silicon tetraethoxide in the solution, was analyzed as $\mathrm{(EtO)_4Si}$ by GC. The five kinds of products were obtained (**1**−**5** in Table 1). Major liquid product (**1**) was separated by distillation under reduced pressure and identified on the basis of GC-MS, infrared spectroscopy, and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, as well as comparison with the spectra of authentic compounds prepared by the $\mathrm{LiAlH_4}$ reduction of corresponding organochlorosilane.[13] Other minor products (**2**−**5**) were assigned on the basis of GC-MS. The yields of the liquid products were determined by GC using n-eicosane as the internal standard. i-$\mathrm{Bu_2AlH}$ and $\mathrm{AlCl_3}$ were also used as catalysts.

$\mathrm{PhSiH_3}$ and $\mathrm{Et_3SiH}$ were also reacted instead of $\mathrm{SiH_4}$ for 20 h at 120 °C in a 100 mL glass flask under nitrogen atomosphric pressure. Five kinds of products were obtained by the reaction between $\mathrm{PhSiH_3}$ and ethynylbenzene (**6**−**10** in Table 1). After the reaction, the major liquid products (**6**, **7**) were separated and identified on the bases of GC-MS, infrared spectroscopy, and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Other minor products (**8**−**10**) were assigned on the basis of GC-MS.

