The Polymerization of Vinylaminosilanes. The Unique Stability of Silicon–Nitrogen Bonds toward Alkyllithium Compounds

MARILYN R. STOBER, KEITH W. MICHAEL, AND J. L. SPEIER

Organic Research Laboratory, Dow Corning Corporation, Midland, Michigan

Received March 13, 1967

n-Butyllithium has been found to initiate anionic polymerizations of vinyldimethyldimethylaminosilane (I), vinylmethylbisdimethylaminosilane (II), vinyltrisdimethylaminosilane (III), and N-methyl-*sym*-divinyltetramethyldisilazane (IV). Copolymers of these were prepared with styrene, α-methylstyrene, and isoprene. The amino groups attached to silicon were essentially inert toward organolithium reagents. Their presence permitted anionic polymerization of the vinyl groups to form polymers and copolymers that were very reactive toward electrophilic reagents in reactions centered about the silicon atoms.

Cason and Brooks[1] found that phenyllithium or *n*-butyllithium would add to the double bond of vinyltriphenylsilane so as to make 2-phenylethyl- or *n*-hexyltriphenylsilane. Later they extended their discovery[2] to show that a variety of organolithium reagents would add to both vinyltriphenylsilane and vinyltrimethylsilane. The homologous allylsilanes did not react. Vinyltrimethylsilane gave very poor yields of 2-phenylethyl- or *n*-hexyltrimethylsilane. Mostly it formed high-boiling fractions and intractable materials suggesting that polymerization was the chief reaction rather than addition. Polymers made in this way were reported recently.[3] Nametkine, *et al.*, showed that compounds of the formula $R_3SiCH{=}CH_2$ polymerized in the presence of small amounts of ethyllithium in heptane to make high molecular weight polymers with R = Me, Et, Bu, and Ph.

Polymers made in this manner from vinylsilanes were desired with chemically reactive groups attached to the silicon. Even at low temperatures, organolithium reagents undergo metathesis with commonly known electronegatively substituted silanes according to eq 1.

$$SiX + RLi \longrightarrow SiR + LiX \qquad (1)$$

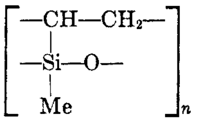
Siloxanes, silicon hydrides, halides, alkoxides, and aryloxides react, destroying the organolithium reagents[4] necessary for polymerizations. A group on silicon satisfactory for our purposes needed to be nearly inert toward organolithium reagents and not cause the vinyl group to lose the unusual property of undergoing this kind of polymerization, but it also needed to be reactive toward other types of reagents. This group was found.

Results

n-Butyllithium proved to be nearly inactive toward dimethylamino groups attached to silicon in the series of compounds $Me_xSi(NMe_2)_{4-x}$, where $x = 1$, 2, or 3. In hexane at room temperature, very little reaction occurred even in 68 hr. In the series, where $x = 1$, 2, or 3, the extent of reaction was <1, 1, and 7%, respectively.

Vinylsilanes of the formula $CH_2{=}CH_2Me_xSi(NMe_2)_{3-x}$, in which $x = 0$, 1, or 2, and $(CH_2{=}CHMe_2Si)_2NMe$ polymerized by reaction with a small amount of *n*-butyllithium with no detectable interference by the silicon–nitrogen bonds. These monomers also formed copolymers with styrene, α-methylstyrene, and isoprene. The speed of polymerization and the ease of copolymerization was clearly a function of x in the above formula. Vinyldimethyldimethylaminosilane (I) was most reactive of the series both alone and in copolymers. No low molecular weight species could be detected even when an equivalent of butyllithium was present. The polymers and copolymers were soluble white solids. Hydrolysis and condensation of these in the presence of acids gave insoluble, infusible solids. Vinylmethylbisdimethylaminosilane (II) formed a precipitate of fine white powder, mp >300°, with *n*-butyllithium. The insolubility of this polymer in the monomer apparently prevented complete polymerization of the monomer by removing the growing polymer–lithium compound from solution. Washing the insoluble powder with methanol removed monomer and lithium from it without removing dimethylamino groups.

Carefully controlled hydrolysis of this polymer in benzene led to a most interesting product. Instead of forming a highly cross-linked structure, a very soluble polymer was obtained with mp >300°. The unusual properties and the analyses of this product suggest that it is a "ladder" polymer of the formula

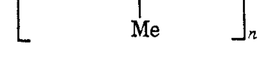


$$\left[\begin{array}{l} -CH-CH_2- \\ \quad | \\ -Si-O- \\ \quad | \\ \quad Me \end{array}\right]_n$$

A copolymer of II with styrene was prepared with more difficulty than was the case for I.

Vinyltrisdimethylaminosilane (III) was the least reactive of the series. It formed low molecular weight polymers slowly with *n*-butyllithium and copolymers in the presence of tetrahydrofuran (THF) and styrene or α-methylstyrene. Hydrolysis and complete condensation of the copolymer with α-methylstyrene gave a white solid which remained soluble in benzene, indicating intramolecular siloxane formation.

N-methyl-*sym*-divinyltetramethyldisilazane $(CH_2{=}CHSiMe_2)_2NMe$ (IV) in dilute solution formed a soluble polymer having a molecular weight of 2600. The solubility of this product and the absence of residual unsaturation in it suggests a structure made up of rings.



---

[1] L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).

[2] L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).

[3] N. S. Nametkine, A. V. Topchiev, and S. G. Dourgarian, *J. Polymer Sci.*, Part C, Polymer Symposia No. 4, 1053 (1963).

