

Alkenylsilane의 제조와 고분자화반응

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Preparation and Polymerization of Alkenylsilanes

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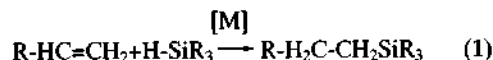
요 약. 실릴트리플레이트($\text{Ph}_{3-n}\text{SiH}(\text{OTf})_n$)는 낮은 온도에서 트리페닐실란과 트리플산($\text{CF}_3\text{SO}_3\text{H}$)의 반응에 의해 형성되며 이러한 화합물은 새로운 기능성 실란 유도체의 제조에 이용되고 있다. 실릴트리플레이트와 알켄일-, 알킨일마그네슘 브롬라이드 그리고 유기리튬 화합물과의 반응에 의해 새로운 실란 화합물 Ph_2SiHR ($\text{R} = \text{C}\equiv\text{CPh}, \text{CH}=\text{CH}_2, \text{CH}_2\text{CH}=\text{CH}_2, (\text{CH}_2)_2\text{CH}=\text{CH}_2, (\text{CH}_2)_3\text{CH}=\text{CH}_2$)을 높은 수율로 얻었다. 합성된 알켄일-, 알킨일실란은 백금촉매 하에서 카보실란 고분자($(\text{Ph}_2\text{SiCH}=\text{CPh})_n, \text{Ph}_2\text{Si}(\text{CH}_2)_m$; $m=2-4, n\geq 10$)와 5~6 환고리 화합물을 형성하였다. 모든 생성물들은 NMR, UV, IR, 질량분석, 그리고 원소분석법에 의해 확인되었다.

ABSTRACT. The silyltriflates $\text{Ph}_{3-n}\text{SiH}(\text{OTf})_n$ have been produced by the reaction of triphenylsilane and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) at low temperature. These highly reactive compounds are a valuable reagent for the synthesis of numerous new functional substituted silane derivatives. The reaction of silyltriflates with alkenyl- and alkyne magnesium bromide as well as organolithium compounds gave new silanes Ph_2SiHR ($\text{R} = \text{C}(\text{CPh}), \text{CH}=\text{CH}_2, \text{CH}_2\text{CH}=\text{CH}_2, (\text{CH}_2)_2\text{CH}=\text{CH}_2, (\text{CH}_2)_3\text{CH}=\text{CH}_2$) in high yields. The hydrosilation of prepared alkenyl- and alkenylsilanes Ph_2SiHR in the presence of a platinum catalyst (Pt/C) at high temperature (200°C) gave carbosilane polymers ($(\text{Ph}_2\text{SiCH}=\text{CPh})_n$ and $(\text{Ph}_2\text{Si}(\text{CH}_2)_m)_n$; $m=2-4, n\geq 10$) along with five- and six-membered silaalkane ring compounds derived from intramolecular hydrosilation reactions. All of the prepared compounds are confirmed by NMR, UV, IR and mass spectroscopy as well as elemental analysis.

INTRODUCTION

In recent years, much attentions have been directed to silicon containing polymers which have regularly alternating arrangements of silicon atoms in polymer backbone.¹ Such carbosilane polymers are obtained from various silicon containing novel materials. It is well known that the Wurtz type reaction of halosilane offers various silicon containing polymers.² However, the preparation of organosilicon polymers by this method that could contain small amount of siloxane units in the polymer backbones has limitation. Therefore, new synthetic routes to organosilicon polymers have been developed without using alkali metal halides.³ The reactions are most conveniently carried out in

the presence of a transition metal catalyst. The addition of hydrosilane to multiple bonds, called to hydrosilation, is a well-known process in organosilicon chemistry.⁴



The effective transition metal catalysts include the electron-rich metals Ru(0), Rh(I), Rh(III), Rh(V), Pt(II), and Pt(VI).^{3,4} As can be seen from the literature, several of the catalysts are also effective in the hydrosilation of olefins.⁵

The development of organosilicon chemistry requires new methods of synthesis not only for the generation of specific compounds but also for the

ability to manipulate functional groups on the compounds without the disturbance of other groups. Therefore, the highly reactive silyltriflates ($R_{4-n}Si(OTf)_n$; $OTf=OSO_2CF_3$) are valuable reagents for our purpose. The general preparation method of many silyltriflates is the following sequence:



The silyltriflates were prepared by phenylsilane with 1–4 equiv. triflic acid in nonpolar media such as pentane and toluene at $-78^\circ C$. These general preparative methods allow the synthesis of a large number of variously structured silyltriflates.^{6,7} The preparation and some chemical reactions of new organogermanium compounds with one or two triflate groups⁸ and a simple synthetic application to dendrimeric carbosilanes by the use of silyltriflates are known.⁹ We are interested in the preparation of carbosilane polymers from alkenylsilane by the use of unimolecular rearrangement. Therefore, the formation of monomeric alkenylsilane was prepared by the use of silyltriflates.

