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Substitution Reactions at Silicon under Strongly Acidic Conditions: Ligand Metathesis between Methyltrichlorosilane and Octamethylcyclotetrasiloxane°

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ABSTRACT

A study of the reactions between methyltrichlorosilane ($MeSiCl_3$) and octamethylcyclotetrasiloxane (D_4) in the presence of trifluoromethanesulfonic acid (HOTf) showed that nucleophilic substitution in $CHCl_3$ solution at the trifunctional silicon was surprisingly slow in comparison with the rate of equilibration/polymerization of D_4. The reaction rate at $MeSiCl_3$ was significantly faster with water present and faster still in THF. In these reactions, there was no evidence for SiOH groups (^{29}Si NMR), even in the presence of excess water. The overriding criterion for relative reactivity toward nucleophilic substitution under strongly acidic conditions is the relative leaving group ability of the groups on silicon. Once $MeSiCl_3$ begins to participate in the redistribution reactions, mono- **3** *and tri-* **5**, *but not di-substituted* **4** *systems are formed ($MeSiCl_{3-x}(D_nSiMe_2Z$ (Z = OTf, Cl$))_x$, $x = 1, 3$), likely through an intramolecular reaction. The mechanisms of nucleophilic substitution at silicon under these conditions are discussed.*

INTRODUCTION

Chlorosilanes occupy a key position in silane and silicone chemistry due to their availability through the Rochow process [2]. They engage in a variety of reactions [3], arguably the most important of which, as it is the foundation of the silicone industry, involves nucleophilic substitution reactions with water and organosilanols [4] to form **Si–O**–Si bonds (Scheme 1).

$$R_3SiCl \xrightarrow[R' = H,\ SiR_2R'']{R'OH} HCl + R_3SiOR' \xrightarrow[R' = H]{R_3SiCl} R_3SiOSiR_3 + HCl$$

SCHEME 1

The reactivity of functional silanes, including chlorosilanes, toward nucleophilic substitution normally increases with increasing numbers of electronegative functional groups such as chloride [4]. For example, the relative reactivity of methylchlorosilanes toward alcoholysis was determined to decrease in the sequence $MeSiCl_3 > MeSi(OEt)Cl_2 > Me_2SiCl_2 > MeSi(OEt)_2Cl > Me_2Si(OEt)Cl > Me_3SiCl$ [5]. Kinetic studies of the hydrolysis reactions of phenyltrichlorosilane showed that the hydrolysis of the first chlorine atom of $PhSiCl_3$ was much faster than that of the remaining two [6].

Siloxanes, including polymeric linear diorganopolysiloxanes [polydimethylsilicones (PDMS)] and silicone cyclics such as octamethylcyclotetrasiloxane (D_4) can undergo reversible polymerization reactions in the presence of acids or bases [7]. These siloxy redistribution reactions are also nucleophilic substitutions. Although some controversy exists regarding the exact mechanism of polymerization, Chojnowski [8,9] and Sigwalt [10,11] and co-workers have suggested that the primary mech-

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°It is a pleasure to dedicate this paper to my father, Prof. Adrian Gibbs Brook, who has been a great inspiration.

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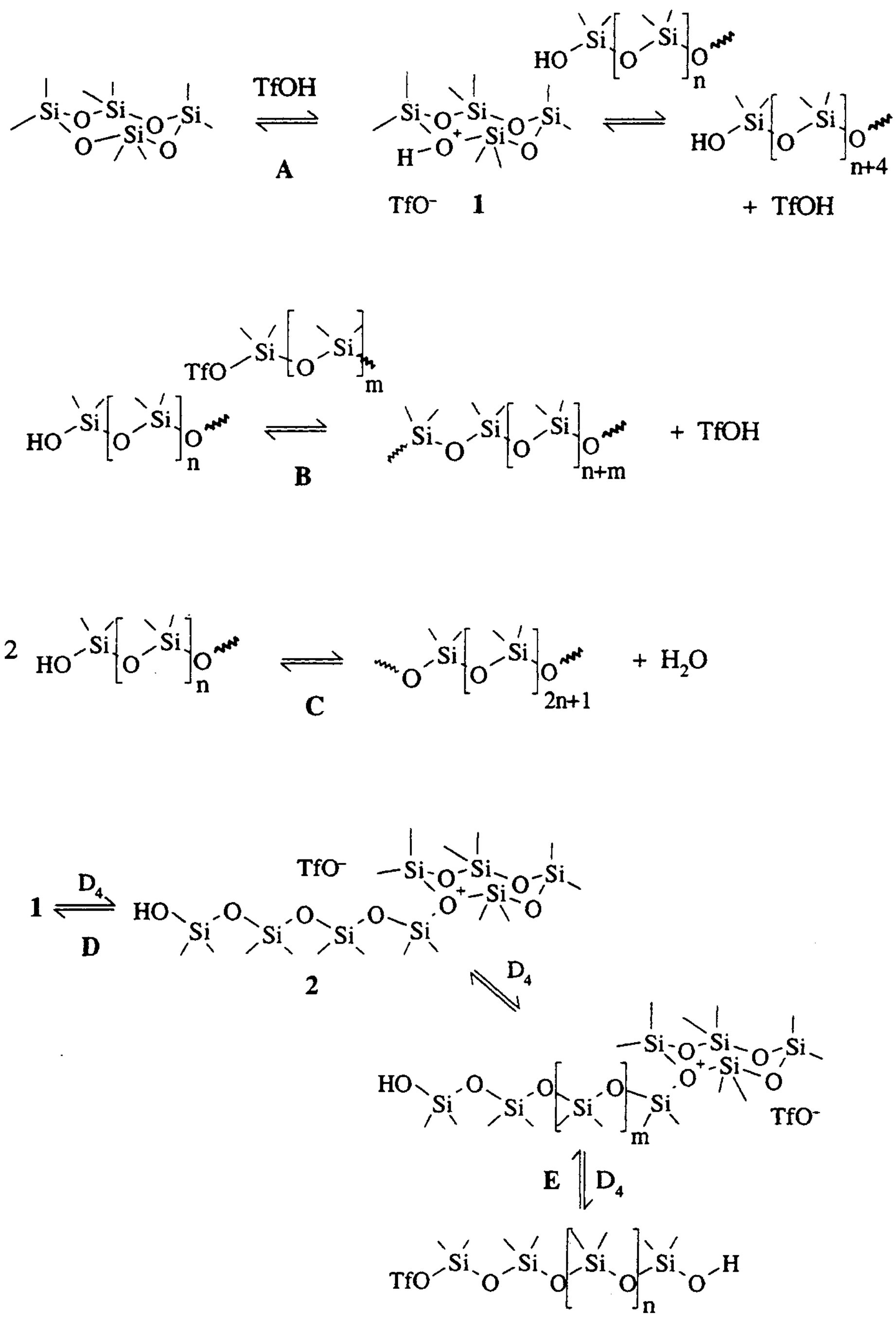
anisms of cationic polymerization initiated with triflic acid (HOTf) involve acid-catalyzed condensation, whereby protonation giving disiloxonium ion **1** is followed by silanol attack at an activated silicon center (Scheme 2A); additional condensation mechanisms involve silanol attack at silyltriflates (Scheme 2B) or condensation of two silanols giving water (Scheme 2C) [8,9]. Alternatively, ring-opening polymerization can occur by the nucleophilic attack of a disiloxane monomer on an active propagating center **1** to give higher molecular weight materials via a trisiloxonium ion **2** (Scheme 2D); as a result of "backbiting," both polymerization processes are reversible (Scheme 2E).

