Articles

Synthesis and Characterization of A Carbosilane Dendrimer Containing Allylic End Groups

Chungkyun Kim*, Eunmi Park, and Eunju Kang

Department of Chemistry, Dong-A University, Pusan 604-714, Korea

Received October 10, 1995

A silane dendrimer with 48 allylic end groups has been synthesized in excellent yield, *via* repetitive alkenylation-hydrosilation cycles. Starting with hexaallylethylenedisilane ($((CH_2=CHCH_2)_3SiCH_2)_2$ as the core molecule (**G0**), a succession of alternate platinum catalyzed hydrosilation (Pt/C, 10% platinum content on active carbon) of all allyl groups with methyldichlorosilane and the allylation of all $SiCl_2$ groups with allylmagnesium bromide in THF provided 3rd generation (**G3**) as carbosilane dendrimer. All the generations of dendrimer have been characterized by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis.

Introduction

Much interest has been developed in a group of macromolecules known as dendrimers.[1] A literature search shows that the number of publications in this field has increased exponentially over several years.[1g] A very extensive review of the organic dendrimer and related synthesis has appeared.[1a~e] The preparation of the first carbosilane dendrimer introduced by Made *et al.* was performed by repetitive alkenylation and hydrosilation cycles.[2] More recently, Seyferth *et al.* prepared the carbosilane dendrimer with vinyl groups by the reaction of corresponding chlorosilane with vinylmagnesium bromide.[3] Another type of dendrimeric polysilane was prepared and characterized by Lambert and co-workers,[4] whose electronic properties should be as interesting as those of linear polysilane. Masamune and co-workers prepared dendrimeric polysiloxane containing SiH groups,[5] and Sakurai *et al.* prepared polysilane dendrimer.[6]

In this paper, we wish to describe the synthesis of carbosilane dendrimer based on hexaallylethylenedisilane ($N_I=6$) as the core molecule (**G0**) and hydrosilation with methyldichlorosilane (**GnP**) in the presence of platinum catalyst (Pt/C) and allylation with allylmagnesium bromide (**Gn**) as the growth steps. The final product was a carbosilane dendrimer whose periphery contained 48 allylic end groups with a molecular weight of 5634. This model is more branched than previous syntheses[2,3] for the preparation of the vinyl and allyl groups containing organosilane dendrimers.

Experimental

All preparations were carried out in dried solvents under nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. The mass spectra were obtained on a HP 5280 spectrometer by EI ionization at 70 eV. HPLC was performed on a Waters Delta Prep 4000 HPLC equipped with a Bondapark C18, 125A and 25×100 mm catridge column. Elemental analysis was carried out by the Korean Basic Science Center in Seoul. Melting point was measured on a Buchi 510 melting point appratus in sealed glass capillaries.

The following abbreviations are used in those experiments: **Gn** refers to each generation of dendrimeric silane with allylic end groups (n=0-3); **GnP** refers to each generation of dendrimeric silane with dichloromethylsilane on its terminal point (n=0-3); N_I refers to initiator core (in our experiment, initiator core has 6 branching sites ($N_I=6$)) and N_B refers to branching for each new layer ($N_B=2$ in our experiments).

G0P. A mixture of 6.38 g (39.5 mmol) of trichlorovinylsilane, 7.58 g (55.96 mmol) of trichlorosilane and 0.03 g of platinum based on hydrosilation catalyst (Pt on activated carbon, 10% Pt content) was stirred for 24 h at room temperature. When the completed reaction was checked by ^1H NMR spectroscopy, excessive $HSiCl_3$ was removed under vacuum. The catalyst was filtered off in pentane. The pentane was evaporated leaving a residue, which contained only $Cl_3SiCH_2CH_2SiCl_3$ (**G0P**) confirmed by ^1H NMR. The product was sublimated at 80 ℃/ 10^{-1} torr, which obtained 10.80 g (36.34 mmol, 92%) of **G0P** ($Cl_3SiCH_2CH_2SiCl_3$) as white crystals (mp 41 ℃). The **G0P** was very sensitive to moisture. The ^1H and ^{13}C NMR chemical shifts of the **G0P** are given in Table 3.

