Journal of Organometallic Chemistry, 410 (1991) 1–12
Elsevier Sequoia S.A., Lausanne
JOM 21746

Dearylation of α,ω-diphenylpermethylated oligosilanes with triflic acid

Karen E. Ruehl and Krzysztof Matyjaszewski *

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213 (USA)

(Received October 18th, 1990)

Abstract

The relative rates of displacement of phenyl groups for a series of α,ω-diphenylpermethylated oligosilanes with the formula $Ph(SiMe_2)_nPh$ ($n = 2–5$) were studied. Triflic acid was utilized in the displacement reactions which occur as a two-step process with protonation at the *ipso*-carbon atom as the rate limiting step. The results showed the displacement of the first phenyl group is more facile than the second group. The largest difference in reactivities is found for the disilane. Competitive displacement reactions between various oligomers were analyzed to establish the influence of the chain length of oligosilanes on the relative reactivities of the terminal phenyl groups. Both the first and second phenyl group displacement reactions are faster for the longer chain oligomers than the shorter analogs. The ^{13}C NMR spectra of the oligosilanes indicate the highest electron density on the *ipso*-carbon atoms in the disilane, in contrast to its lowest reactivity. This is interpreted by the increased stabilization of the positive charge in the transition state with an increase in the chain length. Thus, the reactivities of oligosilanes are governed by the structures of the transition states rather than the ground states.

Introduction

Polysilanes have unique electronic properties. The sigma catenated system absorbs in the ultraviolet. As the number of silicon atoms in the chain increases, up to approximately 50 catenated silicons, the UV absorption shifts bathochromically [1]. The delocalization of electrons in the backbone resembles the behavior of polyenes. The absorption phenomena have been extensively studied and explained by the electronic delocalization in various substituted polysilanes [2]. On the other hand, chemical reactivity as a function of electronic delocalization and catenation length has not been thoroughly studied.

Model compounds are necessary to understand the reactivity differences for silicon chains with various lengths. Boberski and Allred [3] studied a nucleophilic substitution reaction on α,ω-dichloro permethylated silanes. Each member of the series, the disilane to the hexasilane, was allowed to react with one equivalent of methylmagnesium iodide. Statistically, if the rate constant of the first displacement reaction, k, is equal to the second rate constant, k', the monofunctionalized product should be formed in 50% yield at equimolar conditions. The concentration

0022-328X/91/$03.50

of the monofunctionalized product for each of the oligosilanes exceeded 50% of the total concentration; therefore the unreacted oligomers are more reactive than the monofunctionalized compounds. The highest concentration of monofunctionalized product was found for the hexasilane, whereas the lowest was found for the disilane. The difference in the reactivities of the unreacted and the monofunctionalized compounds was found to be dependent upon the chain length and explained by through-bond interactions between the two chain ends, either chloro/chloro or chloro/methyl. The through-bond interactions between remote ends which increase with the chain length has been supported by ^{1}H NMR spectroscopy [4] as well as a reduction potential studies [5]. Differences in reactivity have been explained by different electronic ground states for each of the oligomers.

West et al. [6] studied the α,ω-dichloro permethylated silane series by ^{13}C and ^{29}Si NMR spectroscopy. In contrast to the results of Boberski and Allred, it was found that the effect of the chlorine was attenuated along the silicon chain. The effect was negligible when four atoms away from the halogen. The NMR data reported no long range electronic transmission from chlorine in halopermethyloligosilanes. This ruled out the ground states as responsible for the reactivity differences.

The dearylation of arylsilanes with trifluoromethanesulfonic acid (triflic acid) has previously been studied [7]. Recently, it was reported that in the reaction of 1,2-diphenyltetramethyldisilane with triflic acid the rate of the first phenyl displacement is faster than the second [8]. In order to correlate the reactivities of oligomeric silanes with their chain length, a series of electrophilic substitution reactions (protodesilylation) with triflic acid for oligomers of various length with the formula $Ph(SiMe_2)_nPh$ ($n = 2$–5) were performed. The chain length, as well as the terminal group, strongly affects the relative substitution rates for all oligosilanes.

Experimental

Preparation of $C_6H_5(SiMe_2)_nC_6H_5$, $n = 2$–5

To a 1000 ml, 1-neck reaction flask fit with a septum, 600 ml of dry THF, $C_6H_5SiMe_2SiMe_2Cl$ [9] (60 ml, 0.274 mol), and lithium (1.89 g, 0.274 mol) were added. The reaction was stirred under nitrogen and after two hours a light red color appeared [10,11]. The solution was stirred for an additional hour and the red color deepened. The solvent was removed using a rotary evaporator. The lithium salts were precipitated in benzene and filtered off. The benzene was evaporated leaving a residue, which according to ^{1}H NMR contained 1,2-diphenyltetramethyldisilane (10%), 1,3-diphenylhexamethyltrisilane (30%), 1,4-diphenyloctamethyltetrasilane (38%), and 1,5-diphenyldecamethylpentasilane (22%). The residue was separated by fractional distillation. Each of the oligosilanes has been analyzed by HPLC and UV. The maximum wavelength absorbance, extinction coefficients, and boiling points correlate well with literature values [12,13] and are given in Table 1. ^{1}H NMR chemical shifts of each oligosilane are given in Table 2.

