Reaction of 26 with Et_2NH and Formation of 43. To a suspension of 2.55 g (5 mmol) of **26** in 20 mL of CH_2Cl_2 at 0 °C was added 730 mg (10 mmol) of diethylamine in 5 mL of CH_2Cl_2. A homogeneous pale-yellow solution formed and was stirred for 30 min. The ^1H NMR of this solution shows equimolar amounts of urea **24**, diethylammonium triflate, and **43**. The solution was extracted with 400 mg of KOH dissolved in 20 mL of H_2O, and the organic layer was dried over Na_2SO_4. After removal of solvent, a yellow oil remains that crystallized upon addition of 20 mL of ether. After filtration and recrystallization from $CHCl_3$/ether, 1.17 g (73%) of pale-yellow crystalline **43** was obtained: mp 59–61 °C; IR (KBr) 1607, 1560 (s, $\mathrm{C}\overset{-}{\cdots}\mathrm{N}$), 1310 (s), 1265 (vs), 1223 (s), 1148 (vs), 1033 (vs); NMR ($CDCl_3$; internal standard, Me_4Si) δ 1.23 (t, J = 7.5 Hz, 6 H), 3.00 (s, 6 H), 3.36 (q, J = 7.5 Hz, 4H), 3.81 (s, 4 H). Anal. Calcd. for $C_{10}H_{20}F_3N_3O_3S$(319.35): C, 37.61; H, 6.31; N, 13.16. Found: C, 37.5; H, 6.13; N, 13.3.

Reaction of 26 with $NaBH_4$ and Formation of 44. A mixture of 510 mg (1 mmol) of **26** and 38 mg (1 mmol) of $NaBH_4$ in 10 mL of CH_3CN is refluxed for 3 h with vigorous stirring. After removal of solvent, the residue is extracted with two 15-mL portions of boiling CH_2Cl_2. After removal of CH_2Cl_2, the residual oil is extracted twice with 20-mL portions of ether, yielding 113 mg (100%) of urea **24**. The residual oil, 124 mg (50%), corresponds to **44**: IR (film) 1665 (s, $\mathrm{C}\overset{-}{\cdots}\mathrm{N}$), 1275, 1250 (s, br), 1225, 1157, 1032 (all s); NMR (CH_3CN; internal standard, Me_4Si), δ 3.16 (s, 6 H), 3.94 (s, 4 H), 8.03 (br, s, 1 H). NMR of the original reaction mixture indicates an equimolar amount of **44** and **24**.

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Aluminum Chloride Catalyzed Skeletal Rearrangement of Permethylated Acyclic Polysilanes

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Abstract: Permethylated linear polysilanes, $Me(Me_2Si)_nMe$ with n = 4–10 and 12, underwent skeletal rearrangement to give branched isomers in almost quantitative yields when treated with a catalytic amount of aluminum chloride in refluxing benzene. From the linear polysilanes with n = 4, 5, and 6, $(Me_3Si)_3SiMe$, $(Me_3Si)_4Si$, and $(Me_3Si)_3SiSiMe_2SiMe_3$ were obtained, respectively, as single isomers. The polysilanes with n = 7, 8, and 9 were converted into an equilibrium mixture, each consisting of a pair of branched isomers: $(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3$ (**15**) and $(Me_3Si)_3SiSiMe(SiMe_3)_2$ (**16**); $(Me_3Si)_3SiSiMe_2SiMe(SiMe_3)_2$ (**18**) and $[(Me_3Si)_3Si]_2$ (**19**); and $(Me_3Si)_3SiSiMe_2SiMe_2SiMe(SiMe_3)_2$ and $[(Me_3Si)_3Si]_2SiMe_2$ respectively. Under identical conditions, from **15** an equilibrium mixture of **15** and **16** was formed, while from **19** an equilibrium mixture of **18** and **19** was formed. Isomerization of the polysilane with n = 10 produced $[(Me_3Si)_3SiSiMe_2]_2$ as a single product, and the polysilane with n = 12 was converted to a single isomer $[(Me_3Si)_3SiSiMe_2SiMe_2]_2$. The ^{29}Si NMR chemical shifts for permethylated linear polysilanes with n = 4–12 and for isomerization products are recorded.

Isomerization of saturated hydrocarbons catalyzed by Lewis acids has been extensively studied; many papers dealing with the skeletal rearrangements of linear and cyclic hydrocarbons have been published.[2] However, no interest had been shown in the rearrangements of catenate compounds other than carbon-chain compounds until 1969, when we found a first example of the skeletal rearrangement of dodecamethylcyclohexasilane in the presence of a catalytic amount of anhydrous aluminum chloride.[3] Further work showed that the rearrangement is a general one for permethylated cyclic and acyclic polysilanes.

In this paper, we report the behavior of some permethylated linear and branched polysilanes toward a catalytic amount of aluminum chloride.

Results and Discussion

Isomerization of Lower Polysilanes. In a preliminary experiment[4] we found that the linear permethylated polysilanes, $Me(Me_2Si)_nMe$ with $n = 4 \sim 6$, underwent readily skeletal rearrangement, giving rise to the corresponding branched isomers when refluxed in benzene in the presence of a catalytic amount of anhydrous aluminum chloride. Thus decamethyltetrasilane[5-7] (**1**) was converted to tris(trimethylsilyl)methylsilane (**2**) as the sole product. Monitoring the progress of the reaction by VPC revealed

$$\underset{\mathbf{1}}{Me(Me_2Si)_4Me} \xrightarrow{AlCl_3} \underset{\mathbf{2}}{(Me_3Si)_3SiMe}$$

that a trace of compound whose retention time was identical with that of 1-chloro-2-(trimethylsilyl)hexamethyltrisilane always appeared in the early stage of the reaction and remained throughout.

In sharp contrast to acid-catalyzed isomerization of the saturated hydrocarbons which never yielded neopentyl derivatives, that of permethylated polysilanes afforded tetrakis(silyl)silane derivatives. Thus, the aluminum chloride catalyzed rearrangement of dodecamethylpentasilane[6] (**3**) gave tetrakis(trimethylsilyl)silane (**4**) in almost quantitative yield. In all respects, products **2** and

$$\underset{\mathbf{3}}{Me(Me_2Si)_5Me} \xrightarrow{AlCl_3} \underset{\mathbf{4}}{(Me_3Si)_4Si}$$

4 were identical with the respective authentic samples prepared by known methods.[8,9]

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(3) Ishikawa, M.; Kumada, M. *Chem. Commun.* **1969**, 567.