Product Characterization. **1**, n-$\mathrm{BuC{\equiv}CSiH_3}$: ^{1}H NMR ($\mathrm{CDCl_3}$/TMS) δ 3.75 (s, 3H, $-\mathrm{Si}H_3$), 2.17 (t, 2H, $J_{\mathrm{cd}} = 7.0$ Hz, $\mathrm{H_3Si{-}C{\equiv}C{-}C}H_2\mathrm{{-}CH_2{-}}$), 1.44 (m, 2H, $J_{\mathrm{ab}} = 7.3$ Hz, $J_{\mathrm{bc}} = 7.3$ Hz, $\mathrm{{-}CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_3}$), 1.35 (m, 2H, $J_{\mathrm{bc}} = 7.3$ Hz, $J_{\mathrm{cd}} = 7.0$ Hz, $\mathrm{{-}CH_2{-}C}H_2\mathrm{{-}CH_3}$), 0.85 (t, 3H, $J_{\mathrm{ab}} = 7.0$ Hz, $\mathrm{{-}CH_2{-}C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3/CDCl_3}$,77 ppm): δ 111.96 (s, $\mathrm{H_3Si{-}C{\equiv}}C{-}$), 71.44 (s, $\mathrm{H_3Si{-}}C\mathrm{{\equiv}C{-}}$), 30.30 (s, $\mathrm{{-}C{\equiv}C{-}}C\mathrm{H_2{-}}$), 21.86 (s, $-C\mathrm{H_2{-}}C\mathrm{H_2{-}CH_3}$), 19.65 (s, $-C\mathrm{H_2{-}CH_3}$), 13.35 (s, $\mathrm{{-}CH_2{-}}C\mathrm{H_3}$). ^{29}Si NMR ($\mathrm{CDCl_3}$/TMS): δ −88.16 (m, $-Si\mathrm{H_3}$). IR (neat): ν(Si−H, C≡C) 2170 cm^{-1}, ν(C−H) 2872, 2933, 2959 cm^{-1}, $\delta(\mathrm{SiH_3})$ 925 cm^{-1}, $\delta(\mathrm{SiH_3})$ 684 cm^{-1}. MS (m/z): (EI-mode) 70 (base peak), 55, 83, 97, 111 (M − H)$^+$; (CI-mode) 113 (M + H)$^+$. These spectral data coincided with those of $\mathrm{H_3Si{-}C{\equiv}C{-}CH_2CH_2CH_2CH_3}$, which was prepared by the $\mathrm{LiAlH_4}$ reduction of $\mathrm{Cl_3Si{-}C{\equiv}C{-}CH_2CH_2CH_2CH_3}$. **2**, ($n$-$\mathrm{BuC{\equiv}C)_2SiH_2}$: MS ($m/z$): (EI-mode) 109 (base peak), 108, 107, 121, 191 (M − H)$^+$, 192 (M)$^+$, 177 (M − $\mathrm{CH_3}$)$^+$. **3**, n-$\mathrm{BuCH{=}CH{-}SiH_3}$: MS ($m/z$): (EI-mode) 72 (base peak), 58, 43, 85, 99 (M − $\mathrm{CH_3}$)$^+$, 114 (M)$^+$, 113 (M − H)$^+$. **4**, (n-$\mathrm{BuCH{=}CH)_2SiH_2}$: MS ($m/z$) (EI-mode) 84 (base peak), 83, 85, 97, 111, 196 (M)$^+$, 195 (M − H)$^+$, 181 (M − $\mathrm{CH_3}$)$^+$. **5**, (n-$\mathrm{BuC{\equiv}C)Si(CH{=}CH}$-$n$-$\mathrm{Bu)H_2]}$: MS ($m/z$) (EI-mode) 83 (base peak), 109, 95, 179 (M − $\mathrm{CH_3}$)$^+$, 193 (M − H)$^+$. **6**, $\mathrm{PhC{\equiv}CSi(Ph)H_2}$: ^{1}H NMR ($\mathrm{CDCl_3/CDCl_3}$, 7.26 ppm) δ 4.85 (s, 2H, $-\mathrm{Si}H_2-$), 7.36−7.84 (m, 10H, Ph−H). ^{13}C NMR ($\mathrm{CDCl_3/CDCl_3}$, 77 ppm): δ 84.9 (s, $\mathrm{Si{-}}C\mathrm{{\equiv}C{-}}$), 109.6 (s, $\mathrm{C{\equiv}}C\mathrm{{-}Ph}$), 122.17 (s, Ph−), 128.10 (s, Ph−), 128.16 (s, Ph−), 128.95 (s, Ph−), 129.02 (s, Ph−), 130.10 (s, Ph−), 131.91 (s, Ph−), 135.07 (s, Ph−). ^{29}Si NMR ($\mathrm{CDCl_3}$/TMS): δ −59.55 (s, $-Si\mathrm{H_2}-$). IR (neat): ν(Si−H,C≡C) 2154 cm^{-1}, ν(C−H) 3068 cm^{-1}, δ(C−H) 743, 796, 845 cm^{-1}. MS (m/z): (EI-mode) 208 ((M)$^+$, base peak), 130, 207 (M − H)$^+$. **7**, $\mathrm{(PhC{\equiv}C)_2Si(Ph)H]}$: ^{1}H NMR ($\mathrm{CDCl_3/CDCl_3}$, 7.26 ppm) δ 5.21 (s, 1H, $-\mathrm{Si}H-$), 7.23−7.92 (m, 15H, Ph−H). ^{13}C NMR ($\mathrm{CDCl_3/CDCl_3}$, 77 ppm): δ 85.7 (s, $\mathrm{Si{-}}C\mathrm{{\equiv}C{-}}$), 108.6 (s, $\mathrm{C{\equiv}}C\mathrm{{-}Ph}$), 122.2 (s, Ph−), 128.4 (s, Ph−), 129.4 (s, Ph−), 130.6 (s, Ph−), 132.3 (s, Ph−), 134.9. ^{29}Si NMR ($\mathrm{CDCl_3}$/TMS): δ −63.62 (s, $-Si\mathrm{H}-$). IR (neat): ν(Si−H,C≡C) 2162 cm^{-1}, ν(C−H) 3055 cm^{-1}, δ(C−H) 757, 811, 846 cm^{-1}. MS (m/z): (EI-mode) 308 ((M)$^+$, base peak), 307 (M − H)$^+$, 230. **8**, $\mathrm{PhCH{=}CHSi(Ph)H_2}$: MS ($m/z$) (EI-mode) 132 (base peak), 210 (M$^+$), 105, 209 (M − H)$^+$. **9**, $\mathrm{PhCH[Si(Ph)H_2]{-}CH_2Si(Ph)H_2]}$: MS ($m/z$) (EI-mode) 162 (base peak), 240, 209, 318 (M$^+$). **10**, $\mathrm{PhC{\equiv}CSi(Ph)(CH{=}CH{-}Ph)H]}$: MS ($m/z$) (EI-mode) 310 ((M$^+$), base peak), 206, 231, 309 (M − H)$^+$.