Preparation of $(p\text{-}MeOC_6H_5)Me_2SiSiMe_2(p\text{-}MeOC_6H_5)$

Magnesium turnings (0.52 g, 0.02 mol) and 10 ml of THF were added to a flame-dried 3-neck reaction flask fit with a condenser, addition funnel, and a stopper. The flask was continuously purged with nitrogen. A solution of 1-bromo-

Table 1

Physical properties of various oligosilanes

	λ_{max} (nm)	ϵ ($mol^{-1} cm^{-1}$)	b.p. (m.p.) (°C)
$Ph(SiMe_2)_2Ph$	236.5	16,400	73/0.25 Torr
$Ph(SiMe_2)_3Ph$	242.0	18,630	133/0.25 Torr
$Ph(SiMe_2)_4Ph$	251.5	20,300	165/0.25 Torr
$Ph(SiMe_2)_5Ph$	255.0	20,600	190/0.001 Torr
$(p\text{-}MeOC_6H_5)Me_2SiSiMe_2(p\text{-}MeOC_6H_5)$	239.5	34,450	(44–46)
$(p\text{-}NO_2C_6H_5)Me_2SiSiMe_2(p\text{-}NO_2C_6H_5)$	295.5	17,650	(176–178)

4-methoxybenzene (2.7 ml, 0.02 mol) in 10 ml of THF was added via the addition funnel. The reaction mixture was heated until an exothermic reaction sustained refluxing. The reaction was stirred for 15 minutes under reflux. A solution of $ClMe_2SiSiMe_2Cl$ [14] (2 ml, 0.01 mol) in 10 ml of THF was added dropwise to the refluxing Grignard solution. The reaction mixture was stirred overnight and then filtered with a glass frit. The solvent and any volatile products were distilled off. ^1H NMR did not show any impurities in the residue (purity > 98%). The preparative yield was > 70%. Chemical shifts of the disilane are given in Table 2. The maximum wavelength absorbance, extinction coefficient and melting point of the disilane correspond to literature values [10] and are given in Table 1.

Preparation of $(p\text{-}NO_2C_6H_5)Me_2SiSiMe_2(p\text{-}NO_2C_6H_5)$

The intermediate, *p*-nitrophenyl lithium, was prepared using a modified literature procedure [15]. 100 ml of THF and 1-iodo-4-nitrobenzene (4.96 g, 0.02 mol)

Table 2

^1H NMR chemical shifts of various oligosilanes [a]

	$SiMe_2Ar$	$SiMe_2X$ [b]	$SiMe_2$
1 $Ph(SiMe_2)_2Ph$	0.40		
2 $Ph(SiMe_2)_2OTf$	0.57	0.59	
3 $TfO(SiMe_2)_2OTf$		0.78	
4 $Ph(SiMe_2)_3Ph$	0.35		0.15
5 $Ph(SiMe_2)_3OTf$	0.48	0.52	0.31
6 $TfO(SiMe_2)_3OTf$		0.72	0.46
7 $Ph(SiMe_2)_4Ph$	0.41		0.11
8 $Ph(SiMe_2)_4OTf$	0.46	0.58	0.22, 0.20
9 $TfO(SiMe_2)_4OTf$		0.69	0.41
10 $Ph(SiMe_2)_5Ph$	0.43		0.17, 0.08
11 $Ph(SiMe_2)_5OTf$	0.48	0.64	0.29, 0.24, 0.19
12 $TfO(SiMe_2)_5OTf$		0.68	0.39, 0.36
13 $(p\text{-}MeOC_6H_5)Me_2SiSiMe_2(p\text{-}MeOC_6H_5)$ [c]	0.38		
14 $(p\text{-}MeOC_6H_5)Me_2SiSiMe_2OTf$ [c]	0.57	0.58	
15 $(p\text{-}NO_2C_6H_5)Me_2SiSiMe_2(p\text{-}NO_2C_6H_5)$ [c]	0.47		
16 $(p\text{-}NO_2C_6H_5)Me_2SiOTf$		0.90	

[a] Aromatic protons of compounds No. 1, 2, 4, 5, 7, 8, 10, and 11 absorb as multiplets from 7.3 ppm to 7.5 ppm. [b] $X = CF_3SO_3-$, $p\text{-}MeOC_6H_5-$, or $p\text{-}NO_2C_6H_5-$. [c] Aromatic protons of compounds No. 13, 14, 15, and 16 yield AB-type pattern. Chemical shifts of aromatic protons are as follows: 6.85 ppm and 7.28 ppm (13), 6.90 ppm and 7.28 ppm (14), 7.48 ppm and 8.13 ppm (15), 7.89 ppm and 8.36 ppm (16).

were introduced into a one neck, 250 ml reaction flask fit with a septum and purged with nitrogen. The solution was cooled to − 110 ° C with an ethyl bromide/N_2 bath. The viscous mixture was stirred while phenyllithium (0.02 mol in 10 ml 70 : 30 cyclohexane : diethyl ether) was added dropwise. After the addition, the solution was stirred for additional 60 minutes. $ClMe_2SiSiMe_2Cl$ [14] (1.84 ml, 0.01 mol) was added slowly. After addition, the mixture was kept at − 110 ° C for 7 hours and then allowed to warm to room temperature where it was stirred overnight. The solvents were removed by evaporation and residue extracted with toluene. Toluene was evaporated and a solid residue extracted in boiling hexane, leaving a crystalline disilane (yield 2%, m.p. 176–178 ° C). No impurities were observed in ^{1}H NMR spectrum (purity > 98%). Chemical shifts of the disilane are given in Table 2. The product was characterized by HPLC and UV. The maximum wavelength absorbance and extinction coefficient are given in Table 1.