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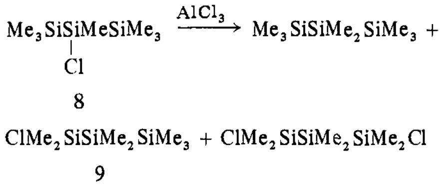
Tetradecamethylhexasilane[6a,7] (**5**) also underwent skeletal rearrangement under similar conditions to give 2,2-bis(trimethylsilyl)octamethyltetrasilane (**6**) quantitatively. When this reaction was followed by VPC, an unidentified peak was observed as a shoulder on the peak corresponding to the starting polysilane **5**, along with a small peak, presumably due to a chloro derivative[10] of the branched hexasilane in the early stage of the reaction. With increasing reaction time, both the starting and the new compound were transformed completely into the final product **6**. At this point, no other isomer was detected by spectroscopic analysis. Interestingly, similar treatment with aluminum chloride of 2,3-bis(trimethylsilyl)octamethyltetrasilane (**7**), prepared from 1,2-dimethyltetrachlorodisilane and trimethylchlorosilane by lithium condensation, afforded **6** quantitatively. The ^{1}H NMR spectrum of **6** exhibits signals at δ 0.10 and 0.21 attributable to Me_3Si protons attached to silicon in the 3-position and an overlapping resonance due to the $(Me_3Si)_3Si$ and internal Me_2Si protons. The ^{29}Si NMR spectrum of **6** was also consistent with the proposed structure.

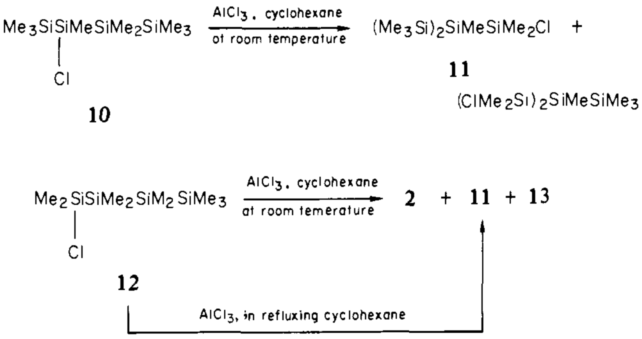
$$\underset{\mathbf{5}}{Me(Me_2Si)_6Me} \xrightarrow{AlCl_3} \underset{\mathbf{6}}{(Me_3Si)_3SiSiMe_2SiMe_3} \xleftarrow{AlCl_3} \underset{\mathbf{7}}{Me(Me_3Si)_2SiSiMe(SiMe_3)_2}$$

Mechanism. In all rearrangement reactions described above, a small amount of a chloropolysilane was detected by VPC analysis in early stages of the reaction. We therefore assume that a trace of a chloropolysilane is formed initially, which undergoes isomerization to the branched polysilane. The formation of such a chloropolysilane may be a result of the reaction of the starting polysilane with aluminum chloride, either alone or in association with hydrogen chloride possibly contained in traces in the catalyst. The fact that hexamethyldisilane reacts with hydrogen chloride at room temperature in the presence of a catalytic amount of aluminum chloride to give chloropentamethyldisilane supports this assumption.[11] With a view to getting an insight into the mechanism of the skeletal rearrangement, we first examined the behavior of 2-chloroheptamethyltrisilane[12] (**8**) in the presence of a catalytic amount of aluminum chloride in cyclohexane. At room temperature, no reaction occurred over a period of 24 h. However, refluxing for 5 h caused redistribution to take place, giving octamethyltrisilane, 1-chloroheptamethyltrisilane[12] (**9**), and 1,3-dichlorohexamethyltrisilane[6a,11] in 15, 52, and 21% yield, respectively, in addition to 12% of unchanged **8**. No 1,2-dichlorohexamethyltrisilane was detected by either VPC or spectroscopic analysis. Attempts to separate **9** from **8** by VPC using several different kinds of columns were unsuccessful. Therefore the yields of **8** and **9** were determined by ^{1}H NMR spectroscopy of the mixture isolated by preparative VPC. Next we prepared a pair of isomeric chlorotetrasilanes, 2-chloro- and 1-chlorononamethyltetrasilane (**10** and **12**, respectively), and studied their behavior toward aluminum chloride in cyclohexane. Treatment of the internal chlorotetrasilane **10** with the catalyst in cyclohexane at room temperature for 4 h led to complete transformation into the branched isomer. 1-Chloro-2-(trimethylsilyl)hexamethyltrisilane (**11**) was obtained in 90% yield in addition to a trace of 1,3-dichloro-2-(trimethylsilyl)pentamethyltrisilane (**13**). On the other hand, treatment of 1-chlorononamethyltetrasilane **12** in cyclohexane for 24 h afforded no isomerization product.[13] Compound **12** underwent isomerization only at refluxing temperature to give the branched isomer **11** in 59% yield together with **2** (13%) and **13** (28%). This result suggests that at higher temperature an intermolecular methyl–chlorine exchange occurs initially between two molecules of **12**, yielding the internal chlorotetrasilane such as **10**, which in turn undergoes rearrangement (Scheme I). In fact, it is known that the aluminum chloride catalyzed intermolecular methyl–chlorine exchange between trimethylchlorosilane and some lower homologues of the permethylated polysilanes easily occurs.[14]

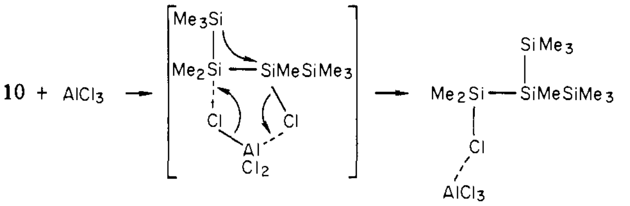


$$\underset{\mathbf{8}}{Me_3Si\underset{\substack{|\\ Cl}}{Si}MeSiMe_3} \xrightarrow{AlCl_3} Me_3SiSiMe_2SiMe_3 + \underset{\mathbf{9}}{ClMe_2SiSiMe_2SiMe_3} + ClMe_2SiSiMe_2SiMe_2Cl$$

Scheme I



From the above-mentioned observations it seems likely that complex formation of the chloropolysilanes with aluminum chloride plays an important role in the present rearrangement. Examination of molecular models shows that such a complex with an internal chloropolysilane is unfavored on steric grounds, and this steric interaction can be relieved through rearrangement to a complex of a terminal chloro isomer.