[4] (a) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950); (b) H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **72**, 4280 (1950); (c) C. Eaborn, *J. Chem. Soc.*, 2840 (1952); (d) H. Gilman, H. N. Benedict, and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954).

A concentrated solution of IV polymerized to form an insoluble polymer. The soluble polymer had an absorption in the infrared at 880 cm^{-1} which seems to be characteristic of this six-membered disilazane ring. The insoluble polymer had the same absorption along with another at 900 cm^{-1} thought to be characteristic of a linear N-methyldisilazane. In THF, styrene formed a copolymer with IV very smoothly. The product was cross-linked and insoluble and showed the two absorptions at 880 and 900 cm^{-1}. During the preparation of the soluble polymer of IV at room temperature, the polymerization was still continuing after 5 days. During the preparation of a copolymer of (III) with α-methylstyrene, the orange-red color of poly-α-methylstyryllithium[5] persisted in solution for 6 days. Exposure to air destroyed this color within minutes. These examples illustrate that organolithium reagents were present and active during these polymerizations for long periods of time. Had these reagents reacted with the dimethylamino groups on silicon, lithium dimethylamide would have been made. Such a reaction would terminate polymerization unless lithium dimethylamide was capable of initiating the growth. This latter possibility is not the case in these experiments. Lithium dialkylamides did not cause polymerization of any of the monomers used in this work. Furthermore, no exchange of unlike amine groups occurred in the systems illustrated.

$$SiNR_2 + LiNR'_2 \not\rightleftharpoons SiNR'_2 + LiNR_2$$

Discussion

The stability of the silicon–nitrogen bond toward n-butyllithium is increased as the number of amino substituents is increased; thus, in stability, $MeSi(NMe_2)_3 > Me_2Si(NMe_2)_2 > Me_3SiNMe_2$. Although the trend is consistent with known steric effects for organometallic reagents at silicon, steric factors alone cannot account for the nonreactivity of Me_3SiNMe_2.[6]

In the limit, two possible schemes may be postulated for the reaction of an aminosilane with a nucleophile. Equation 2 presents the idea that the silicon is not readily attacked by the nucleophile Y. Equation 3 allows facile attack on the silicon by the nucleophile and energy requirements giving only slow decomposition of the intermediate to products. The scheme represented by eq 3 may be ruled out on the basis of lack of any exchange where the nucleophile was R_2NLi with Me_3SiNR_2' (R = Et and Me, R' = Me and Et). Here the entering and leaving group are nearly equivalent and the reaction profile must be nearly symmetrical. The amino–silicon bond must prevent the nucleophile from entering into bonding interactions with the silicon.

$$Y + \equiv SiN= \xrightarrow{\text{slow}} \text{transition state} \xrightarrow{\text{fast}} \equiv SiY + N\equiv \qquad (2)$$

$$Y + \equiv SiN= \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{intermediate} \xrightarrow{\text{slow}} \equiv SiY + N\equiv \qquad (3)$$

Double-bond character has long been ascribed to bonds of various groups to silicon in order to explain their seemingly anomalous properties. Double-bond character of the silicon–nitrogen bond is referred to in explaining why silylisothiocyanate is linear[7] and trisilylamine is planar.[8] As a consequence of dπ–pπ bonding, electron density at silicon is thought to be increased and nucleophilic attack at silicon is therefore difficult in aminosilanes. This concept was adopted by Wannagat who noted that "the majority of SiN compounds are insensitive to hydrolysis, provided a pH value of 8 is not exceeded."[9] None of these considerations would lead one to predict that organolithium reagents should prove to be nearly unreactive toward the amino–silicon bond.

$$H_3Si\ddot{N}=C=S \longleftrightarrow H_3\overset{-}{Si}=\overset{+}{N}=C=S$$

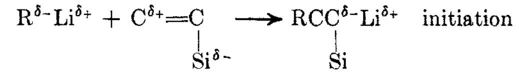
$$H_3Si\ddot{N}(SiH_3)_2 \longleftrightarrow H_3\overset{-}{Si}=\overset{+}{N}(SiH_3)_2$$

The vinyl–silicon bond has been described as containing resonance contributions from dπ–pπ interactions.[10]

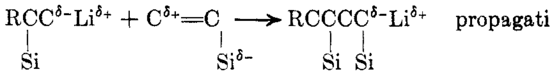
$$SiC=C \longleftrightarrow \overset{-}{Si}=C\overset{+}{C}$$

Resonance of this kind should provide the polarization of the vinyl group necessary for anionic polymerization. The absence of such resonance can then explain the fact that allylsilanes are unaffected by RLi.[2] If the vinyl group competes with amino groups for the d orbitals of silicon, interaction of the vinyl groups with silicon may decrease as the number of amino groups increases. Qualitatively, the ease of polymerization was I > II > III. This trend is also in line with steric effects. The three bulky dimethylamino groups on III could retard the addition of RLi to the vinyl group as well as shield the new organolithium compounds.

Brooks[1] has shown that RLi adds to vinylsilanes so as to produce a secondary lithium compound (eq 4).