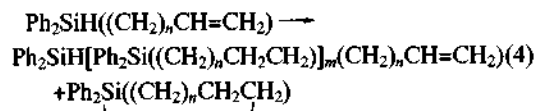
If it is possible to remove the phenyl groups in the Ph_3SiH with triflic acid, then the triflates that would be formed $Ph_{3-n}SiH(OTf)_n$ ($n=1\sim 3$).^{6i,9} It could provide an entry into a variety of oligomers with new substitution patterns. It was this goal in mind that a study of the reactions of the triphenylsilane with 1 equiv. of triflic acid was initiated. In previous studies by Uhlig, competitive cleavages of Si-Ph bonds were observed and formed various substituents.⁶ The silyltriflate $Ph_{3-n}SiH(OTf)_n$ ($OTf=OSO_2CF_3$) was prepared by the substitution of phenyl groups of corresponding silane for the trifluoromethane sulfonate (triflate) group.

The alkenylsilanes with variable substituents were synthesized by the reaction of prepared silyltriflate and corresponding Grignard reagents as well as lithium organyls, which were produced with high regioselectivity. And these groups could be quantitatively replaced by other nucleophilic reagents with short reaction time at low temperature.^{6,9}



The preparation of carbosilane polymers and un-

imolecular rearrangement reactions through catalytic hydrosilation of the given compounds (1–6) was made. It was polymerized by the catalytic thermal decomposition reaction of alkenyl- and alkenylsilanes at $200^\circ C$, albeit only 1-butenyl and 1-pentenylsilane (5 and 6). In this condition, 1-butenylsilane (5) produced five-membered ring (60%) and polymers (40%), while 1-pentenylsilane (6) produced only sixmembered ring (100%):



In this paper, we wish to report (a) the convenient synthetic way of silyltriflates, (b) its alkenylations and (c) the polymerization and rearrangement of prepared compounds using the hydrosilation catalyst.

EXPERIMENTAL

All preparations and transformations were carried out in dried conditions under nitrogen atmosphere. 1H and ^{13}C NMR spectra were measured by a Bruker AC 200 Spectrometer. FT-IR spectra were recorded by an IFS 55-Spectrophotometer (Bruker) and HPLC results were obtained by a Delta Prep 4000 (Waters). The mass spectra were obtained on a HP 5280 Spectrometer (Hewlett Packard) by ionization at 70 eV. Elemental analysis was carried out by the Seoul Branch of the Korean Basic Science Institute. SEC measurement were carried out by Dongju Company (Pusan). Triphenylsilane and trifluoromethanesulfonic acid (TfOH) were commercially available. Platinum (Pt/C; Pt on carbon, 10% Pt content) as a heterogeneous catalyst was dried under vacuum at room temperature before use. Alkenylmagnesium bromide and lithium phenylacetylene were prepared from the corresponding literature methods.¹⁰

$Ph_2SiH(C\equiv CPh)$ (1). Trifluoromethane sulfonic acid (0.75 mL, 8.48 mmol) was added dropwise to triphenylsilane (2.21 g, 8.48 mmol) in 50 mL toluene at $-78^\circ C$. The reaction mixture was stirred for 1 h at $-78^\circ C$ and for an additional 2 h

at room temperature. After the addition of 1.1 equiv. of the sodium acetylide to the reaction mixture was finished, it was stirred for 1 h at room temperature and for an additional 3 h refluxed. The removal of the solvent gave a yellow solid which was filtered with pentane. The pentane was removed from the resultant to give a yellow solid (2.40 g). The recrystallization from pentane and Et₂O (10:2) gave a yellow solid (mp 52 °C, 1.90 g, 67%). ¹H NMR (ppm, CDCl₃); δ=5.31 (s, 1H, SiH), 7.26~7.76 (m, 15H, 3Ph). ¹³C NMR (ppm, CDCl₃); δ=87.57 (SiC≡), 109.56 (≡CPh), 128.16, 128.36 (C-o), 129.15, 130.14 (C-m), 132.22, 135.27 (C-p). Mass spectrum (70 eV); m/z (ion, rel. int.%) =284 (M⁺, 100%), 283 ((M-H)⁺, 38%), 207 ((M-Ph)⁺, 56%), 206 ((M-PhH)⁺, 92%), 129 ((M-2PhH)⁺, 49%). Anal. Calcd. for C₂₀H₁₆Si: C, 84.46; H, 5.67. Found: C, 83.57; H, 5.41.

Ph₂SiH(CH=CH₂) (2). Trifluoromethane sulfonic acid (2.07 mL, 23.5 mmol) was added dropwise to triphenylsilane (6.12 g, 23.5 mmol) in 50 mL toluene at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and for an additional 2 h at room temperature. The THF in vinylmagnesium bromide (25 mmol) was evaporated by vacuum at another flask and 25 mL toluene was added. To vinylmagnesium bromide dissolved in toluene was added dropwise the resulting triflate solution. The reaction mixture was stirred overnight at room temperature. The toluene was removed from the reaction mixture which was filtered with pentane. The pentane was removed from the resultant to give a colorless liquid (3.10 g). The residue was distilled at 60 °C/10⁻¹ torr. The product 2 was obtained as a clear, colorless liquid with 1.67 g (7.59 mmol, 33%). ¹H NMR (ppm, CDCl₃); δ=5.19 (d, 1H, SiH, J=2.9 Hz), 5.91~6.03 (m, 2H, =CH₂), 6.27~6.45 (m, 1H, CH=), 7.38~7.69 (m, 10H, 2Ph). ¹³C NMR (ppm, CDCl₃); δ=128.02 (C-o), 129.72 (C-p), 132.67 (=CH₂), 133.31 (C_{quart}), 135.45 (C-m), 136.98 (CH=). Mass spectrum (70 eV); m/z (ion, rel. int.%)=210 (M⁺, 28%), 182 ((M-CH₂CH₂)⁺, 45%), 132 ((M-PhH)⁺, 100%), 107 ((PhSiH)⁺, 15%), 105 ((M-Ph, CH₂CH₂)⁺, 62%), 53 ((M-2Ph)⁺, 20%). Anal. Calcd. for C₁₄H₁₄Si: C, 79.94; H, 6.71.