The combination of chlorosilanes (e.g., $MeSiCl_3$) and dimethylsiloxanes (e.g., D_4) can be used in the preparation of silicone resins and elastomers. However, the detailed chemistry of the reactions remains unclear [12]. During work attempting the metathesis of trihalosilanes with D_4 for the preparation of star polymers under acidic conditions [13], we found that, in the absence of

SCHEME 2



impurities, the reaction *rate* of the trifunctional species was significantly slower than the polymerization of the D units; small amounts of impurities tremendously affected the rate of nucleophilic substitution at Cl_3SiR and, additionally, the ultimate product distribution of these reactions. The object of the present article is to try to shed light on these reactions. Specifically, we chose to examine why the trifunctional silane is less reactive than the difunctional silane in $CHCl_3$, particularly given the enhanced reactivity to substitution normally associated with Si–Cl when compared with Si–O bonds [3,14]. We report our results on the nucleophilic substitution/metathesis reactions of polychlorosilanes and cycloorganosiloxanes in the presence of acidic catalysts, using $MeSiCl_3$ and D_4 as a model system.

RESULTS

The high sensitivity of chemical shifts to structural differences [15] makes ^{29}Si NMR a unique tool for providing detailed information on different silicon structural units [16], average chain lengths [17], and the degree of condensation [18] of silicon-containing compounds, including oligomers and polymers. Therefore, an examination of products by solution ^{29}Si NMR of the HOTf-catalyzed reactions between D_4 and $MeSiCl_3$ under a variety of experimental conditions was undertaken. The reaction conditions examined included the systematic variation of the reaction time, temperature, solvent, concentrations of both the reactants and the catalyst, and impurities, specifically water. Our particular interest was in the relative rate of reaction, although, in some cases, the reaction was allowed to equilibrate completely. The components of the mixtures were determined by comparison of chemical shift values with assignments reported in the literature [15–18] or previously made by us [19] (see Tables 1 and 2A and B); the relative concentration of each component was taken from the integration of peaks and reported as area % (see the Experimental section).

In the absence of catalysts, neither $MeSiCl_3$ nor D_4 underwent reaction over a period of 7 months at ambient temperature. When catalyzed by HOTf in $CDCl_3$, $MeSiCl_3$ reacted only reluctantly with D_4. Although the ring-opening polymerization and redistribution reactions of D_4 (Scheme 2) occurred immediately upon the addition of HOTf, even at 0°C, nucleophilic substitution at $MeSiCl_3$ by the dimethylsiloxy segments was extremely slow by comparison (>95% D_4 reacted, Tables 1 and 2, entries 1–4; for reaction conditions, see Table 3). Higher acid concentrations did not significantly alter this situation (Tables 1 and 2, entries 4–6).

The addition of water to the reaction mixture increased the rate of reaction at $MeSiCl_3$ (Tables 1 and 2, entries 7–9). The only observed products involved nucleophilic attack by disiloxanes; although water is another nucleophile present in solution, no SiOH-containing molecules were detected. Similarly, changing to the more coordinating solvent THF from $CDCl_3$ dramatically increased the reaction rate between $MeSiCl_3$ and D_4 (Tables 1 and 2, entries 10–13).

Once the $MeSiCl_3$ began to react, it could be seen that exchange of Cl for OSi ligands took place sequentially (Scheme 3). The major products observed were the mono- **3** and tri-substituted compounds **5**. The disubstituted product **4** represented less than 4% of the Me_2Si units in the reaction mixture irrespective of the degree of equilibration in the reaction (Table 1).