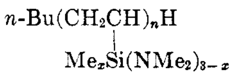
$$R^{\delta-}Li^{\delta+} + C^{\delta+}=\underset{Si^{\delta-}}{\underset{|}{C}} \longrightarrow RC\underset{Si}{\underset{|}{C}}{}^{\delta-}Li^{\delta+} \quad \text{initiation} \qquad (4)$$



$$R\underset{Si}{\underset{|}{C}}C^{\delta-}Li^{\delta+} + C^{\delta+}=\underset{Si^{\delta-}}{\underset{|}{C}} \longrightarrow RC\underset{Si}{\underset{|}{C}}C\underset{Si}{\underset{|}{C}}{}^{\delta-}Li^{\delta+} \quad \text{propagation} \qquad (5)$$

Repetition of the process of eq 5 results in polymerization. The use of an equal amount of n-BuLi with I gave only polymer. The adduct, $\equiv SiHCLiCH_2R$, must then be vastly more reactive than n-BuLi, *i.e.*, eq 5 must be faster than eq 4. The mode of addition seems likely to be that found by Brooks,[1] but was not proved for the above examples.

The structure of the polymers from I, II, and III is likely to be



$$n\text{-}Bu(CH_2\underset{Me_xSi(NMe_2)_{3-x}}{\underset{|}{CH}})_nH$$

where x = 0, 1, and 2. Hydrolysis and condensation of the product obtained from I with styrene led to a

---

(5) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

(6) The incorporation of sufficiently bulky groups on silicon results in a substituted silane, chlorosilane, or ethoxysilane which is not reactive with RLi under mild conditions. See, for example, H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950); J. S. Peake, W. H. Nebergall; and Y. T. Chen, *J. Am. Chem. Soc.*, **74**, 1526 (1952); H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947).

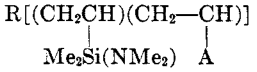
(7) A. G. MacDiarmid and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 411 (1955).

(8) K. Hedberg, *J. Am. Chem. Soc.*, **77**, 6491 (1955).

(9) U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 232 (1964).

(10) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, p 390.

solid no part of which was soluble in refluxing toluene. A copolymer had formed, showing that novel systems are now available of the type



$$R[(CH_2\underset{\displaystyle Me_2Si(NMe_2)}{\underset{|}{C}}H)(CH_2{-}\underset{\displaystyle A}{\underset{|}{C}}H)]$$

where A = any group that activates vinyl groups for homogeneous anionic polymerizations. The aminosilyl groups can be hydrolyzed and condensed to polysiloxanes or converted to other functional groups.[11]

Experimental Section

Instrumental Analyses.—Vapor phase chromatographic (vpc) analyses were obtained on an F & M Model 300 programmed temperature gas chromatograph equipped with a 6-ft-long stainless steel column packed with 25% Dow Corning 200 gum on Chromosorb W. H^1 nmr analyses were obtained with a Varian Associates Model A-60 using 1% tetramethylsilane in carbon tetrachloride. A Perkin-Elmer Model 521 grating spectrometer was used to obtain infrared spectra in carbon tetrachloride or in mineral oil mulls. Melting points and boiling points are uncorrected.

Solvents.—Hexane and pentane (J. T. Baker Chemical Co.) were washed with concentrated sulfuric acid and stored over Linde 4-A Molecular Sieves. Tetrahydrofuran (THF) (J. T. Baker Chemical Co.) was taken from freshly opened bottles. Thiphene-free benzene (Fisher Scientific Co.) was azeotropically dried.

Reagents.—Isoprene (Phillips Petroleum Co.), styrene, and α-methylstyrene (Fisher Scientific Co.) were dried over Linde 4-A Molecular Sieves. Diethylamine (Fisher Scientific Co.), dimethylamine, and methylamine (Matheson Co.), and solutions of *n*-butyllithium and *t*-butyllithium in hydrocarbons (Foote Mineral Co.) were used as purchased.

Organosilicon Compounds.—Trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, vinyltrichlorosilane, vinylmethyldichlorosilane, and vinyldimethylchlorosilane were products of Dow Corning Corp. and were greater than 97% pure by vpc. *n*-Butyltrimethylsilane was prepared as a vpc standard by the action of *n*-butyllithium on trimethylchlorosilane.

Preparation of Aminosilanes.—A chlorosilane in pentane was treated with an amine at 25° or lower and filtered free of amine hydrochloride. The salt was washed with pentane. The combined washings and filtrates were distilled to obtain the following aminosilanes: **trimethyldimethylaminosilane**, 72% yield, n^{25}_{D} 1.3928, bp 85° (lit.[12] n^{20}_{D} 1.3958, bp 85°); **dimethylbisdimethylaminosilane**, 78% yield, n^{25}_{D} 1.4157, bp 127.5° (lit.[13] n^{22}_{D} 1.4169, bp 128°); **methyltrisdimethylaminosilane**, 82% yield, n^{25}_{D} 1.4306, bp 160.5° (lit.[13] n^{22}_{D} 1.4324, bp 161°); **trimethyldiethylaminosilane**, 84% yield, n^{25}_{D} 1.4080, bp 127.5° (lit.[14] n^{20}_{D} 1.4112, bp 128°).

Also obtained were aminosilanes I–IV. **Vinyldimethyldimethylaminosilane** (I) was obtained in 56% yield, n^{25}_{D} 1.4170, bp 107°, d^{25}_{4} 0.773, MR 0.326 (calcd 0.326). The H^1 nmr spectrum consisted of signals with τ values of 9.92 (SiMe), 7.58 (NMe), and 4.7–3.8 ($SiCH{=}CH_2$) in the ratio of 6.1:6.0:3.0.

Anal. Calcd for $C_6H_{15}NSi$: Si, 21.7; neut equiv, 129. Found: Si, 21.2; neut equiv, 132.