Preparation of $CF_3SO_3(SiMe_2)_nSO_3CF_3$, n = *2–5*

1. Isolated oligomer reactions. Each of the oligomers, $C_6H_5(SiMe_2)_nC_6H_5$, was dissolved in $CDCl_3$ in an NMR tube which was purged with nitrogen. Utilizing a microsyringe fit with a teflon tipped plunger, small increments, 0.5–1 μl, of triflic acid were added sequentially and a ^{1}H NMR spectrum after each step was obtained. Each individual reaction was completed in less than a minute. Also, the product distribution was found to remain constant for over an hour or until the next increment of acid was added. ^{1}H NMR shifts of the monofunctionalized and difunctionalized compounds are given in Table 2.

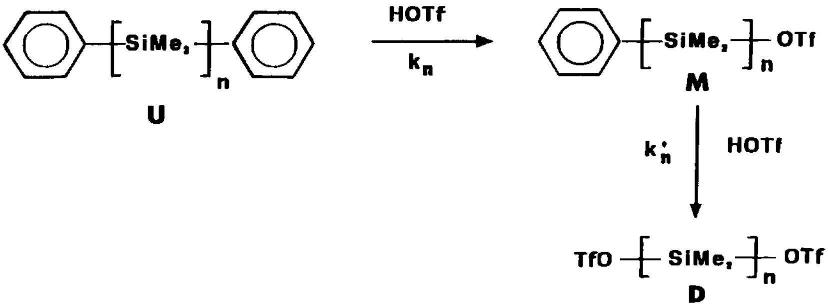
2. Competitive oligomer reactions. Two of the oligomers, $C_6H_5(SiMe_2)_nC_6H_5$, were dissolved in $CDCl_3$ in an NMR tube which was purged with nitrogen. Again, small increments, 0.5–1 μl, of triflic acid were added sequentially via a microsyringe fit with a teflon plunger and a ^{1}H NMR spectrum after each step was obtained.

3. Competitive reactions between various substituted disilanes. In an NMR tube purged with nitrogen, 1,2-diphenyltetramethyldisilane and 1,2-bis(*p*-methoxyphenyl)tetramethyldisilane were dissolved in $CDCl_3$. Small increments, 0.5–1 μl, of triflic acid were added sequentially with a microsyringe. A ^{1}H NMR spectrum after each step was obtained. The reactions were completed within less than a minute and the product distribution remained constant. The procedure was repeated for a competitive reaction between 1,2-diphenyltetramethyldisilane and 1,2-bis(*p*-nitrophenyl)tetramethyldisilane. For this competitive reaction, unreacted triflic acid was seen along with 1,2-bis(*p*-nitrophenyl)tetramethyldisilane after the completion of the faster reaction with 1,2-diphenyltetramethyldisilane. The ^{1}H NMR chemical shifts of the monofunctionalized products are given in Table 2.

Results

1. Isolated oligomer reaction

Reactions of triflic acid with diphenyloligosilanes were monitored by ^{1}H NMR. The overall reaction consisted of two consecutive steps (Scheme 1). The proportion of the unreacted (U), monofunctionalized (M), and difunctionalized (D) species were calculated from normalized ^{1}H NMR integrations for each increment of the added acid. Reactions were fast and complete in less than two minutes, no change in the spectra was observed after longer time. No unreacted acid was found for the



Scheme 1

acid/silane ratio less than 2. A small amount of impurities ascribed to silicon–silicon bond cleavage by acid were sometimes observed. The integration of the Si–Me region in each of the ^{1}H NMR spectra allowed for the determination of the relative proportion of species present. A proportion of unreacted, monofunctionalized, and difunctionalized species versus $[\text{acid}]_0/[\text{Ph(SiMe}_2)_n\text{Ph}]_0$ ratio was plotted for each compound in the series. Plots for each oligomer are given in Fig. 1. Points correspond to the experimental data, whereas the solid line correspond to calculated theoretical dependences for given k/k' ratios.