General procedure for allylation (preparation of Gn). The solution of 9.00 g (30.30 mmol) of **G0P** (Cl_3SiCH_2

Table 1. Analytical Data of Dendrimeric Silanes

Compds.	Formula	Molecular mass*	No of end groups	Analysis (found/calcd., %) C	H
G0	$C_{20}H_{34}Si_2$	330.66	6	72.26/72.65	10.33/10.36
G1	$C_{62}H_{118}Si_8$	1088.30	12	68.17/68.43	10.83/10.93
G2	$C_{146}H_{286}Si_{20}$	2603.59	24	67.13/67.35	10.98/11.07
G3	$C_{314}H_{622}Si_{44}$	5634.15	48	67.69/66.94	10.53/11.13

*: calculated mass

Table 2. NMR Spectroscopic Data of G0-G3 Dendrimeric Silanes

Compds.		MeSi	-CH_2	=CH_2	=CH
G0	^{1}H		0.53 (s, 4H) 1.58, 1.62 (d, 12H J=8 Hz)	4.73-5.02(m, 12H)	5.64-5.91(m, 6H)
	^{13}C		3.29, 19.13	113.55	134.30
G1	^{1}H	−0.01 (s, 18H)	0.35 (s, 4H, G0P) 0.58-0.68 (m, 24H, G0)	4.70-4.90(m, 24H)	5.63-5.87(m, 12H)
			1.23-1.44 (m, 12H, G0)		
			1.53, 1.57 (d, 24H, J=8 Hz, G1)		
	^{13}C	−5.71 (G1)	4.76 (G0P) 17.00, 18.14, 18.37 (G0) 21.50 (G1)	113.10	134.77
G2	^{1}H	−0.06 (s, 18H, G1)	0.35 (s, 4H, G0P) 0.52-0.67 (m, 72H, G1-G0)	4.81-4.90(m, 48H)	5.68-5.90(m, 24H)
		−0.01 (s, 36H, G2)	1.20-1.45 (m, 36H, G1-G0)		
			1.53, 1.57 (d, 48H, J=8 HZ, G2)		
	^{13}C	−5.67 (G2) −4.94 (G1)	4.79 (G0P) 17.18, 18.62, 19.18 (G0)	113.09	134.78
			18.01, 18.29, 18.84 (G1) 21.50 (G2)		
G3	^{1}H	−0.07 (s, 54H, G2-G1)	0.42 (s, 4H, G0P) 0.50-0.67 (m, 168H, G2-G0)	4.72-4.90(m, 96H)	5.66-5.91(m, 48H)
		−0.01 (s, 72H, G3)	1.18-1.43 (m, 84H, G2-G0)		
			1.53, 1.57 (d, 96H, J=8 Hz, G3)		
	^{13}C	−5.66 (G3)	17.16, 18.56, 19.05 (G1)	113.10	134.74
		−4.92 (G2-G1)	17.99, 18.29, 18.81 (G2) 21.49 (G3)		

Table 3. Spectroscopic Data of G0P-G3P Dendrimeric Silanes

Compds.		MeSi	$MeSiCl_2$	CH_2
G0P	^{1}H			1.58 (s, G0P)
	^{13}C			16.29 (G0P)
G1P	^{1}H		0.77 (s, 18H, G1P)	0.43 (s, 4H, G0P)
				0.65-0.76 (m, 12H, G0)
				1.15-1.24 (m, 12H, G0)
				1.43-1.64 (m, 12H, G0)
	^{13}C		5.53	4.28 (G0P)
				15.45, 17.37, 25.89 (G0)
G2P	^{1}H	−0.01 (s, 18H, G1)	0.77 (s, 36H, G2P)	0.38 (s, 4H, G0P)
				0.50-0.68 (m, 36H)
				1.10-1.24 (m, 36H)
				1.41-1.62 (m, 36H)
	^{13}C	−5.06	5.51	4.74 (G0P)
				17.06, 18.57, 18.80 (G0)
				17.34, 17.53, 25.92 (G1)
G3P	^{1}H	−0.06 (s, 18H, G1)	0.77 (s, 72H, G3P)	0.37 (s, 4H, G0P)
		−0.02 (s, 36H, G2)		0.50-0.70 (m, 84H)
				1.18-1.23 (m, 84H)
				1.42-1.63 (m, 84H)
	^{13}C	−5.03 (G2)	5.53	4.76 (G0P)
		−4.93 (G1)		18.51, 18.60, 18.70 (G1-G0)
				17.35, 17.51, 25.93 (G2)