Vinylmethylbisdimethylaminosilane (II) was obtained in 77% yield, n^{25}_{D} 1.4337, bp 83° (100 mm), d^{25}_{4} 0.824, MR 0.316 (calcd 0.316). Characteristic infrared absorptions were ν (NCH) 2795, ($SiCH{=}CH_2$) 1590, ($SiCH_3$) 1250, and (SiN) 980 cm^{-1}. The H^1 nmr spectrum consisted of signals with τ values of 9.95 ($SiCH_3$), 7.54 (NCH_3), and 4.7–3.6 ($SiCH{=}CH_2$) in the ratio 3.0:12.0:2.9.

Anal. Calcd for $C_7H_{18}N_2Si$: C, 53.1; H, 11.5; N, 17.7; Si, 17.7. Found: C, 53.0; H, 11.48; N, 17.6; Si, 17.6.

Vinyltrisdimethylaminosilane (III) was obtained in 68% yield, n^{25}_{D} 1.4447, d^{25}_{4} 0.8634, bp 82° (30 mm), MR 0.308 (calcd 0.308). Characteristic infrared absorptions were ν (NCH) 2790, ($SiCH{=}CH_2$) 1585, and (SiN) 97.5 cm^{-1}. The H^1 nmr spectrum consisted of signals with τ values of 7.57 (NCH_3) and 4.6–4.0 ($SiCH{=}CH_2$) in the ratio 18:3.1.

Anal. Calcd for $C_8H_{21}N_3Si$: C, 51.2; H, 11.3; N, 22.4; Si, 14.98. Found: C, 51.0; H, 11.3; N, 22.3; Si, 14.93.

N-Methyl-*sym*-divinyltetramethyldisilazane (IV) was obtained in 65% yield, n^{25}_{D} 1.4490, d^{25}_{4} 0.835, bp 116° (100 mm), MR 0.321 (calcd 0.324). Characteristic absorptions in the infrared were ν (NCH) 3800, ($SiCH{=}CH_2$) 1595, ($SiCH_3$) 1250, and (SiN) 910 cm^{-1}. The H^1 nmr spectrum consisted of signals with τ values of 9.87 ($SiCH_3$), 7.52 (NCH_3), and 4.6–3.5 ($SiCH{=}CH_2$) in the ratio 12.0:3.0:6.1.

Anal. Calcd for $C_9H_{21}NSi_2$: C, 54.2; H, 10.6; N, 7.02; Si, 28.2. Found: C, 54.6; H, 10.7; N, 7.05; Si, 28.7.

Vinyldimethylmethylaminosilane was also obtained in 29% yield, n^{25}_{D} 1.4151, d^{25}_{4} 0.773, bp 95°, MR 0.324 (calcd 0.324). Characteristic infrared absorptions were ν (NH) 3430, (NCH) 2817, ($SiCH{=}CH_2$) 1595, ($SiCH_3$) 1250, and (SiN) 840 cm^{-1}. The H^1 nmr spectrum consisted of signals with τ values of 9.94 ($SiCH_3$), 7.52 (center of doublet, NCH_3), and 4.6–3.5 ($SiCH{=}CH_2$) in the ratio 6.1:3.0:3.0.

Anal. Calcd for $C_5H_{13}NSi$: C, 52.1; H, 11.4; N, 12.1; Si, 24.3. Found: C, 52.0; H, 11.1; N, 11.9; Si, 23.6.

Polymerizations.—Dry bottles were fitted with stoppers through which two glass tubes were placed. One tube was closed with a septum so reagents could be added and samples removed by means of a syringe. The other tube was used to maintain a slight pressure of helium in the system. The contents of each bottle were stirred by a magnetic stirrer or were shaken as the following polymers were prepared.

Polymers of Vinyldimethyldimethylaminosilane (I). Homopolymers.—A 15% solution of *n*-butyllithium in hexane (0.4 ml, 6×10^{-4} mole) was added to I (3.5 g, 0.027 mole). The solution became warm and grew viscous in a short time. After 0.5 hr all volatile material was removed at 1 mm to leave a solid residue, 0.6 g, mp 90–95°, soluble in pentane. Characteristic infrared absorptions were ν (NCH) 2795, ($SiCH_3$) 1249, and (SiN) 988 cm^{-1}. No vinylic absorption was present. The absence of ν (CCH_3) 1375 cm^{-1} indicated that the content of butyl groups in the polymer was low. The H^1 nmr spectrum indicated no vinylic protons and consisted of signals with τ values of 9.92 ($SiCH_3$), 8.87 (broad aliphatic), and 7.60 (NCH_3) in the ratio 6:4:6. This ratio corresponds to one butyl group per ten monomer units.

Anal. Calcd for $Bu(CH_2CHSiMe_2NMe_2)_{10}H$: N, 10.4; Si, 20.8. Found: N, 10.0; Si, 20.8.

An effort was made in the following way to detect any products of this kind in which *n* might be 1 or 2. I (38.8 g, 0.30 mole) was added to *n*-butyllithium (0.30 mole) in hexane (190 ml) during 1.5 hr at room temperature. An exothermic reaction occurred and vpc analysis indicated that all of I had reacted. Trimethylchlorosilane (32.6 g, 0.30 mole) was added. After 0.5 hr, vpc analysis showed that all of the trimethylchlorosilane had reacted; approximately 90% of it had been converted to *n*-butyltrimethylsilane, showing that about 0.27 mole of *n*-butyllithium remained in the solution after the vinylsilane had disappeared. No peaks appeared on the chromatograph that could correspond to $n\text{-}Bu(C_2H_3SiMe_2NMe_2)_{1(\mathrm{or}\ 2)}SiMe_3$. No trimethyldimethylaminosilane was present, indicating that no $LiNMe_2$ had been formed by reaction of *n*-butyllithium with I.

