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CYCLIC FLUOROSILICONE POLYMERS AND COPOLYMERS.(U)

1980 O R PIERCE, K M LEE

F49620-77-C-0012

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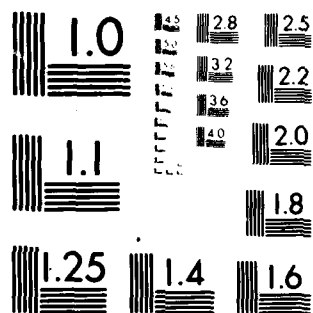
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CYCLIC FLUOROSILICONE POLYMERS AND COPOLYMERS
CONTRACT NO. F 49620-77-C-0012
FINAL REPORT FOR PERIOD
1 JANUARY 1977 to 31 JANUARY 1980

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CYCLIC FLUOROSILICONE POLYMERS AND COPOLYMERS

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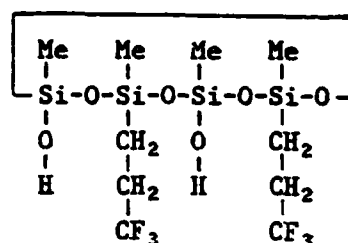
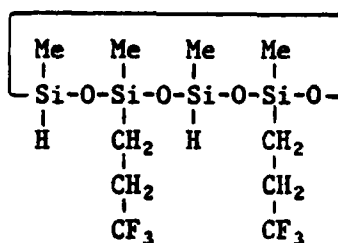
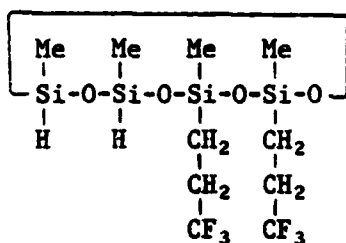
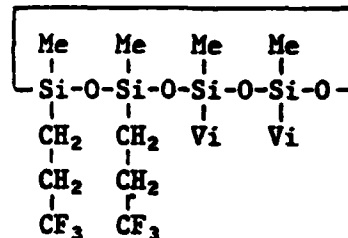
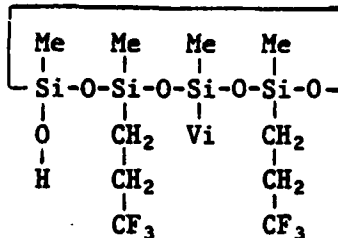
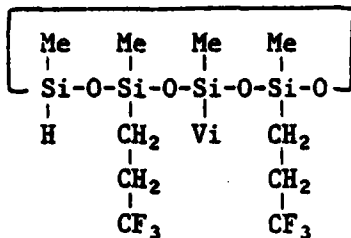
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several reactions were examined as potential routes to reactive cyclic tetrasiloxanes and their precursors. The reactions examined in some detail were cohydrolysis, siloxy-chloride exchange, hydrolysis of SiCl, SiOMe and SiH and acetoxy-silanol condensations. Using these reactions several intermediates were prepared and the new compounds were characterized (see tables). From the intermediates, six reactive cyclic tetrasiloxanes were prepared and characterized, these are listed on the reverse of this page. 409414		

Unclassified

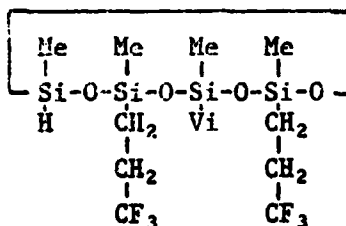
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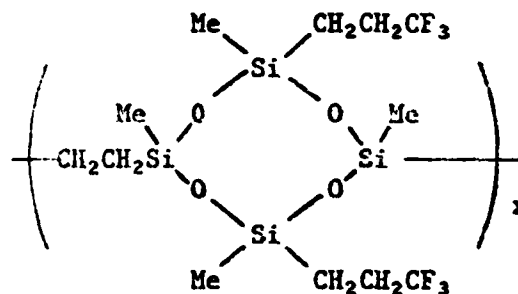


Two of these compounds were studied in polymerization reactions:

1)