DISCUSSION

The commercial importance of silicones stimulated the investigation of their ligand redistribution reactions [20–24]. The equilibration between chlorosilanes and siloxanes has also been studied. This metathesis reaction is much less efficient and needs catalysts such as acids, quaternary ammonium halides, silicon selective nucleophiles [25], organometallic species, or high temperatures [26,27]. For example, PDMS reacts with dimethyldichlorosilane in sealed tubes at 380–400°C to produce D_3, D_4, and α-ω-dichlorooligodimethylsiloxanes [28]. The reactions of $RSiCl_3$ at 250–300°C with D_3 or D_4 were reported to result in formation of $Cl_2(R)Si(OSiMe_2)_{3m}Cl$ (R = Me, Et, C_6H_5 and $CH_2 = CH$) [29] and $Cl_2(R)Si(OSiMe_2)_4Cl$ (R = Et and C_6H_5) [30], respectively. Seminal ^1H NMR studies by Moedritzer [31] elucidated the distribution of products between D_4 and $MeSiCl_3$ at elevated temperatures with $AlCl_3$ catalysis.

Much less work has been done on the relative rates of these processes and the underlying mechanism(s) of nucleophilic substitution at silicon under strongly acidic conditions. In the gas phase, silylium ions are commonly observed [32]. However, in spite of recent reports of X-ray crystal structure data suggesting the existence of these ions in condensed phases [33], evidence for S_N1 reactions in silicon systems is extremely weak.

The available nucleophilic substitution mechanisms are bimolecular and may involve S_N2-type reactions in which the reaction passes through a transition state analogous to the reaction at carbon or formation of a pentacoordinate intermediate (Scheme 4); the redistribution of ligands between two silicon atoms may be a sequential (Scheme 4A) or concerted (Scheme 4B) nucleophilic substitution reaction at both silicon centers.

Recent mechanistic studies of the solvolysis of silyl ethers [34] in buffered polar protic solvents indicate that the reaction occurs by an S_N2 process in which the leaving group is assisted by acid, and the nucleophile by base, in solution. In contrast, in

TABLE 1 The Compositions of the Trifunctional Silicon Moieties (T Units) in the Mixtures of D_4 and $MeSiCl_3$ in the Presence of HOTf under Various Conditions (Given as Relative % T Units, Total = 100)[a]

Entry	$Me\mathbf{Si}Cl_3$	$(Me\mathbf{Si}Cl_2)_2$ (Dj) ***3***	$Me\mathbf{Si}Cl_2$ (D_mM^Z) ***3***	$Me\mathbf{Si}Cl$ $(-D_mM^Z)_2$ ***4***	$Me\mathbf{Si}(-D_n-)$ (D_mM^Z) ***5***	$Me\mathbf{Si}(-D_mM^Z)_3$ ***5***	*D_4 for Comparison*[b]
^{29}Si NMR (ppm)	12.2[c]	−17.4	−19.3(m)	−46.1(m)	−65.3(m)[c] −66.2(m)	−67.0 −67.2(m)	−19.4
1	93.1	1.8	5.1	—	—	—	3.9
2	70.4	6.5	18.7	—	—	4.4	1.8
3	26.9	3.1	27.2	3.9	15.7	23.2	1.1
4	40.5	7.2	39.3	0.7	—	12.3	1.4
5	72.5	3.4	4.3	—	7.3	12.5	8.4
6	71.8	5.5	10.1	0.1	4.7	7.8	0.8
7	63.7	2.8	25.2	—	2.1	6.2	ol[d]
8	*18.6*	*5.7*	*32.2*	*2.7*	*14.3*	*26.5*	*5.1*
9	*20.6*	*5.7*	*30.1*	*1.9*	*10.3*	*31.4*	*7.1*
10	*77.1*	—	*19.1*	—	—	*3.8*	*ol*
11	—	*0.1*	*12.0*	—	*30.7*	*57.2*	*1.9*
12	*58.5*	*0.6*	*38.2*	—	—	*2.5*	*ol*
13	—	*7.1*	*11.4*	—	*49.1*	*33.4*	*21.3*

[a] The chemical shifts of ^{29}Si of the **bold** silicon atom; the conditions of the entries are the same as listed in Table 3.
[b] The numbers given reflect % of total D units.
[c] Refers to multiplet.
[d] ol = overlapped signal.

nonsolvolytic processes (aprotic solvents) and with electronegative leaving groups such as chloride, substitution appears to occur via a pentacoordinate intermediate in which both the leaving group and incoming nucleophile occupy apical positions (Scheme 4A) [35,36]. This pentacoordinate species, particularly in the presence of silaphiles such as F^-, RO^- [37], DMF, DMSO, *N*-methylimidazole [38], etc., may be subject to further nucleophilic attack [39,40] or may decompose to the tetracoordinate product with stereochemical inversion (essentially a stepwise S_N2 reaction).

Several factors are known to increase the relative reactivity of a silicon center toward substitution. In particular, the rate of substitution [35] increases with the following: increasing numbers of electron withdrawing groups; reduced steric size of spectator groups on silicon; nucleophilicity of the incoming nucleophile; and the electronegativity of the leaving group (good leaving groups include the halogens, nitrogen ligands, and, to a lesser extent, oxygen ligands).

As a general rule, therefore, a trifunctional silicon species should be more reactive toward nucleophilic substitution than a difunctional species on the basis of the factors just given. Although Cl is less electronegative than O [41], the presence of three electronegative groups would be expected to make $MeSiCl_3$ much more reactive than D_4 toward nucleophilic substitution and, therefore, ligand redistribution reactions. Furthermore, it is well known that the reactivity of chlorosilanes toward oxynucleophiles is far higher than that of polysiloxanes (consider, for example, the difference in reactivity of dimethyldichlorosilane and D_4 with water). The experimental data in $CHCl_3$ as solvent is inconsistent with this expectation. In order to establish possible reasons for this, it is necessary to examine more carefully the experimental conditions used.