Isomerization of Higher Polysilanes. In the case of higher permethylated polysilanes, we were forced to use a much smaller amount of the substrate for the skeletal rearrangement because of synthetic difficulty. Moreover, the molar ratio of the catalyst to the substrate was higher than in the case of the lower polysilanes. As a result, appreciable amounts of the chloropolysilanes were formed. Therefore, we methylated the resulting products to convert the chloropolysilanes into permethylated polysilanes. Thus, refluxing a benzene solution of hexadecamethylheptasilane[6a] (**14**) with aluminum chloride for 2 h followed by treatment of the resulting solution with methylmagnesium bromide gave 2,2-bis(trimethylsilyl)decamethylpentasilane (**15**) and 2,2,3-tris(trimethylsilyl)heptamethyltetrasilane (**16**) in the ratio of 74:26 in high yield. Attainment of true equilibrium was confirmed by the observation that the same ratio of **15** to **16** was obtained from

$$\underset{\mathbf{14}}{Me(Me_2Si)_7Me} \xrightarrow{AlCl_3} \underset{\mathbf{15}}{(Me_3Si)_3SiSiMe_2SiMe_2SiMe_3} + \underset{\mathbf{16}}{(Me_3Si)_3SiSiMe(SiMe_3)_2} \xleftarrow{AlCl_3} \mathbf{16}$$

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[8] Gilman, H.; Harrel, R. L. *J. Organomet. Chem.* **1966**, *5*, 199.

[9] Gilman, H.; Smith, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 1454.

[10] Treatment of the isomerization product involving a chloro derivative with methylmagnesium bromide afforded only permethylated branched isomer **6**.

[11] Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493.

[12] Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

[13] The reaction of **12** with a catalytic amount of aluminum chloride in benzene at room temperature for 40 h gave isomerization product **11** in 10% yield, in addition to 90% of the starting **12**.

[14] Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

Table I. ^{29}Si Chemical Shifts for Permethylated Polysilanes (ppm in $CDCl_3$)

compound	chemical shifts (ppm in $CDCl_3$)					
	^{a}Si	^{b}Si	^{c}Si	^{d}Si	^{e}Si	^{f}Si
$Me_3\overset{a}{Si}\text{-}SiMe_3$	−19.7					
	−19.6[a]					
$Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}SiMe_3$	−16.1	−48.6				
	−16.1	−48.7[b]				
$Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}SiMe_2\text{-}SiMe_3$	−15.2	−44.9				
	−15.1	−44.7[c]				
$Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}SiMe_2\text{-}SiMe_3$	−15.1	−43.6	−40.9			
	−15.0	−43.4	−40.7[c]			
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2)_2$	−15.1	−43.4	−39.5			
	−14.9	−43.1	−39.2[c]			
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2)_2\overset{d}{Si}Me_2$	−15.0	−43.3	−39.3	−38.2		
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}\overset{d}{Si}Me_2)_2$	−15.0	−43.3	−39.2	−37.9		
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}\overset{d}{Si}Me_2)_2\overset{e}{Si}Me_2$	−15.0	−43.3	−39.1	−37.8	−37.4	
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}\overset{d}{Si}Me_2\text{-}\overset{e}{Si}Me_2)_2$	−15.0	−43.3	−39.1	−37.8	−37.6	
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}\overset{d}{Si}Me_2\text{-}\overset{e}{Si}Me_2)_2\overset{f}{Si}Me_2$	−15.0	−43.2	−39.1	−37.8	−37.5	−37.5
$(Me_3\overset{a}{Si}\text{-}\overset{b}{Si}Me_2\text{-}\overset{c}{Si}Me_2\text{-}\overset{d}{Si}Me_2\text{-}\overset{e}{Si}Me_2\text{-}\overset{f}{Si}Me_2)_2$	−15.0	−43.1	−39.0	−37.6	−37.4	−37.3
$(Me_3\overset{a}{Si})_3\overset{b}{Si}Me$	−12.5	−88.1				
$(Me_3\overset{a}{Si})_4\overset{b}{Si}$	−9.8	−135.5				
	−9.8	−135.5[b]				
$(Me_3\overset{a}{Si})_2Me\overset{b}{Si}SiMe(SiMe_3)_2$	−11.7	−81.4				
$(Me_3\overset{a}{Si})_3\overset{d}{Si}\overset{c}{Si}Me_2\overset{b}{Si}Me_3$	−9.5	−14.7	−39.8	−131.9		
$(Me_3\overset{a}{Si})_3\overset{d}{Si}\overset{c}{Si}Me(\overset{b}{Si}Me_3)_2$	−9.2	−11.7	−79.8	−129.4		
$(Me_3\overset{a}{Si})_3\overset{e}{Si}\overset{c}{Si}Me_2\overset{d}{Si}Me(\overset{b}{Si}Me_3)_2$	−9.5	−11.1	−29.2	−78.8	−126.0	
$(Me_3\overset{a}{Si})_3\overset{b}{Si}Si(SiMe_3)_3$	−9.5	−130.0				
$(Me_3\overset{a}{Si})_3\overset{f}{Si}\overset{c}{Si}Me_2\overset{d}{Si}Me_2\overset{e}{Si}Me(\overset{b}{Si}Me_3)_2$	−9.4	−11.7	−31.8	−33.2	−81.2	−128.6
$(Me_3\overset{a}{Si})_3\overset{c}{Si}\overset{b}{Si}Me_2Si(SiMe_3)_3$	−9.2	−26.0	−118.2			
$(Me_3\overset{a}{Si})_3\overset{c}{Si}\overset{b}{Si}Me_2SiMe_2Si(SiMe_3)_3$	−9.2	−29.0	−126.5			
$[(Me_3\overset{a}{Si})_3\overset{d}{Si}\overset{b}{Si}Me_2\overset{c}{Si}Me_2]_2$[d]	−9.5	−31.4	−35.7	−128.0		

[a] Calculated value using the following equation: $\delta(Me_4Si) = \delta(Si(OMe)_4) + 78.4$ ($\delta(Si(OMe)_4) = 58.9$); reference 16. [b] Reference 17. [c] Reference 18. [d] In benzene.