Found: C, 78.06; H, 7.16.

Ph₂SiH(CH₂CH=CH₂) (3). Trifluoromethane sulfonic acid (1.35 mL, 15.32 mmol) was added to triphenylsilane (3.99 g, 15.32 mmol) in 50 mL toluene at -78 °C. The reaction mixture was stirred for 2 h at -78 °C and for an additional 2 h at room temperature. The Et₂O in allylmagnesium bromide (20 mmol) was evaporated by vacuum at another reaction flask and 25 mL toluene was added. To allylmagnesium bromide was added dropwise the resulting triflate solution. The reaction mixture was stirred overnight at room temperature and refluxed for an additional 1/2 h. The toluene was removed from the reaction mixture which was filtered with pentane. The pentane was removed from the resultant to give a colorless liquid (3.3 g). The residue was distilled at 80 °C/10⁻¹ torr. The product 3 was obtained as a clear colorless liquid with 2.47 g (11.00 mmol, 72%). ¹H NMR (ppm, CDCl₃); δ=2.25~2.31 (dd, 2H, CH₂), 5.03~5.81 (m, 2H, CH₂=), 5.14 (t, 1H, SiH, J=1.0 Hz), 5.88~6.10 (m, 1H, CH=), 7.47~7.73 (m, 10H, 2Ph). ¹³C NMR (ppm, CDCl₃); δ=19.82 (CH₂), 114.80 (CH₂=), 133.65 (CH=), 128.0 (C-o), 129.68 (C-p), 135.20 (C-m), 135.64 (C_{quart}). Mass spectrum (70 eV); m/z (ion, rel. int.%)=224 (M⁺, 74%), 183 ((M-CH₂-CHCH₂)⁺, 100%), 105 ((M-PhH, CH₂CHCH₂)⁺, 80%), 78 ((PhH)⁺, 71%). Anal. Calcd. for C₁₅H₁₆Si: C, 80.30; H, 7.19. Found: C, 81.50; H, 7.08.

Me₂SiH(CH₂CH=CH₂) (3a). The allylmagnesium bromide (50 mmol in Et₂O) was slowly added to 4.57 g (48.29 mmol) of Me₂SiHCl dissolved in 50 mL ether. The reaction mixture was stirred overnight at room temperature and refluxed for an additional 1 h. The etheral solution was carefully removed from the reaction mixture by reduced pressure, and the mixture was filtered with pentane. The pentane was removed from the resultant to give a colorless liquid. The residue was distilled at 30 °C/200 torr. The product 3a was obtained as clear colorless liquid with 3.13 g (30.33 mmol, 63%). ¹H NMR (ppm, CDCl₃); δ=0.02 (d, 6H, Me₂-Si, J=2.0 Hz), 1.57~1.64 (dd, 2H, CH₂), 3.98 (t, 1H, SiH, J=3.7 Hz), 4.99~5.09 (m, 2H, CH₂=), 5.84~6.21 (m, H, CH=). ¹³C NMR (ppm, CDCl₃); δ=

- 5.11 (Me₂Si), 21.73 (CH₂), 113.11 (CH₂=), 134.59 (CH=).

Ph₂SiH(CH₂CH₂CH=CH₂) (4). Trifluoromethane sulfonic acid (1.35 mL, 15.32 mmol) was added to triphenylsilane (3.99 g, 15.32 mmol) in 50 mL toluene at -78°C. The reaction mixture was stirred for 2 h at -78°C and for an additional 2 h at room temperature. The 1-butenylmagnesium bromide (20 mmol in Et₂O) was dried by vacuum at another reaction flask and 25 mL toluene was added. To 1-butenylmagnesium bromide was added dropwise the resulting triflate solution. The reaction mixture was stirred overnight at room temperature and refluxed for an additional 1/2 h. The toluene was removed from the reaction mixture which was filtered with pentane. The pentane was removed from the resultant to give a colorless liquid (3.5 g). The residue was distilled at 80°C/10⁻¹ torr. The product 4 was obtained as a clear colorless liquid with 2.47 g (10.99 mmol, 72%). ¹H NMR (ppm, CDCl₃); δ=1.26-1.36 (m, 2H, SiCH₂), 2.23-2.28 (m, 2H, CH₂), 4.95 (t, 1H, SiH, *J*=5 Hz), 5.00-5.10 (m, 2H, CH₂=), 5.79-6.08 (m, 1H, CH=), 7.40-7.65 (m, 10H, 2Ph). ¹³C NMR (ppm, CDCl₃); δ=11.34 (SiCH₂), 28.36 (CH₂), 113.39 (CH₂=), 127.99 (C-*o*), 129.57 (C-*m*), 134.21 (CH=), 135.15 (C-*p*), 140.60 (C-*quart*). Mass spectrum (70 eV); *m/z* (rel. int.%)=238 (M⁺, 4%), 196 (M-CH₂CHCH₂)⁺, 14%, 183 ((M-CH₂CH₂CHCH₂)⁺, 100%), 160 ((M-Ph)⁺, 25%). Anal. Calcd. for C₁₆H₁₈Si: C, 80.61; H, 7.61. Found: C, 80.70; H, 7.62.