Copolymers. With Styrene.—Styrene (10.4 g, 0.100 mole), I (3.4 g, 0.026 mole) in hexane (30 ml), and THF (1.0 ml) were treated with *n*-butyllithium (0.11×10^{-2} mole). The solution turned orange and increased in viscosity during 3 hr. The bottle was opened to admit air which caused immediate loss of the orange color. Removal of solvents at 50° and 5 mm left a brittle white polymer (13 g, 94% yield) which softened between 88–100° and was soluble in THF or benzene. Characteristic infrared absorptions were ν (NCH) 2792, ($C_{ar}C_{ar}$) 1598, ($C_{ar}C$) 1490, ($SiCH_3$) 1242, and (SiN) 985 cm^{-1}. No vinylic absorption was present.

Anal. Calcd for $[(C_6H_{15}NSi)(C_8H_8)_4]_n$: C, 83.6; H, 8.68; N, 2.56; Si, 5.15. Found: C, 83.3; H, 9.04; N, 2.54; Si, 4.94.

A portion of the polymer in THF was treated with excess dilute hydrochloric acid. Ether and water were added and the organic layer was collected, devolatilized, and dried at 128°. The resulting polymer was extracted with toluene in a Soxhlet extractor for 4 days. No weight loss occurred; the polymer was completely insoluble.

Anal. Calcd for $[(C_4H_9SiO_{1/2})(C_8H_8)_4]_n$: C, 84.7; H, 8.11; Si, 5.50. Found: C, 83.4; H, 8.15; Si, 5.92.

---

[11] For general reactions of aminosilanes, see R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

[12] A. W. Jarvie and A. D. Lewis, *J. Chem. Soc.*, 1073 (1963).

[13] H. H. Anderson, *J. Am. Chem. Soc.*, **74**, 1421 (1952).

[14] R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

With Isoprene.—Isoprene (13.6 g, 0.200 mole) and I (6.5 g, 0.05 mole) in hexane (50 ml) were treated with *n*-butyllithium (0.32×10^{-2} mole) at 25°. After 3 hr most of each monomer remained. THF (2 ml) and *n*-butyllithium (0.32×10^{-2} mole) were added. An exotherm occurred and after a few minutes vpc analysis indicated that both monomers had disappeared. A portion of the solution of polymer was taken up in THF and treated with dilute hydrochloric acid. The organic layer was collected, devolatilized, and dried at 150°, resulting in a soft plastic material which was insoluble in pentane.

Anal. Calcd for $[(C_4H_9SiO_{1/2})(C_5H_8)_{3.4}]_n$: C, 77.5; H, 11.2; Si, 8.62. Found: C, 77.6; H, 11.3; Si, 8.62.

With α-Methylstyrene.—α-Methylstyrene (11.8 g, 0.100 mole) and I (1.3 g, 0.01 mole) in hexane (30 ml) were cooled to −2° and *n*-butyllithium (0.064×10^{-2} mole) was added. No reaction was apparent. THF (6 ml) was added and the solution turned yellow. More *n*-butyllithium was added to a total of (0.22×10^{-2} mole). The solution was bright red and was held at 0° for 3 hr and then allowed to warm slowly to room temperature; it remained red after several hours. By vpc analysis, all of I had disappeared with about 50% of the α-methylstyrene. Lowering the temperature to 0° for 4 hr caused about 70% of the α-methylstyrene to disappear. After exposure to air, which gave an immediate loss of color, volatiles were removed at 80° and 2 mm for 3 hr. A brittle white solid, 8.0 g (61% yield), was obtained which softened at about 95°.

Anal. Calcd for $[(C_6H_{15}NSi)(C_9H_{10})_7]_n$: C, 86.2; H, 8.96; N, 1.5; Si, 2.9. Found: C, 86.4; H, 8.78; N, 1.0; Si, 2.9.

Polymers of Vinylmethylbisdimethylaminosilane (II). Homopolymers.—A 15% solution of *n*-butyllithium in hexane (2.5 ml, 4×10^{-3} mole) was added to II (16.5 g, 0.104 mole). The solution grew warm, rapidly increased in viscosity, and precipitated a solid. After 0.5 hr the mixture was poured into methyl alcohol (200 ml) which caused further precipitation of white solid which was collected by filtration and devolatilized at 25° and 1 mm for 24 hr, leaving a fine, white powder (5.5 g, 33% yield) which did not melt at 300°. The polymer was readily soluble in benzene. Characteristic infrared absorptions were ν (NCH) 2792, ($SiCH_3$) 1247, and (SiN) 985 cm^{-1}. There was no indication of SiOSi, $SiOCH_3$, $SiCH{=}CH_2$, or OH.

Anal. Calcd for $(C_7H_{18}N_2Si)_n$: C, 53.1; H, 11.4; N, 17.7; Si, 17.7. Found: C, 52.8; H, 11.9; N, 17.1; Si, 17.8.