the reaction of pure **16**. Similar treatment of octadecamethyloctasilane[15] (**17**) with aluminum chloride in refluxing benzene again produced two isomers, 2,2,4-tris(trimethylsilyl)nonamethylpentasilane (**18**) and 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetrasilane (**19**) in a ratio of 81:19. The action of aluminum chloride on **19** prepared by an independent route also afforded the equilibrium mixture consisting of **18** and **19** in the same ratio. In this reaction, no 2,2,3-tris(trimethylsilyl)nonamethylpentasilane was detected by either VPC or spectroscopic analysis. Under similar conditions, eicosamethylnonasilane[15] (**20**) was converted into 2,2,5-tris(trimethylsilyl)undecamethylhexasilane (**21**) and 2,2,4,4-tetrakis(trimethylsilyl)octamethylpentasilane (**22**) in a ratio of 4:1 in high yield. No other isomers were detected by spectroscopic analysis. Interestingly, isomerization of docosamethyldecasilane[15] (**23**) and tetracosamethyldodecasilane[15] (**25**) each produced a single product, 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (**24**) and 2,2,7,7-tetrakis(trimethylsilyl)dodecamethyloctasilane (**26**), respectively. The structure of all

$$\underset{\mathbf{17}}{Me(Me_2Si)_8Me} \xrightarrow{AlCl_3} \underset{\mathbf{18}}{(Me_3Si)_3SiSiMe_2SiMe(SiMe_3)_2} + \underset{\mathbf{19}}{(Me_3Si)_3SiSi(SiMe_3)_3} \xleftarrow{AlCl_3} \mathbf{19}$$

$$\underset{\mathbf{20}}{Me(Me_2Si)_9Me} \xrightarrow{AlCl_3} \underset{\mathbf{21}}{(Me_3Si)_3SiSiMe_2SiMe_2SiMe(SiMe_3)_2} + \underset{\mathbf{22}}{(Me_3Si)_3SiSiMe_2Si(SiMe_3)_3}$$

$$\underset{\mathbf{23}}{Me(Me_2Si)_{10}Me} \xrightarrow{AlCl_3} \underset{\mathbf{24}}{(Me_3Si)_3SiSiMe_2SiMe_2Si(SiMe_3)_3}$$

$$\underset{\mathbf{25}}{Me(Me_2Si)_{12}Me} \xrightarrow{AlCl_3} \underset{\mathbf{26}}{(Me_3Si)_3SiSiMe_2SiMe_2SiMe_2SiMe_2Si(SiMe_3)_3}$$

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[15] Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1966**, *5*, 120.

rearranged products could be confirmed unambiguously by mass, ^{1}H NMR, and ^{29}Si NMR spectrometric as well as elemental analyses. The ^{29}Si chemical shifts of the products are listed in Table I, along with permethylated linear polysilanes.

In conclusion, the isomerization of all acyclic permethylated polysilanes reported here leads to the formation of tris(trimethylsilyl)silyl structure expected to be the most thermodynamically stable. In the higher polysilanes, once the tris(trimethylsilyl)silyl structure is constructed at one end of the silicon skeleton, chain branching in the next step occurs at the other end of the chain.

^{29}Si NMR Study. We encountered some difficulties in confirming the structures of the isomerization products arising from higher homologues of permethylated polysilanes by ^{1}H NMR spectroscopic analysis, because in some cases methylsilyl protons in different environments showed overlapping resonances. We thought that ^{29}Si NMR would make it possible to clarify the structures of these compounds. Indeed, chemical shifts of ^{29}Si are highly dependent on the structure of the silicon skeleton.

For obtainment of some information concerning the chemical shifts of silicon atom in various environments, nondecoupled and proton-decoupled ^{29}Si spectra of known permethylated polysilanes were determined. The ^{29}Si chemical shifts of lower homologues of the permethylated linear polysilanes, from disilane through hexasilane, and tetrakis(trimethylsilyl)silane reasonably agreed with reported values.[16-18] The proton-decoupled ^{29}Si NMR spectrum of decamethyltetrasilane **1** showed two singlets at −15.2 and −44.9 ppm upfield from tetramethylsilane. The nondecoupled spectrum of this compound displayed two multiplets at the same positions as above. Selected proton decoupling experiments indicated that the signal at −15.2 ppm can be assigned to the terminal silicon atom and the resonance at −44.9 ppm to the internal one. Thus, when the region of methylsilyl protons (δ 0.00~0.15) was weakly irradiated, gradually from upfield to downfield, the multiplet resonance at −15.2 ppm due to the terminal silicon atom changed into a sharp signal consisting of absorption and emission, while the resonance at −44.9 ppm due to the internal one changed into a broad signal that also showed absorption and emission. Upon irradiation of a region of the internal dimethylsilyl protons, however, the latter became a sharp signal, showing that this is due to the internal silicon atom, while the resonance at −15.2 ppm changed into a broad signal involving emission and absorption.

Assignment of the resonances in the spectrum of 2,2-bis(trimethylsilyl)octamethyltetrasilane (**6**) was also made by its nondecoupled ^{29}Si NMR spectrum. In this case, trimethylsilyl silicon in the tris(trimethylsilyl)silyl group showed a decet at −9.5 ppm along with multiplet signals at −14.7, −39.8, and −131.9 ppm attributed to Me_3Si, Me_2Si, and Si, respectively. In other cases, the chemical shifts for silicon at primary $Me_3Si(Si)$, secondary $Me_2Si(Si)_2$, tertiary $MeSi(Si)_3$, or quaternary $Si(Si)_4$ silicon vary little from compound to compound, so assignment of the signals can be made unambiguously regardless of the chain length of permethylated polysilanes. In all compounds reported here, the primary silicon appears in the region of −5.0~−20.0 ppm, while the secondary silicon shows signals at −25~−49.0 ppm. The tertiary silicon atom is observed at −68.0~−89.0 ppm and the tetrakis(silyl)-substituted silicon at −126.0~−136.0 ppm.

From Table I it can also be seen that the silicon atom of a trimethylsilyl group attached to a secondary silicon atom appears at −15.0~−16.8 ppm. The silicon of the same group bonded to a tertiary and a quaternary silicon atom reveals resonances at −10.1~12.5 ppm and at −5.1~−9.8 ppm, respectively. On the other hand, the resonances of the internal silicon atoms of the dimethylsilyl groups appear at lower fields as the distance of the silicon atom from the end of the chain increases. For instance in the spectrum of dodecamethylpentasilane the two resonances in the internal silicon atoms at −43.6 and −40.9 ppm are due to the silicon atom in the 2- and 3-positions, respectively. In the spectrum of hexadecamethylheptasilane, the internal silicon atoms in the 2-, 3-, and 4-positions appear at −43.3, −39.3, and −38.2, respectively. As the distance from the end of the chain increases, the difference in chemical shift between two adjacent silicon atoms becomes smaller. For long permethylpolysilane chains, the environments of silicons far from the end of the chain becomes essentially equivalent, and coalescence of resonances is expected.