Ph₂SiH(CH₂CH₂CH₂CH=CH₂) (5). Trifluoromethane sulfonic acid (1.35 mL, 15.32 mmol) was added to triphenylsilane (3.99 g, 15.32 mmol) in 50 mL toluene at -78°C. The reaction mixture was stirred for 2 h at -78°C and for an additional 2 h at room temperature. The 1-pentenylmagnesium bromide (20 mmol in Et₂O) was dried by vacuum at another reaction flask and give 25 mL toluene. To 1-pentenylmagnesium bromide was added dropwise the resulting triflate solution. The reaction mixture was stirred overnight at room temperature and refluxed for an additional 1/2 h. The toluene was removed from the reaction mixture which was filtered with pentane. The pentane was removed

from the resultant to give a colorless liquid (3.5 g). The residue was distilled by 100°C/10⁻¹ torr. The product 5 was obtained as a clear colorless liquid with 2.40 g (9.52 mmol, 62%). ¹H NMR (ppm, CDCl₃); δ=1.27-1.33 (m, 2H, SiCH₂), 1.64-1.72 (m, 2H, CH₂), 2.21-2.34 (m, 2H, CH₂C=), 5.00 (t, 1H, SiH, *J*=5 Hz), 5.04-5.15 (m, 2H, CH₂=), 5.78-5.99 (m, 1H, CH=), 7.43-7.70 (m, 10H, 2Ph). ¹³C NMR (ppm, CDCl₃); δ=11.66 (SiCH₂), 23.81 (CH₂), 37.05 (CH₂C=), 114.85 (CH=), 127.94 (C-*o*), 129.49 (C-*m*), 134.46 (CH₂=), 135.11 (C-*p*), 138.41 (C-*quart*). Mass spectrum (70 eV); *m/z* (rel. int.%)=252 (M⁺, 2%), 183 ((M-CH₂CH₂CH₂CHCH₂)⁺, 100%), 175 ((M-Ph)⁺, 6%), 174 ((M-PhH)⁺, 30%), 105 ((PhSi)⁺, 44%). Anal. Calcd. for C₁₅H₁₆Si: C, 80.89; H, 7.99. Found: C, 81.38; H, 8.37.

Ph₂Si(CH₂CH=CH₂)₂ (13). The allylmagnesium bromide (50 mmol in Et₂O) was slowly added to 5.35 g (21.13 mmol) of Ph₂SiCl₂ dissolved in 50 mL ether. The reaction mixture was stirred overnight at room temperature and refluxed for an additional 1 h. The ethereal solution was removed from the reaction mixture by reduced pressure, and the mixture was filtered with pentane. The pentane was removed from the resultant to give a colorless liquid (5.10 g). The residue was distilled by 80°C/10⁻¹ torr. The product 13 was obtained as a clear colorless liquid with 3.27 g (12.39 mmol, 59%). ¹H NMR (ppm, CDCl₃); δ=2.22 (d, 4H, SiCH₂, *J*=8.0 Hz), 4.97-5.09 (m, 4H, CH₂=), 5.82-6.04 (m, 2H, CH=), 7.44-7.65 (m, 10H, 2Ph). ¹³C NMR (ppm, CDCl₃); δ=20.02 (SiCH₂), 114.71 (CH₂=), 127.77 (C-*o*), 129.43 (CH=), 134.97 (C-*m*), 133.67 (C-*p*), 134.02 (C-*quart*). Mass spectrum (70 eV); *m/z* (rel. int.%)=264 (M⁺, 2%), 223 ((M-CH₂CHCH₂)⁺, 100%), 105 (M-Ph, 2 CH₂CHCH₂)⁺, 40%). Anal. Calcd. for C₁₅H₁₆Si: C, 81.76; H, 7.62. Found: C, 81.97; H, 7.33.

Polymerization of 1. A thick-walled glass ampoule was charged with 0.36 g (1.11 mmol) of 1, 5 mL of toluene and 0.03 g of a platinum catalyst (Pt/C). The ampoule was cooled in a liquid nitrogen and sealed under vacuum. The sealed ampoule was heated in an oven at 200°C for 48 h. Subsequently, the ampoule was cooled and open.

The reaction mixture was dissolved in toluene and filtered through a glass filter (No 4). The volatiles were removed from the yellow solution under reduced pressure, leaving a pale yellow glass type polymer **6** (0.25 g, 72%). ^1H NMR (ppm, CDCl_3); $\delta=0.22$ (s, 1H, CH=), 7.01~8.20 (m, Ph). ^{13}C NMR (ppm, CDCl_3); $\delta=128.00$ ~ 132.21 (m, aliphatic C), 134.95~ 138.25 (m, aromatic C). IR (KBr neat, $\nu_{\text{C=C}}$) 1592 cm^{-1} and vibrational frequency of trace of triple bond with low intensity are observed in 2150 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). Anal. Calcd. for $(\text{C}_{20}\text{H}_{16}\text{Si})_n$: C, 84.46; H, 5.67. Found: C, 82.36; H, 6.48.