The theoretical plots were calculated for an array of rate constant ratios, k/k'. The unreacted α,ω-diphenyloligosilane has two phenyl groups to be displaced, whereas the monofunctionalized product has only one. Therefore, equal reactivity of phenyl groups in both compounds corresponds to $k/k' = 2$. Thus, as k/k' approaches 2, the maximum value for the monofunctionalized species approaches the value of 50% of the total concentration. If the unreacted oligomer reacts faster than the monofunctionalized product, then the proportion of the monofunctionalized product is greater than 50%. A master plot of k/k' versus maximum proportion of the monofunctionalized product is shown in Fig. 2. A higher proportion of the monofunctionalized product indicates a greater difference in the displacement rates. The first displacement is faster than the second for all oligomers. The disilane has the largest ratio of the rate constants as seen by the largest proportion of the monofunctionalized product. Table 3 gives the ratios of the rate constants for each of the oligomers.

A concentration of the monofunctionalized product greater than 50% in each of the above cases indicates, as in the Boberski and Allred study, that the monoproduct is less reactive than the unreacted starting material. The greater than 50% concentration in the case of Boberski and Allred [3] is due to the addition of an electron-donating group, methyl, to the silicon chain. The reaction is a nucleophilic substitution reaction which is therefore slowed by replacement of an electron acceptor, chlorine, by a donor. In the triflate case, the reaction is an electrophilic substitution reaction which is therefore retarded by the addition of an electron withdrawing triflate group.

The disilane has the largest maximum concentration for the mono-functionalized product. This trend is the opposite of that seen in the nucleophilic substitution reaction studied by Boberski and Allred [3]. They found the greatest ratio of reactivities for the longest chain analog. In the protodesilylation with triflic acid (electrophilic substitution), the shorter chains have the greatest reactivity ratio.

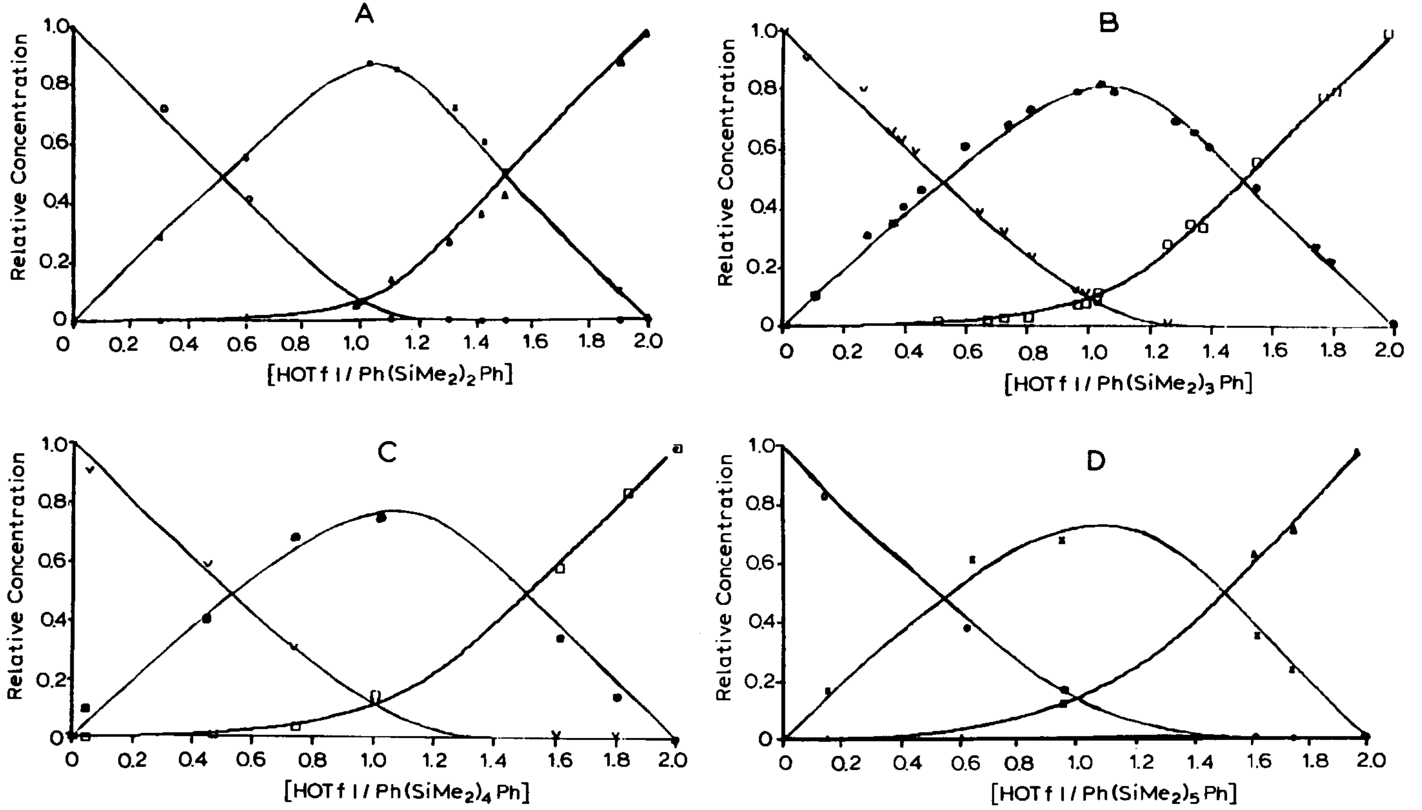


Fig. 1. Proportion of unfunctionalized, monofunctionalized, and difunctionalized species versus $[\text{acid}]_0/[\text{Ph(SiMe}_2)_n\text{Ph}]_0$ ratio for: (A) disilane, (B) trisilane, (C) tetrasilane, and (D) pentasilane in $CDCl_3$ at 25° C.