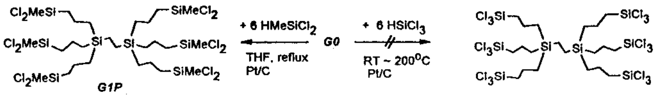
CH_2SiCl_3) in 50 mL Et_2O was added slowly to 200 mL of 1.0 M allylmagnesium bromide (200 mmol). The reaction mixture was refluxed for 6 h (for the synthesis of **G2** and **G3** must be the reaction of the mixture refluxed in THF/Et_2O during overnight). When the completed reaction was checked by ^{1}H NMR spectroscopy, solvents were removed under vacuum. The magnesium salts were precipitated in pentane and filtered off (for the synthesis of **G3**, the reaction mixture was separated by decantation). The organic layer was washed off with distilled water, dried on $MgSO_4$ and concentrated to yield 7.01 g (21.21 mmol, 70%) of $((CH_2CH=CH_2)_3SiCH_2CH_2Si(CH_2CH=CH_2)_3)$ **G0**. The products **G1-G3** were obtained as clear, colorless oil whose viscosity increases with growing generations. The **G3** was purified by preparative HPLC eluting with methanol. ^{1}H and ^{13}C NMR spectroscopic measurements of each generations were shown to be pure dendrimeric silane (Table 2). All the isolated dendrimeric silane of each generation was isolated over 70% yield.

General procedure for hydrosilylation (preparation of GnP). A mixture of 2.60 g (7.80 mmol) of **G0**, 9.40 g (81.70 mmol) of $MeSiHCl_2$ and 0.03 g platinum based on hydrosilation catalyst (Pt on activated carbon, 10% Pt content) was refluxed for 24 h in THF. When the completed reaction was checked by ^1H NMR spectroscopy, excessive $HMeSiCl_2$ and solvent were removed under vacuum. The catalyst was filtered off with pentane or removed by decantation (**G3P**). The pentane was evaporated leaving a residue, which according to NMR contained only $(Cl_2SiMeCH_2CH_2CH_2)_3SiCH_2CH_2Si(CH_2CH_2CH_2SiMeCl_2)_3$ **G1P**. The product, **G1P** of 7.56 g (7.41 mmol, 95%), was obtained as clear, colorless liquid. The ^1H, ^{13}C NMR chemical shifts of the **G1P** are given in Table 3. The product of **G1P-G3P** was obtained as clear, colorless and air-sensitive oil whose viscosity increases with growing generation. All the isolated dendrimeric silane of each **GnP** generations produced almost quantitative yields.