The Reaction Course in Nonpolar Solvents

The Active Nucleophile. In the equilibration of D_4 in $CHCl_3$ with TfOH as catalyst, with or without the presence of $MeSiCl_3$ *or water* (adventitious or added), silanol signals ($\sim Me_2Si{-}O{-}\mathbf{SiMe_2OH}$) were absent; the only end groups present in the reaction media were $\sim Me_2Si{-}O{-}\mathbf{SiMe_2Cl}$ and $\sim Me_2Si{-}O{-}\mathbf{SiMe_2OTf}$ (Table 2A). This indicates that the silanol groups in such systems are the most reactive nucleophiles toward condensation reactions, consistent with the work of Wilczek et al. [9]. The other nucleophiles in solution are TfO^-, water, and disiloxane units (and eventually Cl^-).

Leaving Groups. In the presence of strong acid, protonation of Cl or O significantly improves the leaving group ability of the respective group (Scheme 5A). In the absence of additional water or coordinating solvent (e.g., THF), the disiloxane oxygens or silanols, being more basic, successfully compete with Cl for the protons. That is, the steady state concentration of **6** and **7** (Scheme 5A) will be relatively high compared with that of **8** and **9**. Nucleophilic attack will thus occur preferentially at silicon atoms for which the leaving groups are pri-

TABLE 2 The Compositions of the Difunctional Silicon Moieties (D Units) in the Mixtures of D_4 and $MeSiCl_3$ in the Presence of HOTf under Various Conditions Distal from T Units (Given as Relative % D Units, Total = 100)[a]

Entry	D_4	D–**M**^{Cl}	D–**M**^{OTf}	D–**D**–M^{OTf}	**D**–D–M^{OTf}	D–**D**–M^{Cl}	**D**–D–M^{Cl}	**D**–D_2–IM^Z Z = Cl, OTf	D_n	Me_2SiCl_2
^{29}Si NMR (ppm)	−19.4	3.2	−3.4	−17.7	−21	−21.4	−21.6	−21.7	−22.3	31.8
A	7.4	—	5.3	5.1	—	4.2	ol	12.0	66.0	—
B	8.3	—	4.2	4.7	—	4.8	ol	12.0	66.0	—
1	3.9	1.8	0.6	0.6	0.6	1.3	.4	8.6	64.1	—
2	1.8	2.8	—	—	—	4.9	7.7	ol[b]	71.9	—
3	1.1	6.2	0.3	0.4	0.6	7.7	7.8	ol	62.9	—
4	1.4	2.1	0.8	1.1	0.8	5.9	8.2	ol	66.0	—
5	8.4	5.4	0.7	0.9	ol	9.6	11.8	ol	45.8	—
6	0.8	3.2	1.6	1.5	ol	8.8	13.4	ol	49.1	—
7	5.1	2.1	0.5	0.5	ol	9.4	11.5	ol	51.4	—
9	7.1	6.7	0.6	0.6	ol	8.6	7.9	ol	50.3	—
10	ol	2.6	—	—	—	12.4	ol	36.8	29.3	—
11	1.9	8.3	—	—	—	ol	ol	30.1	20.1	0.1
13	21.3	20.2	—	—	—	ol	ol	ol	34.8	0.4

[a] The chemical shift of the strongest signal of a multiplet is quoted.
[b] ol = overlapped signal.

TABLE 2B The Compositions of the Difunctional Silicon Moieties (D Units) in the Mixtures of D_4 and $MeSiCl_3$ in the Presence of HOTf under Various Conditions Proximate to T Units (Given as Relative % D Units, Total = 100)[a]

Entry	*D_4 for Comparison*	*MeSiCl (**D**–D_2–)$_2$*	*$MeSiCl_2$–**D**–D*	*$MeSiCl_2$–D–**D***	*MeSiCl(D–**D**–D–)$_2$*	*MeSiCl (D_2–**D**–D_n)$_2$, MeSi (D_2–**D**–D_n)$_3$*
^{29}Si NMR (ppm)	−19.4	−19.6	−20.9	−21.3	−21.5	−22
1	3.9	2.7	1.4	0.7	2.7	9.5
2	1.8	2.2	0.3	ol[a]	ol	8.4
3	1.1	5.0	0.6	0.4	ol	7.0
4	1.4	2.7	0.7	ol	ol	10.3
5	8.4	ol	2.5	ol	ol	14.9
6	0.8	5.8	2.3	ol	ol	13.5
7	5.1	ol	3.4	ol	ol	16.1
9	7.1	ol	2.1	ol	ol	16.1
10	ol	ol	ol	ol	ol	18.9
11	1.9	15.8	—	—	23.7	ol
13	21.3	ol	—	—	23.3	ol

[a] ol = overlapped signal.

marily oxygen based; the rate at $MeSiCl_3$ is much slower. Under these circumstances, the trifunctional silane *is less reactive* than the difunctional silane.

Solvent Effects. The replacement of $CDCl_3$ by THF as the solvent led to a very much increased reactivity of $MeSiCl_3$ when compared with the disiloxanes. This is in accord with the previous proposal. Improved solvation of the protons by solvent, in essence lowering the concentration of **6** and **7**, increases the rate of attack at the trifunctional silane (Scheme 5B; see Tables 1 and 2, entries 10 and 12 vs. 1 and 2).