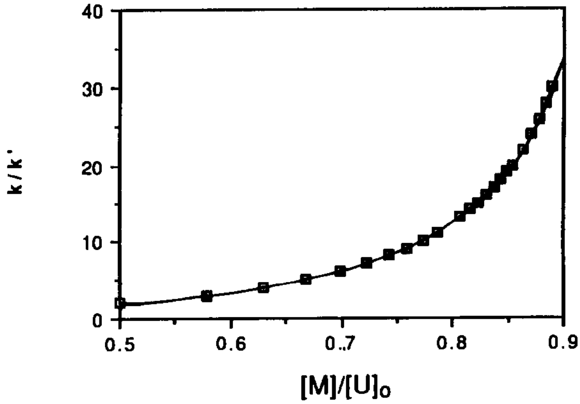


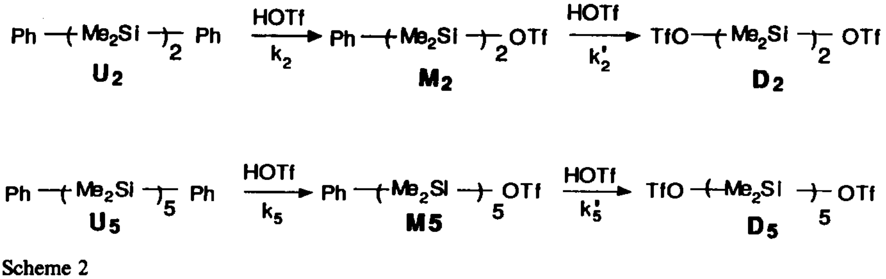
Fig. 2. Dependence of the maximum proportion of monofunctionalized product on the rate constant ratio.

2. Competitive oligomer reactions

In order to determine the relative reactivities of the various oligomers and their monofunctionalized products parallel reactions (Scheme 2) were run and monitored by ^{1}H NMR. Two members of the series were allowed to react simultaneously with triflic acid. The process is a set of two consecutive and competitive reactions. The reaction scheme is analyzed in two parts. The first part is the competitive reaction between two unreacted diphenyloligosilanes. A plot of the decreasing proportion of each of the unreacted species versus amount of triflic acid provides the ratio of the rate constants k_2 for the disilane and k_5 for the pentasilane (Fig. 3).

The reactivity of oligosilanes increases with the chain length. In each of the competitive reactions the longer chain analog is always more reactive than the shorter one. The largest ratio is observed for pentasilane and disilane ($k_5/k_2 = 1.5$).

The second part of the consecutive, competitive reactions study is the analysis of the relative reaction rates of formation of the difunctionalized products from the monofunctionalized compounds. This is, for example, a comparison of k_2' for the monofunctionalized disilane and k_5' for the pentasilane monoproducts. Again, all of the plots indicate that the longer oligomers are more reactive than their shorter chained counterparts (Fig. 4). The largest ratio is observed for the pentasilane and disilane ($k_5'/k_2' = 5$). This is in good agreement with the ratio predicted from the



$$\underset{\mathbf{U_2}}{\mathrm{Ph}-(\mathrm{Me_2Si})_2-\mathrm{Ph}} \xrightarrow[k_2]{\mathrm{HOTf}} \underset{\mathbf{M_2}}{\mathrm{Ph}-(\mathrm{Me_2Si})_2-\mathrm{OTf}} \xrightarrow[k_2']{\mathrm{HOTf}} \underset{\mathbf{D_2}}{\mathrm{TfO}-(\mathrm{Me_2Si})_2-\mathrm{OTf}}$$

$$\underset{\mathbf{U_5}}{\mathrm{Ph}-(\mathrm{Me_2Si})_5-\mathrm{Ph}} \xrightarrow[k_5]{\mathrm{HOTf}} \underset{\mathbf{M5}}{\mathrm{Ph}-(\mathrm{Me_2Si})_5-\mathrm{OTf}} \xrightarrow[k_5']{\mathrm{HOTf}} \underset{\mathbf{D_5}}{\mathrm{TfO}-(\mathrm{Me_2Si})_5-\mathrm{OTf}}$$

Scheme 2

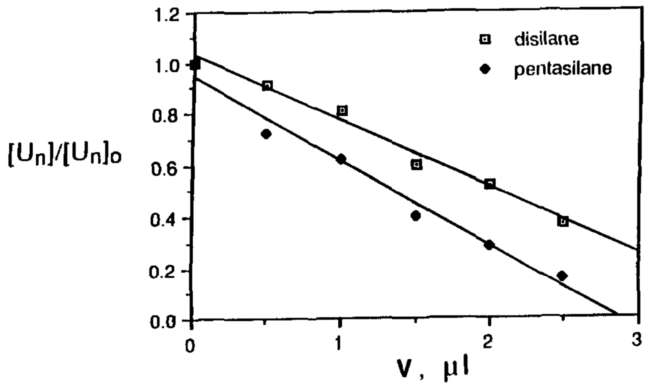


Fig. 3. Dependence of proportion of the unreacted silanes in the initial stage of the competitive reaction between 1,2-diphenyltetramethyldisilane and 1,5-diphenyldecamethylpentasilane with triflic acid in $CDCl_3$ at 25 °C on incremental acid additions.