Experimental Section

General Procedure. ^{1}H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride, using cyclohexane as an internal standard. ^{29}Si NMR spectra were determined with a JEOL Model JNM-PFT-100 spectrometer in deuteriochloroform, using tetramethysilane as an internal standard. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating isomers, **15** and **16**, **18** and **19**, and **21** and **22**. They were easily separated by using a $^{3}/_{8}$ in. × 20 ft column containing SE-30 (30%) on Celite 545.

Materials. All permethylated linear polysilanes were prepared as reported in the literature.[6a,15] Benzene and cyclohexane were dried over lithium aluminum hydride and distilled just before use. Anhydrous aluminum chloride was sublimed before use.

Isomerization of Decamethyltetrasilane (1). In a 25-mL flask fitted with a reflux condenser was placed a mixture of 5.0 g (19.04 mmol) of **1** and 0.10 g (0.75 mmol) of anhydrous aluminum chloride in 20 mL of benzene. The mixture was refluxed for 1 h. At this stage, VPC analysis of the mixture showed that the starting tetrasilane **1** was completely transformed into isomer **2**. The mixture was hydrolyzed with water. The organic layer was dried over potassium carbonate and then distilled under reduced pressure to give 4.6 g (92% yield) of colorless crystals boiling at 106~108 °C (15 mm) [lit.[19] bp 94~96 °C (7 mm)]: mp 54~55 °C, ^{1}H NMR δ 0.03 (3 H, s, MeSi), 0.12 (27 H, s, Me_3Si).

Isomerization of Dodecamethylpentasilane (3). A mixture of 5.0 g (15.6 mmol) of **3** and 0.12 g (0.90 mmol) of anhydrous aluminum chloride in 10 mL of benzene was refluxed for 1 h. After the mixture was hydrolyzed with water, the organic layer was separated and dried over potassium carbonate. The solvent was distilled off to give 4.8 g (96% yield) of **4** as white crystals: mp 263~264 °C after recrystalization from ethanol (lit.[9] 261~263 °C).

Isomerization of Tetradecamethylhexasilane (5). A mixture of 5.0 g (13.19 mmol) of **5** and 0.10 g (0.75 mmol) of aluminum chloride in 20 mL of benzene was refluxed for 1 h. The mixture was hydrolyzed with water. The organic layer was dried over potassium carbonate. The solvent benzene was evaporated and the residue was distilled under reduced pressure (1 mm) to give 4.9 g (98% yield) of **6**: mp 156~157 °C after recrystalization from 95% ethanol; mass spectrum, *m/e* 378; ^{1}H NMR δ 0.10 (9 H, s, Me_3Si), 0.21 (33 H, s, Me_3Si and Me_2Si). Anal. Calcd for $C_{14}H_{42}Si_6$: C, 44.36; H, 11.17. Found: C, 44.16; H, 11.32.

Preparation of 2,3-Bis(trimethylsilyl)octamethyltetrasilane (7). In a 500-mL flask fitted with a stirrer, a dropping funnel and a condenser were placed 15 g (2.2 mol) of finely cut lithium and 94 g (0.86 mol) of trimethylchlorosilane in 200 mL of dry THF. To this was added 41 g (0.18 mol) of 1,2-dimethyltetrachlorodisilane in 150 mL of dry THF over a period of 4 h. The mixture was refluxed for 24 h. The lithium salt and excess of lithium metal were filtered off. The filtrates were hydrolyzed with water, and the organic layer was washed with water and dried over potassium carbonate. After evaporation of the solvent, the residue of the flask was distilled under reduced pressure to give 30 g (44% yield) of white crystals of **7**: bp 142~145 °C (2 mm); mp 88~89 °C after recrystallization from ethanol; mass spectrum, *m/e* 378 (M^+); ^{1}H NMR δ 0.17 (42 H, s, Me_3Si and MeSi). Anal. Calcd for $C_{14}H_{42}Si_6$: C, 44.36; H, 11.17. Found: C, 44.23; H, 11.18.

Isomerization of 7. A mixture of 5.0 g (13.19 mmol) of **7** and 0.08 g (0.60 mmol) of anhydrous aluminum chloride in 20 mL of benzene was refluxed for 1 h. The mixture was hydrolyzed with water and the organic layer was separated and dried over potassium carbonate. The solvent was distilled off and the residue was distilled under reduced pressure to give 4.5 g (82% yield) of **6**.

Reaction of 2-Chloroheptamethyltrisilane[12] (8) with Aluminum Chloride. A mixture of 2.0 g (9.8 mmol) of **8** and 0.25 g (1.9 mmol) of aluminum chloride in 7 mL of cyclohexane was refluxed for 5 h. VPC analysis of the mixture showed the presence of three peaks which have an area ratio of 15:64:21. The mixture was distilled under reduced pressure to give 1.8 g of colorless liquid. The products were isolated by preparative VPC. A compound having the shortest retention time on a

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VPC column was identified as octamethyltrisilane (15% yield), the second peak was found to be a mixture consisting of 2-chloro- (12% yield) and 1-chloroheptamethyltrisilane **9** (52% yield) by the ^{1}H NMR spectrum, and the third compound was identified as 1,3-dichlorohexamethyltrisilane (21% yield). For **9**[20]: ^{1}H NMR δ 0.00 (9 H, s, $\mathrm{Me_3Si}$), 0.04 (6 H, s, $\mathrm{Me_2Si}$), 0.39 (6 H, s, $\mathrm{Me_2Si}$). For 1,3-dichlorohexamethyltrisilane[6a]: ^{1}H NMR δ 0.07 (6 H, s, $\mathrm{Me_2Si}$), 0.43 (12 H, s, $\mathrm{Me_2Si}$).