Results and Discussion

The results are shown in Table 1. The reaction proceeded at 120 °C. Hexynylsilane (**1**) and dihexynylsilane (**2**) were obtained when diethyl ether, THF, or diglyme was used as the solvent. A small amount of the hexenylsilanes (**3**−**5**) was also produced when no solvent was used. The yields of the products indicate

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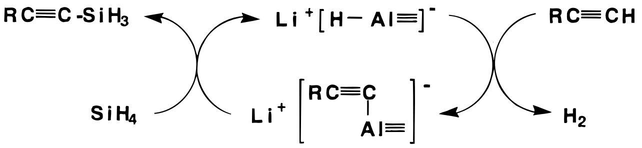
Scheme 1. Mechanism of the Dehydrogenative Coupling Reaction



that the dehydrogenative coupling reactions are selectively catalyzed by $LiAlH_4$.

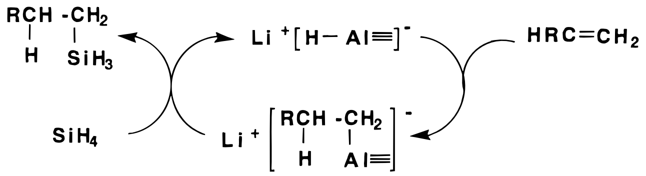
$$\mathrm{SiH_4} + n\text{-BuC}{\equiv}\mathrm{CH} \rightarrow \underset{\mathbf{1}}{n\text{-BuC}{\equiv}\mathrm{CSiH_3}} + \underset{\mathbf{2}}{(n\text{-BuC}{\equiv}\mathrm{C})_2\mathrm{SiH_2}} + \underset{\mathbf{3}}{n\text{-BuC}{=}\mathrm{CHSiH_3}} + \underset{\mathbf{4}}{(n\text{-BuC}{=}\mathrm{CH})_2\mathrm{SiH_2}} + \underset{\mathbf{5}}{(n\text{-BuC}{\equiv}\mathrm{C})\mathrm{SiH_2}(\mathrm{CH}{=}\mathrm{C}\text{-}n\text{-Bu})}$$

It is known that the alkynyl anion is formed by the interaction between $LiAlH_4$ and an alkyne above 110 °C,[13] a reaction accompanied by the generation of hydrogen gas. The dehydrogenation would be caused by the coupling between the hydride of $LiAlH_4$ and the acidic hydrogen of the monosubstituted alkyne. SiH_4 will react with the alkynylaluminate anion to produce the silylated compounds, and $LiAlH_4$ would be regenerated. The proposed mechanism of the dehydrogenative coupling reaction is shown in Scheme 1.

In the case of an alkene, only the hydrosilylation reaction occurred, as has been reported previously (see Scheme 2).[7] The difference in the mechanisms of the two reactions will be determined by the difference in the acidity of the hydrogens of the alkene (HC=C−) and the alkyne (HC≡C−). The solvents diethyl ether, THF, and diglyme, which would support the polarization of hydrogens of an alkyne and Li^+ of $LiAlH_4$, stabilize the intermediate alkynylaluminate anion.

i-Bu_2AlH and $AlCl_3$, which catalyze the hydrosilylation of alkenes with hydrosilanes with a trivalent aluminum compound as an intermediate,[14] showed no catalytic activity. These Lewis acid catalysts would have no interaction with the acidic hydrogen of the alkyne.

Scheme 2. Mechanism of the Hydrosilylation Reaction



$PhSiH_3$, the concentration of which in the reaction solution would be higher than that of SiH_4, also reacted and gave the alkynylated compounds in significant yields. This suggests that the dehydrogenative coupling reactions using $LiAlH_4$ as a catalyst are applicable to other silicon compounds. Et_3SiH did not react. This may be caused by the steric hindrance between the anionic intermediate (four-coordinate aluminate anion) and Et_3SiH.

Alkynylsilanes are usually prepared by the reduction of the corresponding alkynylchlorosilane using an expensive metal hydride.[15] This report offers a new direct route for preparing alkynylsilanes, which have a reactive silyl group ($-SiH_3$) and could be very useful materials.

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