The presence of added water similarly led to an increased participation of $MeSiCl_3$ in the reaction (see Table 1, entries 7–9 and 12–13). This is the result both of the presence of better nucleophiles (H_2O and silanols) in solution and, by virtue of the enhanced basicity of H_2O with respect to $R_3SiOSiR_3$, less effective proton catalysis. Once in solution, Cl^- is a competitive nucleophile with TfO^-, as evidenced by the presence of both Cl and TfO terminated linear silicone chains.

Under the conditions of Lewis basic (co)solvents (THF and/or H_2O), the usual enhanced reactivity of tri- with respect to difunctional silanes is observed when the leaving groups are the same [4,5]. This can be most clearly seen from the production of dimethyldichlorosilane from the mixture of

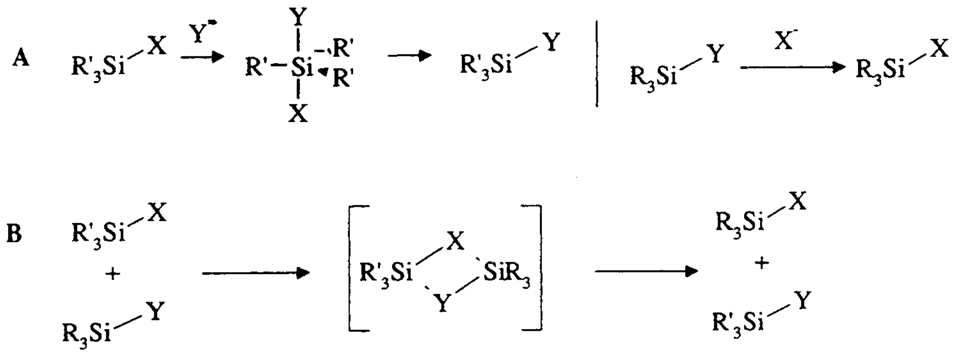
TABLE 3 Experimental Conditions for the Reactions on the Other Tables

Entry	*Solvent*	*D_4 (mM)*	*$MeSiCl_3$ (mM)*	*TfOH (mM)*	*H_2O (mM)*	*Temperature (°C)*	*Time (h)*
A	$CDCl_3$	2.13	—	66	—	0	17
B	$CDCl_3$	PDMS 2.38[a]	—	66	—	25	173
1	$CDCl_3$	2.55	0.85	66	—	0	18
2	$CDCl_3$	2.55	0.85	66	—	25	336
3	$CDCl_3$	2.55	0.85	66	—	25	840
4	$CDCl_3$	2.55	0.85	66	—	75	20
5	$CDCl_3$	1.70	2.27	90	—	75	19
6	$CDCl_3$	1.70	2.27	180	—	75	19
7	$CDCl_3$	2.55	0.85	66	0.093	25	2
8	$CDCl_3$	2.55	0.85	66	0.093	45	75
9	$CDCl_3$	2.55	0.85	66	0.14	25	840
10	THF	2.55	0.85	66	—	25	18
11	THF	2.55	0.85	66	—	45	90
12	THF	2.55	0.85	66	0.093	25	2
13	THF	2.55	0.85	66	0.093	45	20

[a] This value is based on the assumption that no end groups are present in the PDMS and that polymer is composed of $[-(OSiMe_2)_4-]_n$ units (MW = 296) to facilitate comparison with D_4.

$$\mathrm{MeSiCl_3} \rightarrow \underset{\mathbf{1}}{\mathrm{MeSiCl_2[(OSiMe_2)_n\sim]}} \rightarrow \underset{\mathbf{2}}{\mathrm{MeSiCl[(OSiMe_2)_n\sim]_2}} \rightarrow \underset{\mathbf{3}}{\mathrm{MeSi[(OSiMe_2)_n\sim]_3}}$$

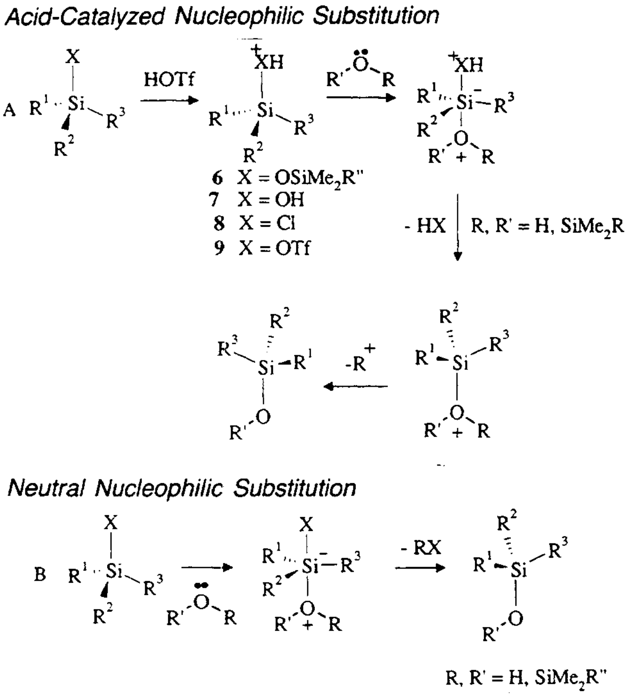
SCHEME 3



SCHEME 4

$MeSiCl_3$, D_4, and HOTf in THF. Me_2SiCl_2 is still present after the complete reaction of $MeSiCl_3$ (see entries 11 and 13 of Tables 1 and 2A). Thus, strongly acidic conditions do not change the relative reactivity to nucleophilic substitution of trifunctional ($MeSiCl_3$) and difunctional silanes (dimethylsiloxanes and Me_2SiCl_2) but selectively activate/catalyze the Si–O bonds as leaving groups.