Polymerization of 2. The same procedure in the polymerization of **1** was used in the reaction of 1.50 g (6.68 mmol) of **2**, toluene (10 mL) and small amount of a platinum catalyst (Pt/C). The same workup procedure yield a pale yellow gel type polymer (1.12 g, 75%). ^1H NMR (ppm, CDCl_3); $\delta=0.59$ ~ 1.61 (m, CH_2), 7.26~ 7.56 (m, Ph). ^{13}C NMR (ppm, CDCl_3); $\delta=5.42$ (CH_2), 127.97 (C-o), 129.58 (C-m), 134.15 (C_{quart}), 135.18 (C-p). Anal. Calcd. for $(\text{C}_{14}\text{H}_{14}\text{Si})_n$: C, 79.94; H, 6.71. Found: C, 79.43; H, 7.10.

Polymerization of 3. The same procedure in the polymerization of **1** was used in the reaction of 1.50 g (6.68 mmol) of **3**, toluene (10 mL) and small amount of a platinum catalyst (Pt/C). The same workup procedure yielded a pale yellow gel type polymer **8** (1.12 g, 75%). ^1H NMR (ppm, CDCl_3); $\delta=0.62$ ~ 1.38 (m, SiCH_2), 1.40~ 1.75 (m, CH_2), 7.09~ 7.70 (m, Ph). ^{13}C NMR (ppm, CDCl_3); $\delta=17.14$ (SiCH_2), 20.84 (CH_2), 113.46 (C_{quart}), 127.65 (C-o), 128.92 (C-p), 134.52 (C-m). Anal. Calcd for $(\text{C}_{15}\text{H}_{16}\text{Si})_n$: C, 80.30; H, 7.19. Found: C, 79.46; H, 7.15. Weight average molecular weights (M_w) in the range of 1700~3700 and polydispersity of 2.33, relative to polystyrene standards, were found by exclusion chromatography. They correspond to polymerization degree (n) of 7~15.

Polymerization of 3a. A mixture of 1.50 g (6.68 mmol) of **3a**, and 0.02 g of a platinum catalyst (Pt/C) in ether (25 mL) was stirred for 24 h at room temperature. When the reaction was completed by NMR, the platinum catalyst was re-

moved by filtration. Yield: 1.12 g (75%). After the chromatographic attachment of resulting product **8a**, it was observed only one product by ^1H NMR. ^1H NMR (ppm, CDCl_3); $\delta=0.01$ (s, SiMe_2), 0.03 (s, end chain Si chain SiMe_2), -3.24 (SiMe_2), 19.55 (CH_2), 20.14 ($\text{Si-CH}^{13}\text{C}$). The ratio of intergrated area of 0.01 and 0.03 ppm was about 10 to 1. They correspond to polymerization degree of $n \approx 10$.

Polymerization and Intramolecular Hydrosilation of 4. The same procedure was used in the reaction of 2.79 g (11.72 mmol) of **4**, toluene (10 mL) and 0.03 g of platinum catalyst (Pt/C). The same workup procedure yielded a pale yellow gel type mixed products. Total yield: 2.43 g (10.21 mmol, 87%). By the ratio of integration of methylene groups for compounds **9** and **10** by NMR spectrum showed ca 2 to 3. The volatiles were distilled by $70\text{ }^\circ\text{C}/10^{-1}$ torr from the pale yellow products under reduced pressure, leaving 0.9 g (40%) of **9** as a glass type polymer. Compound **10** was detected by ^1H NMR. And GC-mass spectrum of **10** showed only one signal at molecular mass ($m/z = 238$). **10**: ^1H NMR (ppm, CDCl_3); $\delta=1.08$ ~ 1.32 (m, SiCH_2), 1.82~ 2.05 (m, CH_2), 7.40~ 7.75 (m, Ph). ^{13}C NMR (ppm, CDCl_3); $\delta=12.15$ (SiCH_2), 27.71 (CH_2), 127.85 (C-o), 129.12 (C-m), 134.76 (C-p), 136.93 (C_{quart}). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{Si}$: C, 80.61; H, 7.61. Found: C, 79.98; H, 7.99. Mass spectrum (70 eV); m/z (rel. int.%)=238 (M^+ , 64%), 210 ($(\text{M-CH}_2\text{CH}_2)^+$, 18%), 182 ($(\text{M-(CH}_2)_4^+$, 100%), 160 ($(\text{M-PhH})^+$, 38%), 132 ($(\text{M-PhH, CH}_2\text{CH}_2)^+$, 29%).

9: ^1H NMR (ppm, CDCl_3); $\delta=0.49$ ~ 2.21 (m, CH_2), 7.11~ 7.63 (m, Ph).