Preparation of 2-Phenylnonamethyltetrasilane. To a sodium–potassium alloy prepared from 19.2 g (0.49 mol) of potassium and 2.0 g (0.09 mol) of sodium in 250 mL of heptane was added slowly a mixture of 43 g (0.19 mol) of 1-chloro-1-phenyltetramethyldisilane[21] and 50 g (0.30 mol) of chloropentamethyldisilane in 200 mL of dry benzene. The mixture was refluxed for 5 h and hydrolyzed in the usual way. Fractional distillation gave 23 g (59% yield) of decamethyltetrasilane, bp 60 °C (2 mm), and 22 g (36% yield) of 2-phenylnonamethyltetrasilane: bp 119~120 °C (2 mm); $n^{20}{}_{\mathrm{D}}$ 1.5341; mass spectrum, *m/e* 324; ^{1}H NMR δ 0.04 (9 H, s, $\mathrm{Me_3Si}$), 0.13 (9 H, s, $\mathrm{Me_3SiSiPh}$), 0.18 (6 H, s, $\mathrm{Me_2Si}$), 0.41 (3 H, s, MeSiPh), 7.03~7.31 (5 H, m, ring protons). Anal. Calcd for $\mathrm{C_{15}H_{32}Si_4}$: C, 55.48; H, 9.93. Found: C, 55.34; H, 10.04.

Preparation of 2-Chlorononamethyltetrasilane (10). In a 250-mL three-necked flask fitted with a reflux condenser, a stirrer and an inlet tube for hydrogen chloride was placed a mixture of 10 g (31 mmol) of 2-phenylnonamethyltetrasilane and 0.5 g (3.75 mmol) of anhydrous aluminum chloride in 200 mL of chloroform. Dry hydrogen chloride was passed into the solution for 2 h with ice cooling. Acetone (2 mL) was added to the reaction mixture and the solvent was then distilled off. The residue was distilled under reduced pressure to give 7.0 g (78% yield) of **10**: bp 76~77 °C (3 mm); $n^{20}{}_{\mathrm{D}}$ 1.4710; mass spectrum, *m/e* 282; ^{1}H NMR δ 0.16 (9 H, s, $\mathrm{Me_3Si}$), 0.19 (3 H, s, $\mathrm{Me_aSi(Me_b)}$), 0.20 (9 H, s, $\mathrm{Me_3SiSiCl}$), 0.21 (3 H, s, $\mathrm{Me_bSi(Me_a)}$), 0.54 (3 H, s, MeSiCl). Anal. Calcd for $\mathrm{C_9H_{27}ClSi_4}$: C, 38.18; H, 9.61. Found: C, 37.93; H, 9.45.

Preparation of 1-Phenylnonamethyltetrasilane. To a sodium–potassium alloy prepared from 14.8 g (0.38 mol) of potassium and 1.6 g (0.07 mol) of sodium in 200 mL of heptane was added slowly a mixture of 31 g (0.14 mol) of 1-chloro-2-phenyltetramethyldisilane[12] and 39 g (0.24 mol) of chloropentamethyldisilane in 200 mL of benzene. The mixture was refluxed for 5 h and hydrolyzed. Fractional distillation gave 15 g (24% yield) of decamethyltetrasilane, bp 57~60 °C (2 mm), and 14 g (31% yield) of 1-phenylnonamethyltetrasilane: bp 118~120 °C (2 mm), $n^{20}{}_{\mathrm{D}}$ 1.5314; mass spectrum, *m/e* 324; ^{1}H NMR δ 0.01 (6 H, s, $\mathrm{Me_2Si(SiMe_2)}$), 0.04 (9 H, s, $\mathrm{Me_3Si}$), 0.10 (6 H, s, $\mathrm{Me_2Si}$), 0.37 (6 H, s, $\mathrm{Me_2SiPh}$), 7.19~7.44 (5 H, m, ring protons). Anal. Calcd for $\mathrm{C_{15}H_{32}Si_4}$: C, 55.48; H, 9.93. Found: C, 55.44; H, 10.08.

Preparation of 1-Chlorononamethyltetrasilane (12). Into a mixture of 12.5 g (39 mmol) of 1-phenylnonamethyltetrasilane and 0.5 g (3.75 mmol) of anhydrous aluminum chloride in 60 mL of chloroform was introduced hydrogen chloride over a period of 2.5 h at room temperature. The solvent was evaporated and the residue was distilled under reduced pressure to give 6 g (54% yield) of **12**: bp 71 °C (2 mm); $n^{20}{}_{\mathrm{D}}$ 1.4898; mass spectrum, *m/e* 282; ^{1}H NMR spectrum δ 0.05 (9 H, s, $\mathrm{Me_3Si}$), 0.16 (6 H, s, $\mathrm{Me_2Si}$), 0.20 (6 H, s, $\mathrm{Me_2Si}$), 0.49 (6 H, s, $\mathrm{Me_2SiCl}$). Anal. Calcd for $\mathrm{C_9H_{27}ClSi_4}$: C, 38.18; H, 9.61. Found: C, 37.89; H, 9.47.

Isomerization of 10. A mixture of 3 g (10.60 mmol) of **10** and 0.15 g (1.13 mmol) of anhydrous aluminum chloride in 6 mL of cyclohexane was stirred for 5 h at room temperature. After ca. 1 mL of acetone was added to the mixture in order to deactivate aluminum chloride, the mixture was distilled under reduced pressure to give 2.7 g (90% yield) of **11**: mp 43 °C; ^{1}H NMR δ 0.17 (3 H, s, MeSi), 0.20 (18 H, s, $\mathrm{Me_3Si}$), 0.54 (6 H, s, $\mathrm{Me_2Si}$). Anal. Calcd for $\mathrm{C_9H_{27}ClSi_4}$: C, 38.18; H, 9.61. Found: C, 38.01; H, 9.42.

Attempted Isomerization of 12 in Cyclohexane at Room Temperature. A mixture of 2.0 g (7.06 mmol) of **12** and 0.23 g (1.72 mmol) of anhydrous aluminum chloride in 6 mL of cyclohexane was stirred at room temperature for 24 h. After 2 mL of acetone was added to the mixture, it was distilled under reduced pressure to give 1.7 g of recovered **12**. All spectral data were identical with those of an authentic sample.

Isomerization of 12. A mixture of 2.0 g (7.06 mmol) of **12** and 0.23 g (1.72 mmol) of aluminum chloride in 6 mL of cyclohexane was refluxed for 2 h. The mixture was analyzed by VPC as being **2** (13% yield), **11** (59% yield), and 1,3-dichloro-2-(trimethylsilyl)pentamethyltrisilane (28% yield). After 2 mL of acetone was added to the mixture, the solvent was evaporated, and the residue was then distilled under reduced pressure (2 mm) to give 1.6 g of colorless liquid. The products were separated by preparative VPC. All spectral data for **2** and **11** were identical with those of the authentic samples. For 1,3-dichloro-2-(trimethylsilyl)pentamethyltrisilane: ^{1}H NMR δ 0.24 (9 H, s, $\mathrm{Me_3Si}$), 0.25 (3 H, s, MeSi), 0.50 (12 H, s, $\mathrm{Me_2SiCl}$). Anal. Calcd for $\mathrm{C_8H_{24}Cl_2Si_4}$: C, 31.65; H, 7.97. Found: C, 31.49; H, 7.81.