Solvent effects of this type have been observed in the TfOH-catalyzed polymerizations of silicones. In the absence of a coordinating solvent, "intra-inter catalysis" is observed in which both the intramolecular (cyclization) and intermolecular (chain growth) condensations of silanols are bimolecular [42]. The chain ends, in essence, facilitate nucleophilic substitution by solvating a proton, which simultaneously creates an active leaving group. In solvents capable of proton solvation, the kinetics are quite different; intramolecular attack is unimolecular, whereas condensation is bimolecular. The presence of H_2O and the nature of the solvent are, therefore, very important in determining the ultimate equilibrium mixture and the rate of attaining equilibrium [11,43].



SCHEME 5

The Degree of Nucleophilic Substitution at $MeSiCl_3$

On the basis of the relative rates for sequential alcoholysis of trichlorosilanes [5], it was anticipated that once $MeSiCl_3$ began to participate in the redistribution reaction, the major products would be the mono- **3** and perhaps the disubstituted product **4** for both steric and electronic reasons: as Cl is replaced by much larger siloxy groups, steric factors in particular should reduce the rate of subsequent substitutions. In addition, expansion of the coordination shell is more facile with Cl than O ligands and an extracoordinate species is, importantly, more reactive toward subsequent nucleophilic attack [35]. In fact, however, regardless of the relative concentration of $MeSiCl_3$ in the reaction mixture, the major substitution products were the mono- **3** and trisubstituted species **5**; substantial concentrations of the disubstituted compound **4** were not observed (Table 1).

In analyzing the reasons for the enhanced reactivity of **4**, several factors must be considered. One of these is that silyl triflates are not normally catalysts for the redistribution/equilibration of silicones [11]: neither Me_3SiOTf nor $Me_2Si(OTf)_2$ would catalyze the redistribution of D_4 or PDMS. Indeed, based on the observed ^{29}Si NMR spectra, silyl triflates were the most stable termini of the linear silicones formed. Thus, the relative rates of substitution cannot be attributed to *inter*molecular catalysis by silyl triflates. However, by virtue of an *intra*molecular tether, it is possible that the triflate can activate the trifunctional silane through extracoordination (Scheme 6).

The fast polymerization/depolymerization of the silicone chain with D_4 occurs in the background (Scheme 6A). Once nucleophilic substitution at $MeSiCl_3$ occurs, giving **3**, the triflate may intramolecularly activate the trifunctional silicon by extracoordination **10** (Scheme 6B). This would clearly be easiest with chains of 3–4 Me_2SiO units length (vide infra). Nucleophilic attack by a silicone (shown for D_4) leads to a new pentacoordinate species **11** (Scheme 6C) that collapses by intramolecular transfer of Cl to the silicone chain end **4** (Scheme 6D).

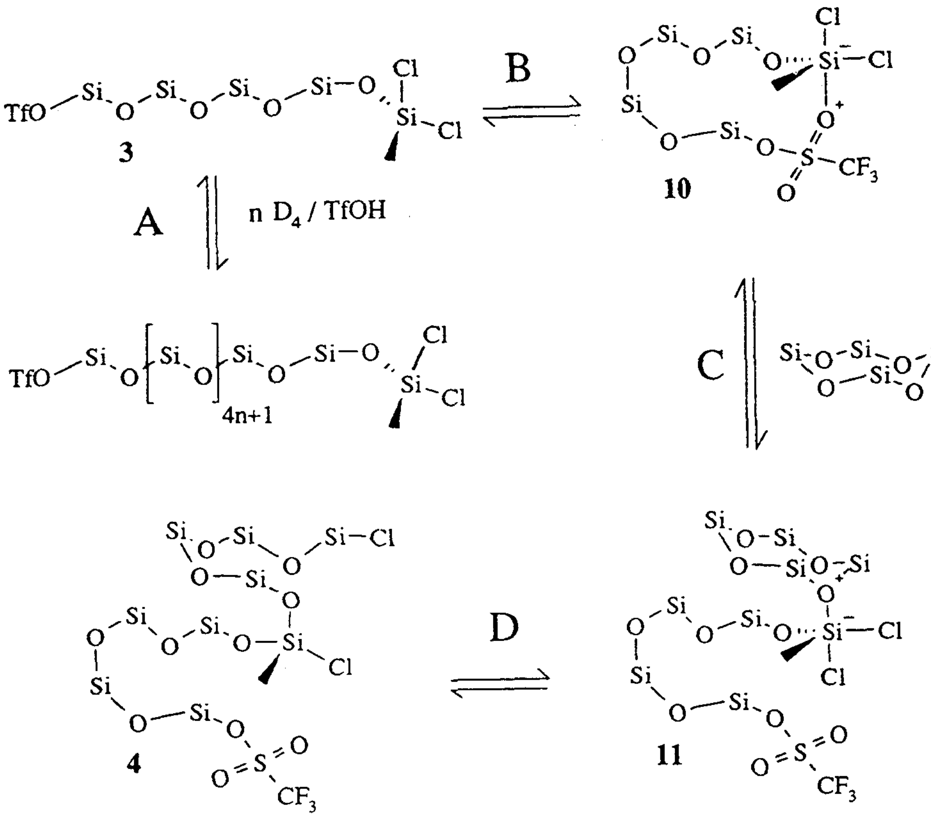
Subsequent substitutions may occur before, after, or during further silicone equilibration (Scheme 7E and H) and may involve intramolecular cleavage of longer silicone chains (Scheme 7E → G) and/or hydrolysis of chlorosilane termini to give silanols that may attack intramolecularly (Scheme 7H → I).