Intramolecular hydrosilation of 5. By the use of the same procedure in the polymerization of **3** was used in the reaction of 1.86 g (7.32 mmol) of **5**, toluene (10 mL) and 0.05 g of platinum catalyst (Pt/C). The same workup procedure yielded a pale yellow liquid (1.30 g, 5.15 mmol, 70%). By the distillation of resultants at $75\text{ }^\circ\text{C}/10^{-1}$ torr, the intramolecular hydrosilation product **12** obtained 1.40 g (1.59 mmol, 63%). ^1H NMR (ppm, CDCl_3); $\delta=0.95$ ~ 1.22 (m, SiCH_2), 1.23~ 1.75 (m, CH_2), 2.01~ 2.25 (m, CH_2), 7.38~ 7.75 (m, Ph). ^{13}C NMR (ppm,

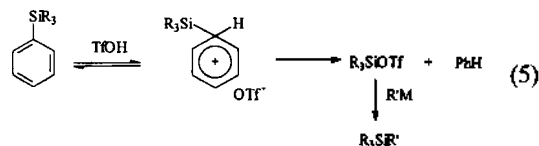
CDCl₃); δ =11.76 (SiCH₂), 20.33 (CH₂), 25.25 (CH₂), 127.66 (C-*o*), 129.13 (C-*m*), 135.40 (C-*p*), 136.82 (C-*quat*). Mass spectrum (70 eV); *m/z* (rel. int.%)= 252 (M⁺, 74%), 175 (M-Ph)⁺, 100%), 147 (M-Ph, CH₂CH₂)⁺, 64%). Anal. Calcd. for C₁₇H₂₀Si: C, 80.89; H, 7.99. Found: C, 80.58; H, 8.01.

Polymerization of 13 with 14. By the use of the same procedure in the polymerization of 3 was used in the reaction of 0.80 g (3.03 mmol) of 13, 0.56 g (3.03 mmol) of 14, toluene (10 mL) and 0.05 g of platinum catalyst (Pt/C). The same work-up procedure yielded a pale yellow gel 1.2 g of 15. ¹H NMR (ppm, CDCl₃); δ =0.70–1.25 (m, SiCH₂), 1.30–1.75 (m, CH₂), 7.35–7.75 (m, Ph). Anal. Calcd. for (C₁₅H₁₆Si)_{*n*}: C, 80.30; H, 7.19. Found: C, 79.25; H, 7.96. Weight average molecular weights in the range *M_w*=1100–1700 and polydispersity is 1.55, relatively to polystyrene standards, were found by exclusion chromatography. They correspond to polymerization degree (*n*) of 5–7.

RESULTS AND DISCUSSION

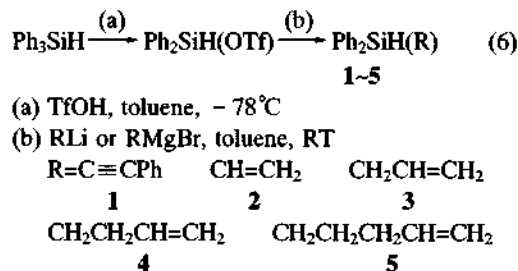
The diphenylsilyltriflate was prepared by triphenylsilane with 1 equiv. triflic acid in toluene. The quantitative formation of diphenylsilyltriflate from triphenylsilane indicates higher reactivity of the first phenyl group than hydrogen or the second and third phenyl groups towards triflic acid. When the reaction of 1 equiv. of triflic acid is used, the resulting products will form only Ph₂SiH(OTf), and by 2 equiv. of triflic acid only PhSiH(OTf)₂⁹ as reported by the reaction with allylmagnesium bromide. These results are the same as those in the previous report by Uhrig.⁶ It is because the triflate group in phenylsilanes leads to strong deactivation of the other phenyl groups at the silicon atom, and because the displacement of the second phenyl group at the same silicon atom is much slower than in the first step.⁶⁽ⁱ⁾ For this reason, in the case of di- or triphenylated oligosilanes, the substitution of triflates is occurred regioselectively. Therefore, if 1 equiv. triflic acid is used, the reaction products will find only the

monosubstituted silyltriflate.



For the preparation of alkenylsilane, Ph₂SiHR (R=C(CPh), (CH₂)_{*n*}CH=CH₂; (*n*=0–3)) was produced by the reaction of diphenylsilyltriflate with corresponding Grignard reagents at low temperature. All the reactions with triflic acid were produced under nonpolar condition. When the reaction of Grignard reagents with silyltriflate was run in a polar medium, the products contained many unknown compounds as minor products, which were informed by ¹H NMR. For example, by the reaction of diphenylsilyltriflate with PhC(CMgBr) (contained trace of THF) the products were 1, diphenylsilane 14, and other many unknown compounds.

In the previous report, the determination of rate constants in the reaction of organic reagents with silylating agent of the type R₃SiX gave the following sequence of the silylating potential: X=Cl < CH₃SO₃ < PhSO₃ < Br < CF₃SO₃ < I.⁹ Therefore, organolithium and organomagnesium compounds react rapidly with silyltriflates at low temperature. The alkenylsilanes 3–5 were prepared in high purity and practically quantitative by ¹H NMR spectroscopic analysis (obtained yields over 70%), albeit only from vinyl diphenylsilane 2, contained as the minor products of diphenylsilane by the reaction of trace of the THF in Grignard reagent with triflic acid. But the major component 2 was obtained from the isolation as volatile material (33%).



The structural characterization of 1–5 was main-

ly based on NMR and mass spectroscopy as well as elemental analysis. The ^1H and ^{13}C NMR spectra are consistent with the proposed structure of alkenylsilane. The NMR spectral data of the given compounds (Ph_2SiHR ($\text{R}=\text{C}(\text{CPh}, (\text{CH}_2)_n\text{CH}=\text{CH}_2$; $n=0\sim 3$)) have four main regions, whose resonance with 4.97~6.45 ppm refers to $\text{CH}=\text{CH}_2$ protons of compounds 2~5, 4.95~5.31 ppm refers to Si-H protons for 1~5, 1.26~2.34 ppm refers to CH_2 protons for 3~5 and 7.26~7.76 ppm refers to all phenyl protons. In all cases, the integration of resonance was employed to further confirm the prepared compounds. More complete information can be gathered by analyzing the ^{13}C NMR spectra of 1~5 (Table 2). Elemental composition and mass spectral data of given compounds had expected value in Table 1.