A different procedure involved II (79 g, 0.50 mole), benzene (5 ml), and *n*-butyllithium (0.026 mole). The exothermic reaction was accompanied by the formation of a copious precipitate of polymer. After 4 hr, vpc analysis showed the disappearance of about 50% of II. The mixture was poured into methyl alcohol (700 ml). The solid polymer was collected and devolatilized at 30° and 1 mm, affording a white solid (38 g, 49% yield) which did not melt up to 300°. The polymer was soluble in benzene and had a molecular weight of 1.6×10^3 (cryoscopic in benzene). The infrared spectrum gave characteristic absorptions at ν (NCH) 2790, ($SiCH_3$) 1250, and (SiN) 980 cm^{-1}.

Anal. Calcd for $(C_7H_{18}N_2Si)_n$: C, 53.1; H, 11.4; N, 17.7; Si, 17.7. Found: C, 53.5; H, 12.1; N, 18.0; Si, 18.0.

A portion of this material (22.3 g, 0.141 equiv of II) was dissolved in benzene (400 ml) and treated with acetic acid (36.0 g, 0.60 mole) causing an exotherm. Distilled water (2.6 g, 0.14 mole) was added to the stirred solution after 1 hr. The water was consumed almost immediately causing an exotherm. Ether was added and the material was washed with water. The organic phase was dried over anhydrous potassium carbonate and devolatilized giving a white powder (7.5 g, 62% yield) which was soluble in cold toluene and did not melt up to 300°. The infrared spectrum showed characteristic absorptions at ν (SiOH) 3450, ($SiCH_3$) 1260, and (SiOSi) 960 cm^{-1}.

Anal. Calcd for $(C_7H_{18}O_2Si)_{10}$: C, 42.8; H, 7.40; Si, 29.5; OH, 3.46. Found: C, 41.7; H, 7.81; Si, 29.9; OH, 3.42.

Copolymers with Styrene.—Compound II (7.9 g, 0.05 mole) in hexane (40 ml) and THF (5 ml) was treated with *n*-butyllitbium (0.48×10^{-2} mole). A mild exotherm occurred but only a small amount of II disappeared (vpc). Styrene (21 g, 0.20 mole) was added slowly over 2 hr. Periodic vpc analysis showed no unreacted styrene at any time and a continuously diminishing amount of II. When the styrene had been added, about one-fourth of II remained and the solution was very viscous. Removal of volatiles at 25° and 1 mm left a brittle solid (24.7 g, 86% yield) which softened between 93–105°. The infrared spectrum showed characteristic absorptions at ν (NCH) 2795, ($C_{ar}C_{ar}$) 1599, ($C_{ar}C$) 1490, ($SiCH_3$) 1248, and (SiN) 975 cm^{-1}. There was no indication of $SiCH{=}CH_2$.

Anal. Calcd for $[(C_7H_{18}N_2Si)(C_8H_8)_{4.5}]_n$: C, 82.4; H, 8.6; N, 4.5; Si, 4.5. Found: C, 82.2; H, 9.1; N, 4.2; Si, 4.5.

Polymers of Vinyltrisdimethylaminosilane (III). Homopolymers.—Compound III (18.7 g, 0.10 mole) was added slowly to *n*-butyllithium (0.11 mole) in hexane (70 ml); after 0.5 hr, vpc analysis showed only hexane and III. After 20 hr, 95% of III had disappeared; no volatile compound except hexane was present. The clear solution was cooled to 0° and treated with excess dimethylamine (16 g, 0.36 mole) which caused an exotherm and salt formation. After 0.5 hr excess amine was permitted to escape and lithium dimethylamide was removed from the solution. Vapor phase chromatography analysis showed no volatile product in the organic layer and only a small amount of III. Removal of volatiles at 80° and 1 mm left a viscous liquid (19.7 g). Infrared analysis showed characteristic absorptions at ν (NCH) 2792 and (SiN) 982 cm^{-1}. There was no evidence for $SiCH{=}CH_2$ or SiOSi. A solution of *n*-butyllithium (0.16×10^{-2} mole) in III (10.5 g, 0.0560 mole) at ambient temperature for 20 hr noticeably increased in viscosity. The solution was cooled in Dry Ice and additional *n*-butyllithium (0.16×10^{-2} mole) was added. No further change in viscosity occurred during 1 hr. The solution was poured into methyl alcohol. An oil separated and was collected and devolatilized at 25° and 2 mm to yield a very viscous oil (4.0 g, 38% yield). Characteristic infrared absorptions were ν (NCH) 2790 and (SiN) 988 cm^{-1}. The H^1 nmr spectrum gave signals with τ values of 7.52 (NCH_3) and 8.6 (broad aliphatic) in the ratio of 18:5.5, indicating an average degree of polymerization of four.

Anal. Calcd for *n*-$Bu(C_8H_{21}N_3Si)_4H$: C, 53.6; H, 11.7; N, 20.8; Si, 13.9. Found: C, 53.4; H, 11.7; N, 20.9; Si, 15.0.

Copolymers. With Styrene.—To III (8.63 g, 0.0460 mole), hexane (40 ml), THF (5 ml), and *n*-butyllithium (0.48×10^{-2} mole) was added styrene (8.2 g, 0.079 mole) over a period of 1.5 hr. The solution turned orange. After the addition was completed, vpc analysis showed that only 10–20% of III had reacted while all of the styrene polymerized. The polymer was precipitated with methyl alcohol and devolatilized at 1 mm to give 9.0 g (53% yield) of a white powder which began to soften at 100°. The infrared spectrum was consistent with a polymer containing mostly polystyrene and showing additional absorptions ν (NCH) 2790 and (SiN) 980 cm^{-1}. There was no evidence of $SiOCH_3$ or $C{=}CH_2$.