Several observations point to the possibility of an intramolecular reaction. An intramolecular substitution process would be facilitated for the siloxane chains near the trifunctional silicon for entropic reasons. The length of the tether of the newly formed silicone unit cannot, for energetic reasons, reasonably be less than 5 atoms; significant ring strain exists even in D_3. In accord with this, the number of D units bonded to the trifunctional silicon atom was always larger than two. If an intermolecular process were dominant, one would expect to observe chains of all lengths to some degree. Finally, consistent with the steric constraints that are present, the final substitution of chlorine by siloxane should be very slow if occurring in an intermolecular process. In fact, however, the third substitution is faster than the second, again suggesting an intramolecular process.

CONCLUSIONS

In the redistribution reaction of $MeSiCl_3$ and D_4, the siloxanes were found to be much more susceptible to nucleophilic attack than chlorosilanes in the presence of strong acids such as HOTf in a solvent which solvates protons poorly. Under these conditions, siloxane oxygens are selectively activated as leaving groups leading to preferential nucleophilic attack at difunctional siloxanes in the presence of Cl_3SiMe. Silanols and H_2O were found to be the most active nucleophilic species in such acidic media.

In the presence of more polar solvents, such as THF and/or added water, which reduce the effectiveness of acidic catalysis, the relative rate of nucleophilic attack at $MeSiCl_3$ vs. siloxanes was



SCHEME 6 (dimethyl groups at silicon omitted for clarity).

significantly increased. Trifunctional silanes, as expected, were found to be more reactive than difunctional silanes with the same leaving groups. Once reaction at the trifunctional site was initiated, further reactions of the siloxy-substituted adducts were facilitated primarily by intramolecular ring-forming reactions.

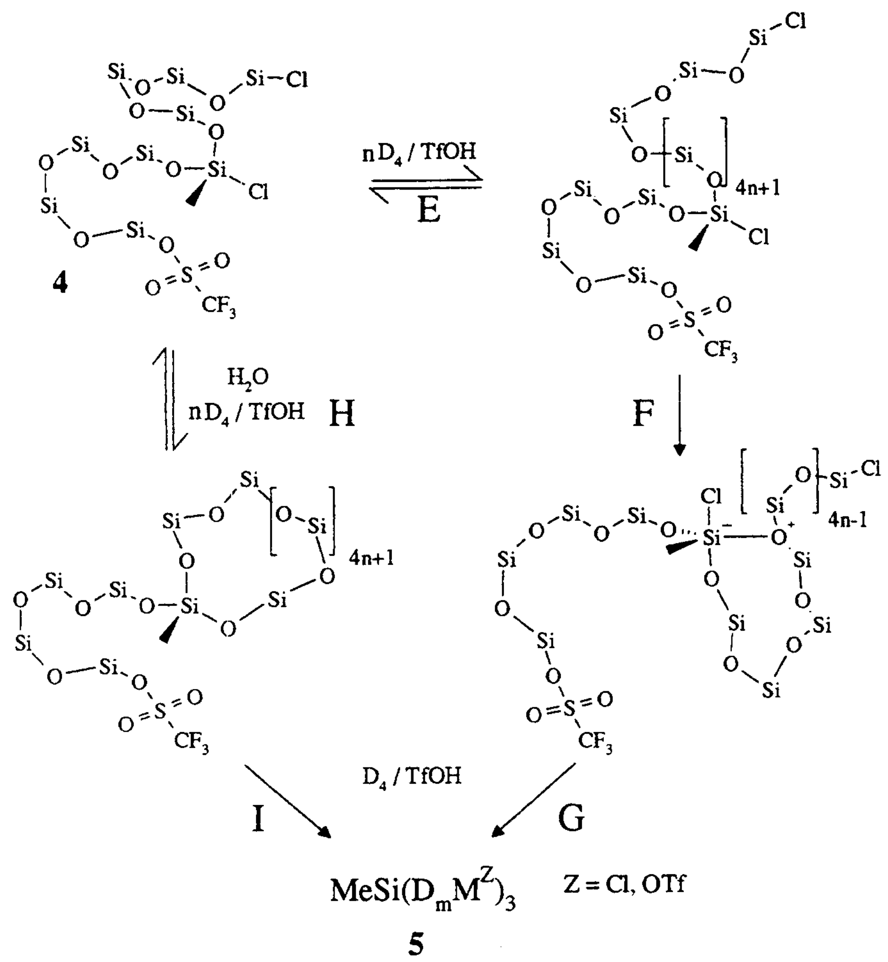
EXPERIMENTAL

Octamethylcyclotetrasiloxane (D_4) and hydroxyl-terminated polydimethylsiloxane (2000 cs, MW 36,000) were purchased from Hüls America Inc. (Bristol, PA); methyltrichlorosilane ($MeSiCl_3$) was a gift from Dow Corning Corp. (Midland, MI). D_4 and $MeSiCl_3$ were distilled and stored under N_2 over 4 Å molecular sieves. Quality control by ^1H NMR before use indicated a purity of >99%. Trifluoromethanesulfonic acid was purchased from Aldrich (Milwaukee, WI), stored under N_2, and used without further treatment. The solvent chloroform-*d* ($CDCl_3$, 99.8%D), the product of MSD Isotopes, was stored under N_2 over molecular sieves. Tetrahydrofuran was obtained from VWR Scientific (London, Canada) and was freshly distilled over K/benzophenone before use.