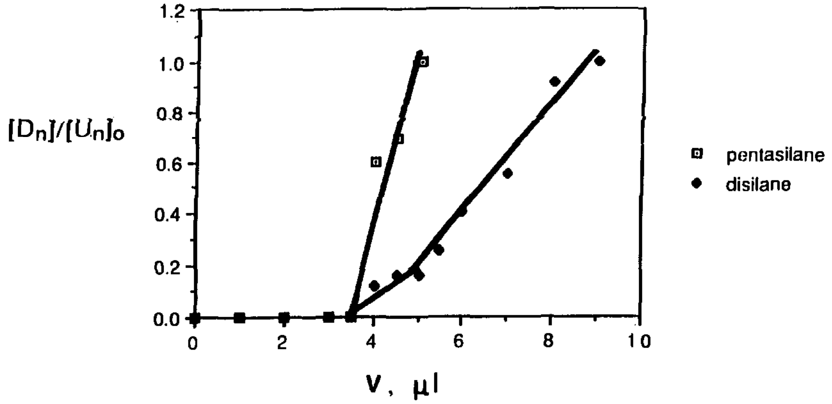


Fig. 4. Dependence of difunctionalized species in the competitive reaction between 1-phenyl-2-trifluoromethanesulfonyltetramethyldisilane and 1-phenyl-5-trifluoromethanesulfonyldecamethylpentasilane with triflic acid in $CDCl_3$ at 25 °C on incremental acid additions.

Table 3

Ratios of dearylation rate constants for various oligosilanes and comparison with the ratio of methylation rate constants

Oligomer	Max. % monoproduct	k_1/k_2	Allred [13], %
Disilane	87.0	23	58
Trisilane	81.0	13	67
Tetrasilane	77.5	10	82
Pentasilane	73.0	7	90 [a]

[a] Value for hexasilane. No data for pentasilane.

Table 4
^{13}C NMR chemical shifts of the *ipso*-carbon atoms for the α,ω-diphenylpermethylated oligosilane ($Ph(Me_2Si)_nPh$) series

n	*ipso*-carbon shift (ppm)
2	139.8
3	140.3
4	140.6
5	140.7

comparison of k_5/k_2 and the ratios given in Table 3 $[k_5'/k_2' = (k_5/k_2)(k_5'/k_5)(k_2/k_2') = 4.9]$.

3. ^{13}C NMR studies

Protodesilylation occurs usually as a two-step process with the protonation at the *ipso*-carbon atom as the rate-limiting step (cf. next section). Therefore, it has been assumed that the electron density at the attacked *ipso*-carbon atom could be correlated with the observed reactivities, if the found trend has its origin in the ground states. The chemical shifts in ^{13}C NMR move upfield for atoms with higher electron densities. Although it is difficult to separate diamagnetic and paramagnetic effects and to account for the change in the conformations of different oligomers, the monotonous trend and absence of odd–even effects suggest possibility of correlations of chemical shifts with electron densities.

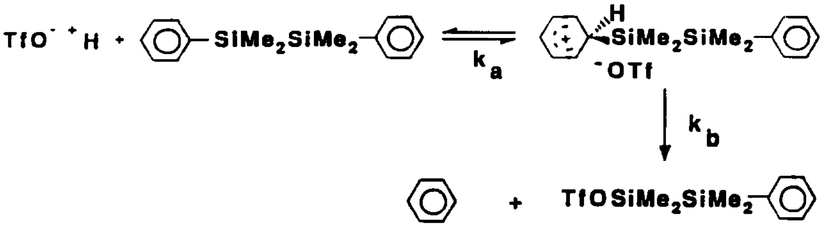
The *ipso*-carbon atoms of α,ω-diphenylpermethylated oligosilanes, as seen in ^{13}C NMR spectra, shift downfield with an increase in the silicon chain length (Table 4). This suggests that the electron density at the *ipso*-carbon atom is greatest for the disilane. Therefore, the disilane is predicted to be more reactive towards protonation than the other members in the series, in contrast to the experimental results. As described in the previous section in all cases the higher analog is more reactive than the shorter chain compound.

Two possible explanations for the observed discrepancies are possible. Either the electronic nature of the ground state is not responsible for reactivity differences, or the triflate anion is such a weak nucleophile that the protonation at the *ipso*-carbon atom is no longer the rate-determining step and the attack of the anion starts to control the overall reaction rate. In the latter case the positive charge on the *ipso*-carbon atom would be more stabilized for the disilane leading to its lower reactivity. This is discussed in the next section.