The polymers were produced by rearrangement of alkenylsilanes in the presence of a platinum catalyst at 200°C in toluene. Compound 6 was readi-

ly prepared by the platinum catalyzed hydrosilation of alkynylsilane 1. IR and ^1H and ^{13}C NMR spectra of polymer 6 clearly indicate the presence of ethenyl groups. ^1H NMR spectrum for 6 shows very weak resonance attributed to the SiH proton at the end point of polymer backbones. By IR, spectroscopic view of 6 was detected at 2150 cm^{-1} of trace of triple bonds of the ethynyl groups in the end groups of polymer backbones with very low intensity, but the new peak at 1590 cm^{-1} for ethenyl groups with strong intensity. For this reason, the compound 1 was converted to polymer 6 with linear structure. The ratio of intensities of signals SiH to vinylic CH in ^1H NMR spectrum was found to be 1 to 15.

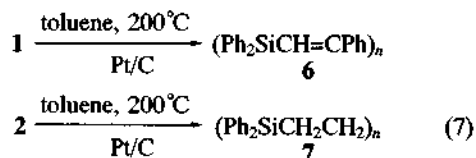


Table 1. Elemental analyses and mass spectroscopic data

Compounds	M_w	Analysis(Found/Calcd.)		MS $m/z(\text{ion}^+$, rel. int.%)
		C	H(%)	
1($\text{C}_{20}\text{H}_{16}\text{Si}$)	284	83.57/84.46	5.41/5.67	284 (M^+ , 100%)
2($\text{C}_{14}\text{H}_{14}\text{Si}$)	210	78.06/79.94	7.16/6.71	210 (M^+ , 28%)
3($\text{C}_{15}\text{H}_{16}\text{Si}$)	224	81.50/80.30	7.08/7.19	224 (M^+ , 74%)
4($\text{C}_{16}\text{H}_{18}\text{Si}$)	238	80.70/80.61	7.62/7.61	238 (M^+ , 4%)
5($\text{C}_{17}\text{H}_{20}\text{Si}$)	252	81.38/80.89	8.37/7.99	252 (M^+ , 2%)
6($\text{C}_{20}\text{H}_{16}\text{Si}$) _n	(284) _n	82.36/84.46	6.48/5.67	
7($\text{C}_{14}\text{H}_{14}\text{Si}$) _n	(210) _n	79.43/79.94	7.10/6.71	
8($\text{C}_{15}\text{H}_{16}\text{Si}$) _n	(224) _n	79.46/80.30	7.15/7.19	
9($\text{C}_{16}\text{H}_{18}\text{Si}$) _n	(238) _n	79.68/80.61	8.06/7.61	
10($\text{C}_{16}\text{H}_{18}\text{Si}$)	238	79.98/80.61	7.99/7.61	238 (M^+ , 64%)
12($\text{C}_{17}\text{H}_{20}\text{Si}$)	252	81.35/80.89	8.01/7.99	252 (M^+ , 74%)
13($\text{C}_{18}\text{H}_{20}\text{Si}$)	264	81.97/81.76	9.33/7.62	264 (M^+ , 2%)
15($\text{C}_{15}\text{H}_{16}\text{Si}$) _n	(224) _n	79.25/80.30	7.96/7.19	

By the same procedure of preparation of 6, polymeric silane 7 was prepared by the platinum catalyzed hydrosilation of 2 at 200°C. ^1H and ^{13}C NMR spectra of polymer 7 clearly indicate the presence of CH_2 groups (multiplet) with very high intensities, but the vinyl groups show very weak resonances between 5.00~6.10 ppm which are attributed to the vinyl proton at the end point of polymer backbones. For this reason, compound 2 was converted to polymer 7 with a linear structure. The ratio of intensities of signals CH_2 (vinylic end groups) to CH_2 (polymer backbones) in ^1H NMR spectrum was found to be 1 to 10. As a similar reaction of the polymerization of 2, the intramolecular hydrosilation of 3 in the presence of a platinum catalyst was observed. ^1H and ^{13}C NMR spectra of polymer 8 clearly indicate the presence of methylene groups in polymer backbone and allylic end groups with a ratio of intensities of signals in ^1H NMR spectrum was found to be 10 to 1. After HPLC attachment of 8, the NMR showed the same results as before. Polydispersity (M_w/M_n) of 8 was found to be 2.3 by the GPC analysis and is consistent with purely linear structure. Weight-