Isomerization of Hexadecamethylheptasilane (14). A mixture of 3.50 g (8.01 mmol) of **14** and 0.22 g (1.65 mmol) of anhydrous aluminum chloride in 20 mL of benzene was refluxed for 2 h. VPC analysis of the mixture showed the presence of **15** and **16** in a ratio of 74:26. To this mixture were added 10 mL of 3.7 M methylmagnesium bromide in ether and 10 mL of THF to convert chloro derivatives into permethylated polysilanes. The mixture was refluxed for 5 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. The solvent was evaporated and the residue was distilled under reduced pressure to give 3.2 g of a mixture of **15** and **16** in a ratio of 74:26. Pure products were isolated by preparative VPC. For **15**: colorless liquid; mass spectrum, *m/e* 436 ($\mathrm{M^+}$); ^{1}H NMR δ 0.12 (9 H, s, $\mathrm{Me_3Si}$), 0.17 (6 H, s, $\mathrm{Me_2Si}$), 0.32 (6 H, s, $\mathrm{Me_2Si}$), 0.26 (27 H, s, $\mathrm{Me_3Si}$). Anal. Calcd for $\mathrm{C_{16}H_{48}Si_7}$: C, 43.96; H, 11.07. Found: C, 43.81; H, 11.01. For **16**: mp 128~130 °C; mass spectrum, *m/e* 436 ($\mathrm{M^+}$); ^{1}H NMR δ 0.20 (18 H, s, $\mathrm{Me_3Si}$), 0.25 (30 H, s, $\mathrm{Me_3Si}$ and MeSi). Anal. Calcd for $\mathrm{C_{16}H_{48}Si_7}$: C, 43.96; H, 11.07. Found: C, 43.92; H, 10.94.

Isomerization of 15. A mixture of 1.01 g (2.31 mmol) of **15** and 0.08 g (0.60 mmol) of anhydrous aluminum chloride in 4 mL of benzene was refluxed for 2 h. To it were then added methylmagnesium bromide (3.7 M, 5 mL) in ether and 10 mL of THF. The mixture was refluxed for 8 h and hydrolyzed with dilute hydrochloric acid. VPC analysis indicated the presence of **15** and **16** in the ratio of 74:26.

Preparation of 2,2,3,3-Tetrakis(trimethylsilyl)hexamethyltetrasilane[22] (19). A mixture of 1.567 g (6.32 mmol) of tris(trimethylsilyl)silane[8] and 1.000 g (6.85 mmol) of di-*tert*-butyl peroxide in 3 mL of benzene was heated at 130 °C for 24 h in a sealed glass tube. The mixture was distilled under reduced pressure to give 1.42 g (92% yield) of white crystals: mp >300 °C (lit.[8] mp 372~374 °C); mass spectrum, *m/e* 494 ($\mathrm{M^+}$); ^{1}H NMR δ 0.28 (54 H, s, $\mathrm{Me_3Si}$). Anal. Calcd for $\mathrm{C_{18}H_{54}Si_8}$: C, 43.65; H, 10.99. Found: C, 43.77; H, 11.11.

Isomerization of 19. A mixture of 2.05 g (3.71 mmol) of **19** and 0.15 g (1.13 mmol) of anhydrous aluminum chloride in 15 mL of benzene was refluxed for 19 h. To this solution were added 6 mL of 3.7 M methylmagnesium bromide in ether and 10 mL of THF at room temperture. The mixture was refluxed for 8 h and hydrolyzed with dilute hydrochloric acid. The organic layer was separated and washed with water to neutral and dried over potassium carbonate. VPC analysis of the mixture showed the presence of **18** and **19** in a ratio of 81:19. The solvent was evaporated and the residue was distilled under reduced pressure (1.5 mm) to give 1.80 g of a mixture of **18** and **19**. Pure **18** and **19** were isolated by preparative VPC. For **18**: mp ca. 45 °C; mass spectrum, *m/e* 494 ($\mathrm{M^+}$); ^{1}H NMR δ 0.18 (18 H, s, $\mathrm{Me_3Si}$), 0.22 (3 H, s, MeSi), 0.24 (27 H, s, $\mathrm{Me_3Si}$), 0.42 (6 H, s, $\mathrm{Me_2Si}$). Anal. Calcd for $\mathrm{C_{18}H_{54}Si_8}$: C, 43.64; H, 10.99. Found: C, 43.36; H, 11.27. The IR, mass, and ^{1}H NMR spectra of **19** were identical with those of the starting compound.

Isomerization of 17. A mixture of 1.02 g (2.06 mmol) of **17** and 0.06 g (0.45 mmol) of anhydrous aluminum chloride in 5 mL of benzene was refluxed for 10 h. To this was added 5 mL of 3.7 M methylmagnesium bromide–ether solution. The mixture was refluxed for 6 h and hydrolyzed with hydrochloric acid. The organic layer was washed with water to neutral. VPC analysis of the reaction mixture showed it to consist of **18** and **19** in the ratio of 81:19.

Isomerization of Eicosamethylnonasilane (20). A mixture of 1.89 g (3.41 mmol) of **20** and 0.27 g (2.03 mmol) of anhydrous aluminum chloride in 10 mL of benzene was refluxed for 12 h. After addition of 10 mL of 3.7 M methylmagnesium bromide and 10 mL of THF to the reaction mixture, the resulting solution was refluxed for 5 h. The mixture was hydrolyzed with dilute hydrochloric acid, and the organic layer was washed with water to neutral. The solvent was evaporated and the residue was distilled under reduced pressure (1 mm) to give 1.50 g (79% yield) of the products. VPC analysis of the products showed the presence of **21** and **22** in the ratio of 4:1. For **21**: mp 75~76 °C; mass spectrum, *m/e* 552 ($\mathrm{M^+}$); ^{1}H NMR spectrum δ 0.32 (18 H, s, $\mathrm{Me_3Si}$), 0.35 (30 H, s, $\mathrm{Me_3Si}$ and MeSi), 0.38 (6 H, s, $\mathrm{Me_2Si}$), 0.40 (6 H, s, $\mathrm{Me_2Si}$). Anal. Calcd for $\mathrm{C_{20}H_{60}Si_9}$: C, 43.40; H, 10.93. Found: C, 43.18; H, 10.81. For **22**: mp 170~172 °C; mass spectrum, *m/e* 537 ($\mathrm{M^+ - 15}$); ^{1}H NMR δ 0.35 (54 H, s, $\mathrm{Me_3Si}$), 0.50 (6 H, s, $\mathrm{Me_2Si}$). Anal. Calcd for $\mathrm{C_{20}H_{60}Si_9}$: C, 43.40; H, 10.93. Found: C, 43.23; H, 10.78.