4. Reactivities of disilanes bearing various aryl groups

Eaborn [16] previously studied the displacement of an aryl group from a monosilane by acids much weaker than triflic acid and found it to be a two-step process. In the displacement of a phenyl group from trimethylphenylsilane by, for example, acetic acid the rate determining step is the protonation of the *ipso*-carbon atom by the acid. This step is followed by a facile attack of the strongly nucleophilic acetate ion on the silicon atom (Scheme 3).

The influence of the substituents in the aryl group was previously studied for protodesilylation under various conditions [16]. The rates increase with the introduction of *para* electron-donating substituents. The Yukawa–Tsuno [17] equation,



Scheme 3

$\log k_{rel} = \rho[\sigma + r(\sigma^+ - \sigma)]$ where $\rho = -5.3$ and $r = 0.65$ [16] for protodesilylation, was used to correlate the reactivity order with substituent structures.

Triflic acid is one of the strongest known protonic acids and triflate is one of the anions with the weakest nucleophilicity. Thus, the protonation at the *ipso*-carbon atom could no longer be the rate-determining step and the attack of the anion could start to control the overall reaction rate.

In order to establish the rate-determining step for the reactions of triflic acid with the oligomeric silane the following disilanes were studied: 1,2-bis(*p*-methoxyphenyl)tetramethyldisilane, 1,2-diphenyltetramethyldisilane, and 1,2-bis(*p*-nitrophenyl)-tetramethyldisilane. They were competitively reacted with triflic acid in order to determine the relative rates of dearylation. The reactions were monitored by ^{1}H NMR and the relative reaction rates were compared.

1,2-Bis(*p*-methoxyphenyl)tetramethyldisilane was found to be more than 10^2 times more reactive than 1,2-diphenyltetramethyldisilane. Also, the monofunctionalized *p*-methoxy compound is 11 times more reactive than the unreacted diphenyl compound. 1,2-Bis(*p*-nitrophenyl)tetramethyldisilane was found to be much less reactive than the diphenyl compound. By ^{1}H NMR it appears that the diphenyl compound was completely reacted before the dinitro compound reacted. Also, it should be noted that unreacted triflic acid is observed in contrast to all other experiments. The major product of the reaction between the dinitro compound and triflic acid is (*p*-nitrophenyl)dimethylsilyl triflate which is formed by silicon–silicon bond cleavage. Protonation at the *ipso*-carbon atom results in a minor product. Thus, the presented results indicate that the protonation step is the rate-determining step in the reaction of various disilanes with triflic acid. The relative rates of reactions using triflic acid are in agreement with the literature value of $\rho = -5.3$ [16] which was determined for weaker acids.

Discussion

The studies of the displacement of phenyl groups with triflic acid for α,ω-diphenylpermethylated oligosilanes with the formula $Ph(SiMe_2)_nPh$ ($n = 2$–5) lead to the following conclusions:

1. Dearylation of the first phenyl group is faster than the second phenyl group. The ratio of the rate constants k/k' decreases from 23 to 7 on passing from disilane to pentasilane, nevertheless the substitution of the phenyl group by triflate group at the remote chain ends affects the observed rate constants. This parallels to some extent previous results described by Allred and Boberski who found large rate

constant differences in the reaction of α,ω-dichloropermethylated oligosilanes with Grignard reagents. However, the effect of the chain length is opposite to that reported previously.

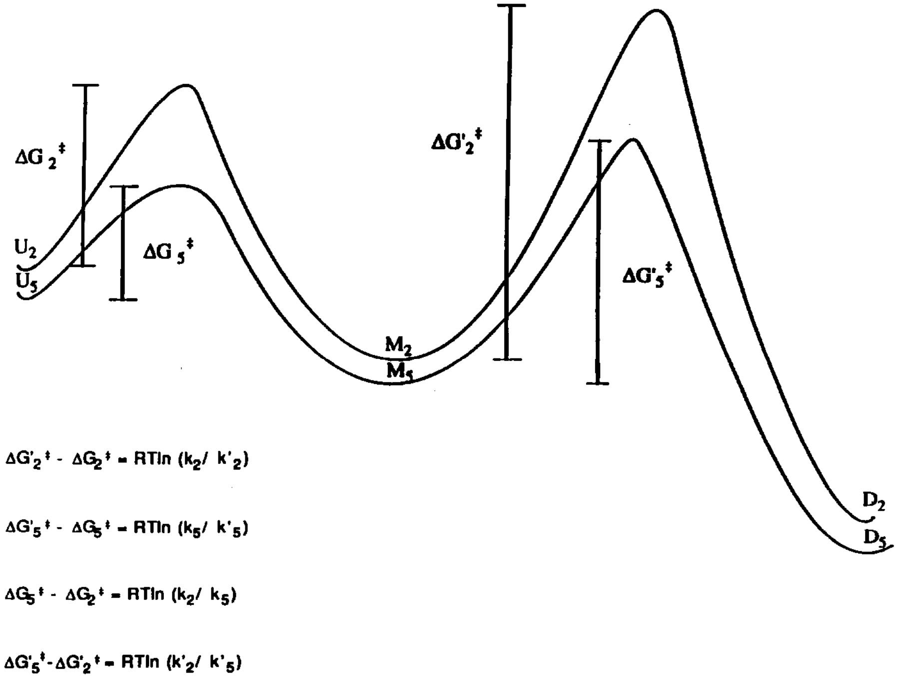
2. Relative rates of protodesilylation reactions increase with the chain length. This is in contrast to previously reported results [3].