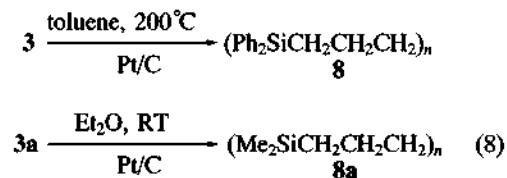
Table 2. NMR spectroscopic data

Comps.		CH ₂	SiH	CH ₂ =	CH=	Ph
1	¹ H	-	5.31(s, ¹ H)			7.26~7.76(m, 15H)
	¹³ C	-				128.16(2Ph- <i>o</i>) 128.36(Ph- <i>o</i>) 129.15(2Ph- <i>m</i>) 130.14(Ph- <i>m</i>) 132.22(2Ph- <i>p</i>) 135.27(Ph- <i>p</i>)
2	¹ H	-	5.19(d, 1H, <i>J</i> =2.9 Hz)	5.91~6.03(m, 2H)	6.27~6.45(m, 1H)	7.38~7.69(m, 10H)
	¹³ C	-		132.67	136.98	128.02(C- <i>o</i>) 129.72(C- <i>p</i>) 133.31(C- <i>quart</i>) 135.45(C- <i>m</i>)
3	¹ H	2.25~2.31(m, 2H)	5.14(t, 1H, <i>J</i> =1.0 Hz)	5.03~5.81(m, 2H)	5.88~6.10(m, 1H)	7.47~7.73(m, 10H)
	¹³ C	19.82		114.80	133.65	128.00(C- <i>o</i>) 129.68(C- <i>p</i>) 135.20(C- <i>m</i>) 135.64(C- <i>quart</i>)
4	¹ H	1.26~1.36 2.23~2.28(m, 2H)	4.95(t, 1H, <i>J</i> =5.0 Hz)	5.00~5.10(m, 2H)	5.79~6.08(m, 1H)	7.40~7.65(m, 10H)
	¹³ C	11.34 28.36		113.49	134.21	127.99(C- <i>o</i>) 129.57(C- <i>m</i>) 135.15(C- <i>p</i>) 140.60(C- <i>quart</i>)
5	¹ H	1.27~1.33 1.64~1.72 2.21~2.34(m, 2H)	5.00(t, 1H, <i>J</i> =5.0 Hz)	5.04~5.15(m, 2H)	5.78~5.99(m, 1H)	7.43~7.70(m, 10H)
	¹³ C	11.66 23.81 37.05		134.46	114.85	127.94(C- <i>o</i>) 129.49(C- <i>m</i>) 135.11(C- <i>p</i>) 138.41(C- <i>quart</i>)
13	¹ H	2.22(d, 4H, <i>J</i> =8.0 Hz)		4.97~5.09(m, 4H)	5.82~6.04(m, 2H)	7.44~7.65(m, 10H)
	¹³ C	20.02		114.71	129.48	127.77(C- <i>o</i>) 133.67(C- <i>p</i>) 134.02(C- <i>quart</i>) 134.97(C- <i>m</i>)

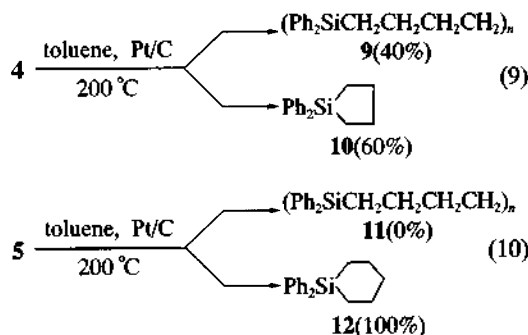
average molecular weights in the range of 1700~3700, relative to polystyrene standards, were found by the size exclusion chromatography. These results can be interpreted that **8** also has a linear structure. They correspond to polymerization degrees of *n*=7~15. But higher value of *M_w* were obtained by using relatively more concentrations and long reaction time.

Platinum catalyzed hydrosilation of **3a** was produced at room temperature in Et₂O. After the chromatographic attachment of resulting product **8a**, it

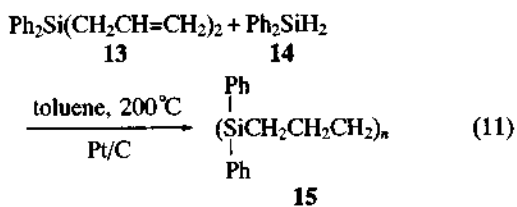
was observed same intergration ratio of before by ¹H NMR. The ratio of intergrated area of methyl groups in polymer backbone and its end chains was about 10 to 1. They correspond to polymerization degree (*n*) of 10.



The intramolecular hydrosilation of alkenylsilane **4** in the presence of a platinum catalyst produced a new carbosilane polymer **9** and a intramolecular hydrosilation product **10**. The formation of compound **10** announced the 1,5-unimolecular rearrangement of **4**. As the same reaction of this, the pyrolysis of **5** in the presence of a platinum catalyst produced only the product **12** by the 1,6-unimolecular rearrangement. In this condition, 1-buthenylsilane (**4**) produced five-membered ring (60%) and polymer (40%), while 1-pentenylsilane (**5**) produced only six-membered ring (100%).



The polymers are light yellow-brown solids and/or highly viscous fluids. All polymers are soluble in the usual organic solvents, such as benzene, toluene, chloroform and THF.



Next, we examined the reaction of $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$ **13** with Ph_2SiH_2 **14** by using the Pt catalyst in the hope of obtaining polymers that have the alternating arrangement of a carbosilane unit with four and five carbons between silicon atom. Thus, the reaction of **13** and Ph_2SiH_2 in the presence of Pt/C in the toluene at 200°C for 24 h gave a polymer **15** whose molecular weight was determined by SEC ($M_n/M_w=1.5$, $M_w=1100-1500$, polymerization degree of $n \approx 5$). Further work will be directed to investigate the physical properties (e.g.,

thermal behavior, conductivities) of the prepared polymers.

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