Isomerization of Docosamethyldecasilane (23). A mixture of 1.30 g (2.13 mmol) of **23** and 0.19 g (1.43 mmol) of anhydrous aluminum chloride in 20 mL of benzene was refluxed for 5 h. To this was added 10 mL of 1.5 M methyllithium–ether solution at room temperature. The

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mixture was refluxed for 2 h and hydrolyzed with water. The solvent was evaporated and the residue was distilled under reduced pressure (1 mm) to give 1.29 g (99% yield) of **24**. VPC analysis of the distillate showed a single peak: mp 225~226 °C after recrystalization from ethanol-benzene (25:8); mass spectrum, *m/e* 610 (M^+); ^1H NMR δ 0.24 (54 H, s, Me_3Si), 0.37 (12 H, s, Me_2Si). Anal. Calcd for $C_{22}H_{66}Si_{10}$: C, 43.20; H, 10.88. Found: C, 42.98; H, 11.27.

Isomerization of Tetracosamethyldodecasilane (25). A mixture of 1.06 g (1.46 mmol) of **25** and 0.09 g (0.68 mmol) of anhydrous aluminum chloride in 10 mL of benzene was refluxed for 5 h. After addition of 10 mL of 1.5 M methyllithium–ether solution to the mixture, the reaction mixture was refluxed for 2 h. The mixture was hydrolyzed with water as usual way. The solvent was evaporated and the residue was distilled under reduced pressure to give 1.00 g (95% yield) of crystals of **26**: mp 236 °C after recrystalization from ethanol–benzene (25:8); mass spectrum, *m/e* 726 (M^+); ^1H NMR δ 0.37 (54 H, s, Me_3Si), 0.48 (12 H, s, Me_2Si), 0.54 (12 H, s, Me_2Si). Anal. Calcd for $C_{26}H_{78}Si_{12}$: C, 42.90; H, 10.80. Found: 42.62; H, 10.92.

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Nucleophilic Addition to Olefins. 5.[1] Reaction of 1,1-Dinitro-2,2-diphenylethylene with Water and Hydroxide Ion in 50% Me_2SO–50% Water. Complete Kinetic Analysis of Hydrolytic Cleavage of the C=C Double Bond in Acidic and Basic Solution

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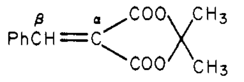
Abstract: Hydrolysis of 1,1-dinitro-2,2-diphenylethylene (**2**) to form benzophenone and dinitromethane (or its anion) was studied in 50% Me_2SO–50% H_2O and also in 50% Me_2SO–50% D_2O. Experiments were conducted over a pH range from ~1 to ~16. The data can be interpreted by Scheme I. Solvent isotope effects, observation of general acid and general base catalysis, and structure–reactivity relationships were used to assign rate-limiting steps under various conditions and to probe into the mechanistic details of the various steps. The major conclusions are the following. (1) The equilibrium constants for OH^- and water addition to **2** to form T_{OH}^- (Scheme I) are of comparable magnitude to those for the corresponding reactions of benzylidene Meldrum's acid (**1**), but the *rate* constants are much lower for **2** than for **1**. This indicates a higher intrinsic kinetic barrier for the nitro-activated olefin and fits into a previously reported pattern, according to which activating substituents that are most effective in delocalizing negative charge lead to the highest kinetic barrier. (2) Carbon protonation of T_{OH}^- follows an Eigen curve similar to that for 1,1-dinitroethane anion (Figure 7) but which is displaced upward by nearly 1 log unit. This indicates a higher intrinsic protonation rate because of a smaller charge delocalization in T_{OH}^- owing to an enhanced steric hindrance to coplanarity of the nitro groups in T_{OH}^-. (3) Intramolecular proton transfer from the OH group to the carbanionic site in T_{OH}^- (k_i in Scheme I) is insignificant, which is in contrast to the behavior of the addition complex between **2** and morpholine. (4) The base-catalyzed breakdown of T_{OH}^0 into benzophenone and dinitromethane anion occurs by rate-limiting oxygen deprotonation (k_3^B, k_3^{OH} in Scheme I), which implies that k_4 for $CH(NO_2)_2^-$ departure from T_{OH}^{0-} is $\gg 2 \times 10^9\ s^{-1}$, a remarkably high rate for a carbanionic leaving group. The water-catalyzed breakdown of T_{OH}^0 proceeds by a different mechanism, which is most likely concerted, with a transition state as **8** or possibly **9**. (5) The acid-catalyzed breakdown of T_{OH}^{2-} occurs by rate-limiting carbon protonation (k_6^{BH} in Scheme I), but the water-catalyzed breakdown follows a different mechanism. Various possibilities are discussed, and a slight preference is given to a preassociation mechanism (Scheme III).

Recently we reported a study of the hydrolysis of benzylidene Meldrum's acid (**1**) which leads to a cleavage of the C=C double bond and the formation of benzaldehyde and Meldrum's acid.[2] The reaction involves four consecutive steps: (1) OH^- or water attack on the β carbon to form an addition complex T_{OH}^-, (2) protonation of the α carbon of T_{OH}^- to form T_{OH}^0, (3) deprotonation of the OH group of T_{OH}^0 to form the tetrahedral intermediate T_{OH}^{0-}, (4) breakdown of T_{OH}^{0-} into benzaldehyde and the anion of Meldrum's acid. Rate constants for the first three steps could be determined, while that for the last step was estimated to be $\geq 10^{10}\ s^{-1}$. This latter value is remarkably high for the departure of a carbanionic leaving group from a tetrahedral intermediate but was accounted for by the low basicity of the carbanion[2] (pK_a value of Meldrum's acid is 4.83).



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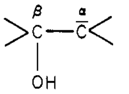

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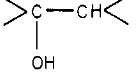

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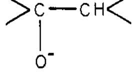

T_{OH}^{0-}

It seemed of interest to investigate other cases in order to ascertain whether this high rate of carbanion departure is particular to **1** or whether it is a general phenomenon.[3] A system

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