Anal. Calcd for $[(C_8H_{21}N_3Si)(C_8H_8)_9]_n$: C, 86.0; H, 8.23; N, 3.4; Si, 2.3. Found: C, 86.4; H, 8.56; N, 2.8; Si, 2.5.

With α-Methylstyrene.—α-Methylstyrene (11.8 g, 0.100 mole) and III (4.7 g, 0.25 mole) in hexane (30 ml) and THF (2 ml) were cooled to −25° and treated with *n*-butyllithium (0.0012 mole) resulting in an orange-red solution. After 20 hr part of the α-methylstyrene disappeared but III remained mostly unreacted. After 6 days at ambient temperature, the solution was still highly colored and about one-half of the α-methylstyrene and two-thirds of III had polymerized. Rapid loss of the orange-red color occurred when the system was opened to the atmosphere. The polymer was precipitated in *t*-butyl alcohol, dissolved in THF, and boiled with dilute HCl for 4 hr. A soft solid formed during this time. Drying at 100° for 6 hr at 1 mm gave a brittle white solid (7.7 g) which was soluble in benzene. The infrared spectrum showed a strong, broad band at ν (SiOSi) 1110 cm^{-1}. A barely detectable absorption at ν (SiOH) 3640 cm^{-1} indicated no more than a trace of uncondensed silanol.

Anal. Calcd for $[(C_2H_3O_{3/2}Si)(C_9H_{10})_{2.6}]_n$: C, 78.9; H, 7.5; Si, 7.2. Found: C, 78.5; H, 8.3; Si, 7.1.

Polymers of N-Methyl-*sym*-divinyltetramethyldisilazane (IV). Homopolymers.—Compound IV (10 g, 0.05 mole) in hexane (10 ml) and *n*-butyllithium (0.16×10^{-2} mole) gave little reaction during 3 hr but formed a gelatinous mass during 3 days. This material was extracted twice with methyl alcohol and devolatilized at 1 mm for 20 hr, giving a brittle polymer (7.2 g, 72% yield) which did not melt up to 300° and which was insoluble. The infrared spectrum showed characteristic absorptions at ν (NCH) 2805, ($SiCH_3$) 1245, and (SiNSi) 900 and 800 cm^{-1}. No $SiCH{=}CH_2$, $SiOCH_3$, or NH was evident.

Anal. Calcd for $(C_9H_{21}NSi_2)_n$: C, 54.2; H, 10.6; N, 7.02; Si, 28.2. Found: C, 54.1; H, 10.8; N, 7.15; Si, 26.9.

When IV (8.8 g, 0.044 mole) in hexane (70 ml) and triethylamine (10 ml) was treated with *n*-butyllithium (0.0062 mole), 60% of IV disappeared during 5 days. The polymer was precipitated in methyl alcohol and devolatilized at 2 mm for 3 days, affording 4.2 g (47% yield) of a white solid (mp 70–75°) with a molecular weight of 2.6 × 10^3. The polymer was completely soluble in cold benzene. Characteristic infrared absorptions were ν (NCH) 2810, ($SiCH_3$) 1245, and (SiNSi) 880 cm^{-1}.

Anal. Calcd for $(C_9H_{21}NSi_2)_n$: C, 54.2; H, 10.6; N, 7.02; Si, 28.2. Found: C, 55.2; H, 11.1; N, 7.12; Si, 27.2.

Copolymers with Styrene.—Compound IV (10 g, 0.050 mole) and *n*-butyllithium (0.48 × 10^{-2} mole) were dissolved in toluene (40 ml) and styrene (6.34 g, 0.0610 mole) was added. The solution turned orange and grew warm. Additional styrene was added for a total of 20 g (0.20 mole). Within 30 min the solution became an orange gelatinous mass. This was extracted with toluene and methyl alcohol and devolatilized at 1 mm for 20 hr to yield a white brittle polymer (16 g, 53% yield) which did not melt to 300° and was insoluble in toluene. Characteristic infrared absorptions were ν (NCH) 2810, ($C_{ar}C_{ar}$) 1600, ($SiCH=CH_2$) 1595, ($SiCH_3$) 1250, and (SiNSi) 900 and 880 cm^{-1}. There was no indication of $SiOCH_3$.

Anal. Calcd for $[(C_9H_{21}NSi_2)(C_8H_8)_{1.2}]_n$: C, 69.0; H, 9.5; N, 4.3; Si, 17.3. Found: C, 68.9; H, 9.5; N, 4.4; Si, 16.8.

In a similar preparation, IV (10.9 g, 0.0544 mole) and styrene (5.2 g, 0.050 mole) in benzene (60 ml) were treated with *n*-butyllithium (0.64 × 10^{-2} mole), resulting in an orange solution and noticeable exotherm. After 0.5 hr the viscous solution was poured into methyl alcohol. The polymer which precipitated was devolatilized at 1 mm for 24 hr to give a brittle white solid (9.5 g, 57% yield) which became quite soft at 90°. This polymer was soluble in benzene and had a molecular weight of 1.4 × 10^3. The infrared spectrum showed more $SiCH=CH_2$ than was present in the earlier preparation.

Anal. Calcd for $[(C_9H_{21}NSi_2)(C_8H_8)_{1.5}]_n$: C, 63.6; H, 9.9; N, 5.3; Si, 21.3. Found: C, 62.2; H, 9.9; N, 5.3; Si, 20.8.