3. Electron density on the *ipso*-carbon atoms deduced from the ^{13}C NMR chemical shifts decreases with the chain length in contrast to the increasing reactivities.

4. Dearylation is faster for compounds with electron donating *para* substituents in agreement with the previous studies for acids which are weaker acids than triflic. This indicates that the protonation at the *ipso*-carbon atom is still the rate-determining step.

The reverse correlation of the electron densities with reactivities could indicate a change in the mechanism and shift of the rate-determining step from the protonation to the attack of weakly nucleophilic triflate. However, the much faster dearylation for the *p*-methoxy derivative than for the unsubstituted phenyl disilane, and nearly absence of dearylation for *p*-nitrophenyl disilane, confirmed protonation as the slowest step.

Therefore, one logical explanation for the observed trends in reactivities is that an energetic difference in transition states may determine the reaction rates. A catenated silicon chain can stabilize a partially positive charge. It has previously been shown that the longer silicon chains have a greater ability to stabilize a charge



$$\Delta G'_2{}^{\ddagger} - \Delta G_2^{\ddagger} = RT\ln (k_2/\ k'_2)$$

$$\Delta G'_5{}^{\ddagger} - \Delta G_5^{\ddagger} = RT\ln (k_5/\ k'_5)$$

$$\Delta G_5^{\ddagger} - \Delta G_2^{\ddagger} = RT\ln (k_2/\ k_5)$$

$$\Delta G'_5{}^{\ddagger} - \Delta G'_2{}^{\ddagger} = RT\ln (k'_2/\ k'_5)$$

Fig. 5. Energy diagram illustrating the ground states and transition states of 1,2-diphenyltetramethyldisilane and 1,5-diphenyldecamethylpentasilane and the corresponding monofunctionalized products.

[5,18]. Upon protonation with triflic acid in the electrophilic substitution reaction a positive charge is generated in the transition state. The charge is more easily stabilized by a longer silicon chain and therefore the longer chain analogs have a transition state of lower energy. The presence (or absence) of the electron-withdrawing (or electron-donating) group at the remote chain end has a strong influence on the stabilization of the charge in the transition state to a larger extent than in the ground state. Thus, the ground states of the unreacted and monofunctionalized compounds are thought to be less responsible than the transition states for the rate differences in the discussed reaction. In all of the oligomer reactions, the change in free energy for the first phenyl displacement is less than that of the second displacement. Thus, a monofunctionalized product build-up is observed. In the competitive reactions, the reactivity ratios of two oligomers are directly related to the differences in the change in free energies of activation (Fig. 5). Protodesilylation is an irreversible reaction. Therefore, a decrease in the free energy is shown for each step, although formally silyl triflates are more reactive than arylsilanes.

Acknowledgements

The financial support from the National Science Foundation for this work is acknowledged. K.M. is grateful for the support from ARCO, Hoechst Celanese, Eastman Kodak, PPG Industries, and Xerox Corp. within a Presidential Young Investigator Award.

References

1 P. Trefonas, R. West, R. Miller and D. Hofer, J. Polym. Sci., Polym. Lett. Ed., 21 (1983) 823.
2 R. Miller and J. Michl, Chem. Rev., 89 (1989) 1359.
3 W. Boberski and A. Allred, J. Am. Chem. Soc., 96 (1974) 1244.
4 W. Boberski and A. Allred, J. Organomet. Chem., 74 (1974) 205.
5 W. Boberski and A. Allred, J. Organomet. Chem., 88 (1975) 73.
6 R. West and D. Stanislawski, J. Organomet. Chem., 74 (1974) 205.
7 D. Habich and F. Effenberger, Synthesis, (1978) 755.
8 K. Matyjaszewski and Y.L. Chen, J. Organomet. Chem., 340 (1988) 7.
9 M. Kumada, M. Ishikawa and S. Maeda, J. Organomet. Chem., 2 (1964) 478.
10 M. Kumada, S. Sakamoto, and M. Ishikawa, J. Organomet. Chem., 17 (1969) 231.
11 K. Ruehl and K. Matyjaszewski, unpublished results.
12 H. Gilman, W.H. Atwell, and G.L. Schwebke, Chem. Ind. (London), (1964) 1063.
13 M. Kumada and K. Tamao, Adv. Organomet. Chem., 6 (1968) 19.
14 H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, Tetrahedron Lett., 45 (1966) 5493.
15 H.A. Brune, B. Stapp and G. Schmidtberg, J. Organomet. Chem., 307 (1986) 129.
16 C. Eaborn, J. Organomet. Chem., 100 (1975) 43.
17 Y. Tsuno, T. Ibato and Y. Yukawa, Bull. Chem. Soc. Jpn., 32 (1959) 960.
18 A. Diaz and R. Miller, J. Electrochem. Soc., 132(4) (1985) 834.