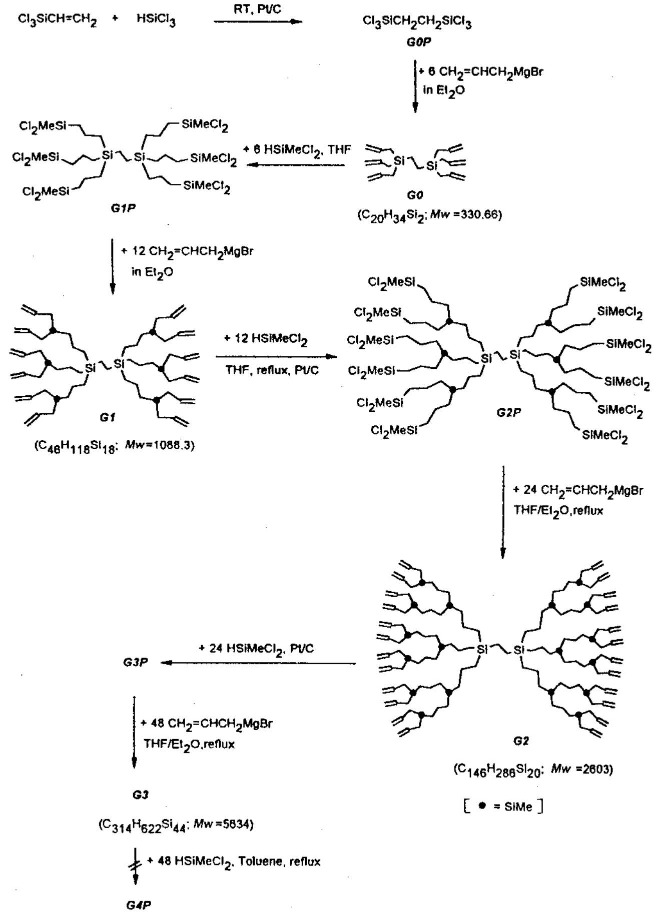
Results and Discussion

The synthesis of our silane dendrimers starts with exhaustive allylation of hexachloroethylenedisilane ($Cl_3SiCH_2CH_2SiCl_3$) with allylmagnesium bromide to produce hexaallylethylenedisilane ($(CH_2CHCH_2)_3SiCH_2)_2$). This six-fold initiator molecule has been attached to six functional core point (N_f), the so called **G0** generation. In the next step, the 6 allyl groups of **G0** are hydrosilated by methyldichlorosilane in the presence of platinum catalyst (Pt/C, 10% content of Pt on activated carbon) for hydrosilation with quantitative yield which is a molecule contained in 12 terminal Si-Cl bonds (Scheme 2). But a reaction of **G0** with trichlorosilane was not completely formed by a molecule containing 6 $SiCl_3$ groups from room temperature and 200 ℃ in toluene. The products observed by ^1H NMR were the half-reacted compounds of **G0** (Scheme 1).

The **G1P** molecule containing 12 growth cores ($N_B=2$) was produced by the reaction of 12 equiv allylmagnesium bromide with a dendrimeric silane having 12 allylic end groups (**G1**) *via* overnight refluxing in THF. The complete reaction of **G1P** to **G1** was confirmed by ^1H NMR spectroscopy. The **G1** generation of silane dendrimer was produced with 12 equiv allylmagnesium bromide in quantitative yield. The **G1** dendrimeric molecule is converted into **G2P** *via* the same hydrosilation process, and **G2P** generation containing 24 Si-Cl bonds was produced *via* alkenylating **G2** containing 24 allylic end groups *via* alkenylation process. By the repetition of the alkenylation and hydrosilation cycle, the third generation could produced to **G3**. The **G3** is purified by HPLC eluting with methanol. All the preparation of each generation dendrimer was made on the basis of the exhaustive yields that can be obtained for the formation of **Gn** from **GnP** and $G_{n+1}P$ from **Gn**. However **G3** with excess of $HSiMeCl_2$ did not completely progress to **G4P** with 48 $SiCl_2$ groups. The major product shown by ^1H NMR was the half-reacted product of previous generation. The reason for this failure is not entirely clear, but possibly due to steric hinderance.



Scheme 1.



Scheme 2. Schematic View of Synthetic Routes for Dendrimeric Silane.

The third generation of our silane dendrimer (**G3**) has 48 allylic end groups. The prepared silane dendrimers (**Gn** and **GnP**) are dramatically provided by the pure substance of NMR spectroscopic views as well as HPLC. By ^{13}C NMR spectroscopic attachments, the growth of molecule through repeated hydrosilation and alkenylation cycle could be demonstrated. The novel carbosilane dendrimers (**Gn**) have been characterized by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The ^1H NMR spectra for **G0-G3** show three main regions: resonances with 4.5-6.0 ppm refers to allylic proton, 0.5-1.5 ppm refer to CH_2 protons, and −0.3-0.0 ppm with single signal refer to MeSi protons. They have also different resonance region between end groups (new generation) and inner core groups (old generation). ^1H NMR spectroscopy allows each different building block to be determined and it also allows subtle structure change for **Gn** and **GnP** type to be clearly detected (Table 2 and 3). For example, a great difference between allylic end group containing generation (**G0-G3**) and hydrosilylated group containing generation (**G1P-G3P**) is also observed by ^1H NMR spectroscopy. In all cases, the intergration of resonance was employed to further confirm the generation number and to ascertain whether the reaction of **Gn** with $HSiMeCl_2$ (or **GnP** with allylmagnesium bromide) reached to completion. More complete information can be gathered from the analysis of the ^{13}C NMR spectra of **Gn** and **GnP** generations. A greater difference betwen **Gn** and **GnP** generator is observed between 25 to −10 ppm. The core groups (old generation) show unique resonance about −5 ppm for MeSi signal and