Stability of Dimethylaminosilanes in the Presence of *n*-Butyllithium.—Trimethyldimethylaminosilane (1.17 g, 0.010 mole), dimethylbisdimethylaminosilane (1.46 g, 0.010 mole), and methyltrisdimethylaminosilane (1.75 g, 0.010 mole) were placed under helium in separate vials fitted with septums. *n*-Butyllithium (0.010 mole) in hexane was added to each vial. Samples were periodically withdrawn and analyzed by vpc for the aminosilane. After 68 and 116 hr at ambient temperature, 93 and 83%, respectively, of the trimethyldimethylaminosilane remained, 99 and 89% of the dimethylbisdimethylaminosilane remained, and 100 and 96% of the methyltrisdimethylaminosilane was unreacted. In all cases, a small amount of precipitate, presumably lithium dimethylamide, became evident. The product from trimethyldimethylaminosilane and *n*-butyllithium was identified as *n*-butyltrimethylsilane by comparison of its retention time with that of an authentic sample.

Stability of Dialkylaminosilane in the Presence of Lithium Dialkylamides.—Diethylamine (0.073 g, 0.0010 mole) and *t*-butyllithium (1.5 *M* in pentane; 0.67 ml, 0.0010 mole) were combined under helium in a vial fitted with a septum. The addition of trimethyldimethylaminosilane (0.117 g, 0.0010 mole) and triethylamine (2.00 ml) dissolved the lithium diethylamide. By the same method, a solution of lithium dimethylamide (0.0010 mole) and trimethyldiethylaminosilane (0.0010 mole) in triethylamine (2.00 ml) was prepared. The solutions were analyzed by vpc. No exchange of amino groups could be detected in either system during 84 hr at ambient temperature.

Registry No.—I, 13391-72-5; II, 13368-45-1; III, 13391-74-7; IV, 7688-44-0; vinyldimethylmethylaminosilane, 7688-43-9.

Organic Photochemistry. III. Photochemical Reaction of 5-Chlorotropolone and Its Methyl Ether[1,2]

TOSHIO MUKAI AND TADAO SHISHIDO[3]

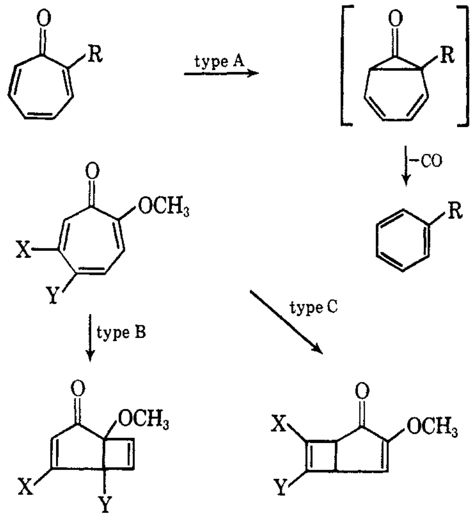
Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

Received December 20, 1966

Irradiation of 5-chlorotropolone methyl ether (I) in methanol using a high-pressure mercury lamp produced three photoproducts: 6-chloro-7-methoxy- and 6-chloro-3-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (II) and (III) and methyl 4-keto-2-cyclopentenylideneacetate (IV). The irradiation of 5-chlorotropolone (XIV) in the same manner afforded four photoproducts, a methanol adduct XV and a dimer XVI, besides III and IV. The structure of XV and XVI including stereochemistry was elucidated and the mechanistic pathway for products was also discussed.

There are three different modes of cyclization, type A, B, and C in Scheme I, in the photo-induced valence isomerization of a troponoid system.[4] Previous studies have established that the nature of the substituents in the troponoid system play a major role in the control of the reaction path.[4] In general, tropolones and their methyl ethers[5,6] and alkyl-substituted derivatives[7] follow type B cyclization, whereas aromatic substituted systems such as colchicine,[8] isocolchicine,[9] and 5-phenyltropolone methyl ether[1] undergo type C isomerization. Type A cyclization has only been observed on irradiation of tropone[4] and 2-phenyltropone.[10]

SCHEME I



---

[1] Preceding paper in this series: T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967).

[2] Support of this work by Sankyo Co. Tokyo is gratefully acknowledged.

[3] From the M.S. Thesis of T. Shishido, Fuji Film Industry Co., Minamiashigara, Kanagawa Prefecture.

[4] O. L. Chapman, *Advan. Photochem.* **1**, 323 (1963).

[5] (a) W. G. Dauben, K. Koch, and W. E. Thiessen, *J. Am. Chem. Soc.*, **81**, 6087 (1959); (b) E. J. Forbes and R. A. Ripley, *Chem. Ind.* (London), 589 (1960).

[6] (a) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958); (b) *ibid.*, **82**, 3642 (1960).

[7] (a) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *ibid.*, **83**, 1768 (1961); (b) *ibid.*, **85**, 2616 (1963).

[8] (a) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955); (b) O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 803 (1963).

[9] (a) W. G. Dauben and D. A. Cox, *ibid.*, **85**, 2130 (1963); (b) O. L. Chapman, H. G. Smith, and P. A. Barks, *ibid.*, **85**, 3171 (1963).

[10] Irradiation of 2-phenyltropone in methanol afforded biphenyl (1.5% yield) and 1-phenyl- and 7-phenyl-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-ones (16%). Details will be reported by the authors.