^{29}Si NMR spectral measurements were made on a BRUKER AC300 NMR spectrometer with a tunable, multinuclear probe at ambient temperature. The normal spectral parameters were as follows: spectral width, up to 12,000 Hz (60 to −140 ppm); frequency, 59.628 MHz; pulse width, 10.7 μs; pulse delay, 5–15 seconds; irradiation mode, decoupling without nuclear Overhauser enhancement; exponential window, 3 (for integration) or 0.3 (for fine structure); number of scans, up to 20,000. The assignments of the signals were based on assignments reported in the literature [15–18] or previously made by us [19]. The magnitudes of the integration of the signals were assumed to be proportional to the relative concentrations of the constituents in the mixture.

General Procedure for the ^{29}Si NMR Examinations of the Mixtures of $MeSiCl_3$ and D_4 in the Presence of HOTf

Reactions were carried out in oven-dried round bottom flasks (50–100 mL) equipped with magnetic stirrers under a nitrogen atmosphere. The solvents, D_4 and $MeSiCl_3$, were measured and transferred with disposable syringes into the reaction vessel. The catalyst HOTf and other additives were then injected with stirring into the solution at 0°C. The reaction mixture was subjected to various treatments. Samples were withdrawn



SCHEME 7 (dimethyl groups at silicon omitted for clarity).

with syringes at different reaction stages and transferred into a 10 mm thin wall NMR tube in which tetramethylsilane was present to serve as an internal standard, and sealed.

Calibration

To calibrate the reaction conditions, the equilibration (polymerization/depolymerization) reactions of D_4 and PDMS in $CDCl_3$ were examined in the presence of HOTf. The equilibrium compositions of the two systems were very close and in agreement with previous reports [8]. (entries A and B, Table 2A).

The Reaction of $MeSiCl_3$ with D_4 without Catalyst

$MeSiCl_3$ (0.82 mL, 7.0 mmol) and D_4 (2.0 mL, 6.4 mmol) were mixed in $CDCl_3$ (1.0 mL) in an NMR tube. The ^{29}Si NMR spectrum, even after the sample had stayed at ambient temperature for 7 months, showed only two sharp signals at $\delta = 12.14$ and -19.40, corresponding to $MeSiCl_3$ and D_4, respectively.

The Reaction of $MeSiCl_3$ with HOTf

$MeSiCl_3$ (1.5 mL, 12.8 mmol) and HOTf (0.5 mL, 5.7 mmol) were mixed in $CDCl_3$ (1.0 mL) at room temperature. There was only a tiny signal at $\delta = 43.41$, Me_3SiOTf, a product of the reaction between Me_4Si and HOTf, in addition to the slightly broadened signal of $MeSiCl_3$ at 12.24 on the ^{29}Si NMR spectrum. Efforts were made to prepare $MeSiCl_2OTf$ from allylmethyldichlorosilane and triflic acid [36]. However, the only clean product after distillation was $MeSiCl_3$.

METATHESIS EXPERIMENTS

The experiments, from which data is to be found in Tables 1 and 2, are summarized in Table 3. The specific quantities used are given below.

A: D_4 (2.4 mL, 7.7 mmol); HOTf (0.05 mL, 0.6 mmol); $CDCl_3$ (1.2 mL); 0°C; 17 hours.

B: Hydroxy-terminated PDMS (2.6 mL, 2000 cs, MW 36,000); HOTf (0.06 mL, 0.72 mmol); $CDCl_3$ (1.0 mL); 23°C; 173 hours.

1: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL; 1.4 mmol); $CDCl_3$ (3.0 mL); 0°C; 18 hours.

2: Sample "1"; 23°C; 336 hours.

3: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL; 1.4 mmol); $CDCl_3$ (3.0 mL); 23°C; 840 hours.

4: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL; 1.4 mmol); $CDCl_3$ (3.0 mL); 75°C; 20 hours.

5: $MeSiCl_3$ (8.0 mL, 68.1 mmol); D_4 (15.85 mL, 51.1 mmol); HOTf (0.48 mL; 2.7 mmol); $CDCl_3$ (6.0 mL); 75°C; 19 hours.

6: $MeSiCl_3$ (8.0 mL, 68.1 mmol); D_4 (15.85 mL, 51.1 mmol); HOTf (0.24 mL; 5.4 mmol); $CDCl_3$ (6.0 mL); 75°C; 19 hours.

7: $MeSiCl_3$ (3.0 mL, 25.5 mmol); D_4 (23.8 mL, 76.7 mmol); HOTf (0.18 mL, 2.0 mmol); H_2O (0.05 mL, 2.8 mmol); 23°C; 2 hours.

8: $MeSiCl_3$ (3.0 mL, 25.5 mmol); D_4 (23.8 mL, 76.7 mmol); HOTf (0.18 mL, 2.0 mmol); H_2O (0.05 mL, 2.8 mmol); 45°C; 75 hours.

9: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL; 1.4 mmol); $CDCl_3$ (3.0 mL); H_2O (0.05 mL, 2.8 mmol); 23°C; 840 hours.

10: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL, 1.4 mmol); THF (3.0 mL); 23°C; 18 hours.

11: $MeSiCl_3$ (2.0 mL, 17.0 mmol); D_4 (15.8 mL, 50.9 mmol); HOTf (0.12 mL, 1.4 mmol); THF (3.0 mL); 45°C; 90 hours.

12: $MeSiCl_3$ (3.0 mL, 25.5 mmol); D_4 (23.8 mL, 76.7 mmol); HOTf (0.18 mL, 2.0 mmol); H_2O (0.05 mL, 2.8 mmol); THF (4.5 mL); 23°C; 2 hours.

13: $MeSiCl_3$ (3.0 mL, 25.5 mmol); D_4 (23.8 mL, 76.7 mmol); HOTf (0.18 mL, 2.0 mmol); H_2O (0.05 mL, 2.8 mmol); THF (4.5 mL); 45°C; 20 hours.

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