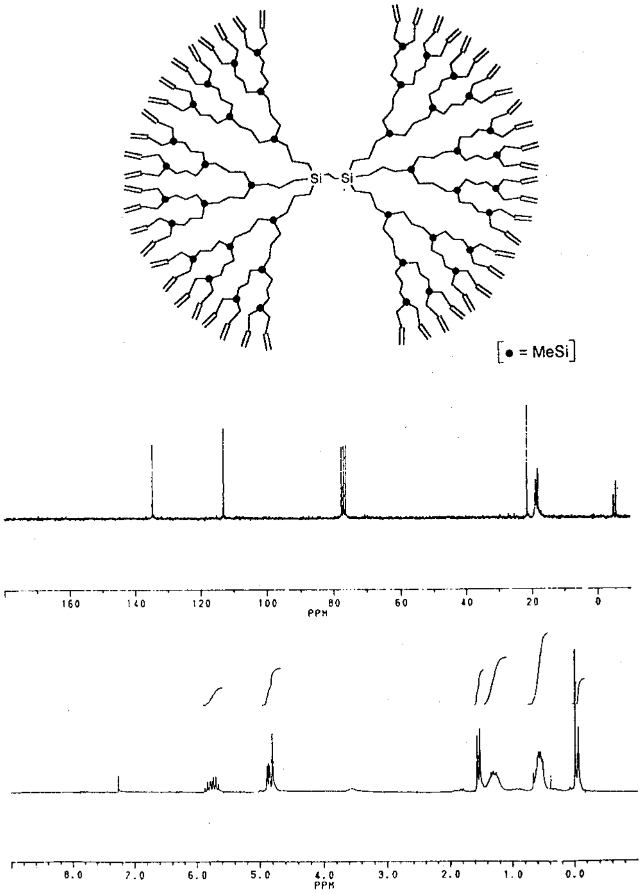


Figure 1. The Schematic View of 3rd Generation of Dendrimeric Silane with 48 Allylic End Groups and its ^{13}C (up) and ^{1}H (down) NMR Spectra.

17-19 ppm for CH_2 signals to assist in controlling the reaction and detecting the exsisting small amounts of impurities which exist in the reaction mixture. Elemental compositon of the dendrimers (**Gn** generation) determined by combustion is very close to the expected value (Table 1).

Acknowledgment. This work was supported by the Korea Sanhak Foundation (1995).

References

1. for reviews, see (a) Tomalia, D. A.; Naylor, A. M.; GoddardIII, W. A. *Angew. Chem.* **1990**, *102*, 119; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem.* **1992**, *104*, 1009; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (c) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichim. Acta* **1992**, *25*, 31. (d) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 192. (e) Tomalia, D. A. *Aldrichim. Acta* **1993**, *26*, 91. (f) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (g) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem.* **1994**, *106*, 2507; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413.
2. (a) Made, A. W.; Leeuwen, P. W. N. M.; Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466. (b) Made, A. W.; Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400.
3. Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682.
4. Lambert, J. B.; Pflung, J. L.; Stern, C. L. *Angew. Chem.* **1995**, *107*, 106; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98.
5. Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7707.
6. Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195.

Reaction of Nitrile Oxides with 3(2*H*)- and 2(5*H*)-Furanones

Hyo Won Lee*, Han-Young Kang, Su-Jin Lee, Ihl-Young Choi Lee†, and Jae Hyun Lee†

**Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea*
†*Korea Research Institute of Chemical Technology, Taejon 305-606, Korea*

Received January 18, 1996

1,3-Dipolar cyclization of various nitrile oxides with 3(2*H*)- and 2(5*H*)-furanones regioselectively furnished the corresponding syn-addition products of 3-oxotetrahydro-furano[4,5-*d*]isoxazolines and 2-oxotetrahydrofurano[3,4-*d*]isoxazolines.

Introduction

Nitrile oxides are reactive 1,3-dipoles, which add to ethylenic and acetylenic dipolarophiles with high regioselectivity to furnish Δ^2-isoxazolines and isoxazoles, respectively. These stereoselectively controlled reaction intermediates serve as useful building blocks that lead to various compounds through chemical modification and ring cleavage. For exam-