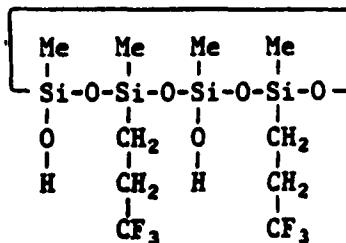


$\xrightarrow{\text{H}_2\text{PtCl}_6}$

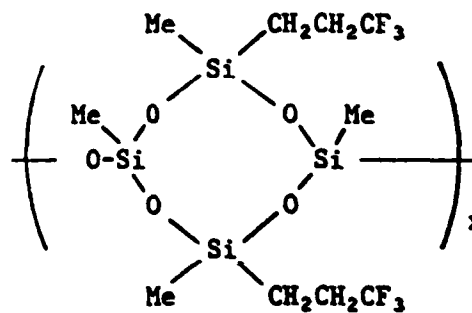


Molecular weight of 43,300 was achieved; and

2)



$\nrightarrow$



Polymerization was not achieved in this system.

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PREFACE

This final report was prepared by the Advanced Research Laboratory, Dow Corning Corporation, Midland, Michigan 48640 under contract no. F 49620-77-C-0012 and covers work preformed during the period 1 January 1977 to 31 January 1980. The sponsoring agency is the Office of Scientific Research, Balling Air Force Base, D.C. 20322. The Project Monitor is Mr. Anthony J. Matuszko.

The personnel assigned to this project were Dr. O. R. Pierce (Principal Investigator)(deceased) and Mr. K. M. Lee (Project Specialist).

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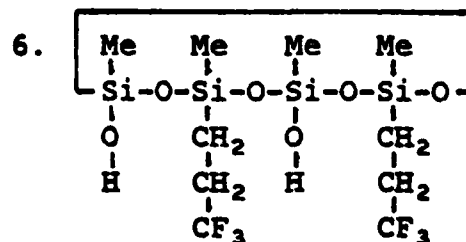
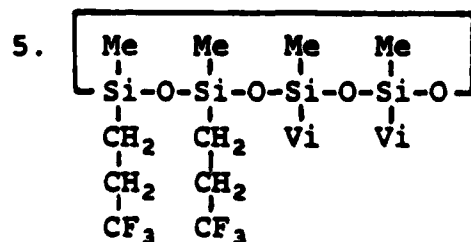
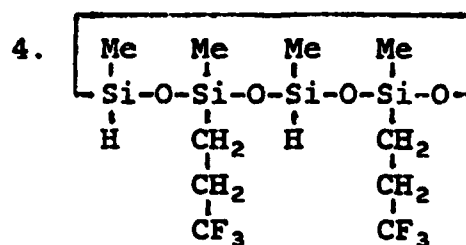
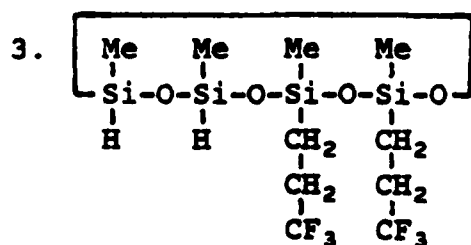
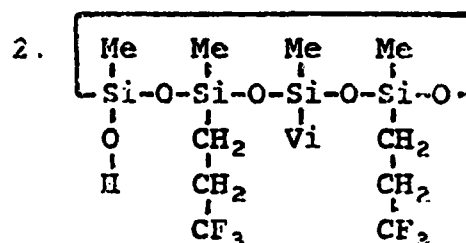
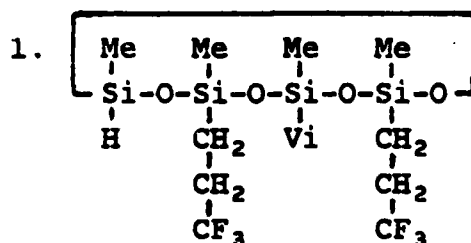
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Table II	Cyclic Siloxanes Characterization
Table III	Siloxy/Chloride Exchange Systems Screened
Table IV	Compounds Prepared by Siloxy/Chloride Exchange

SUMMARY

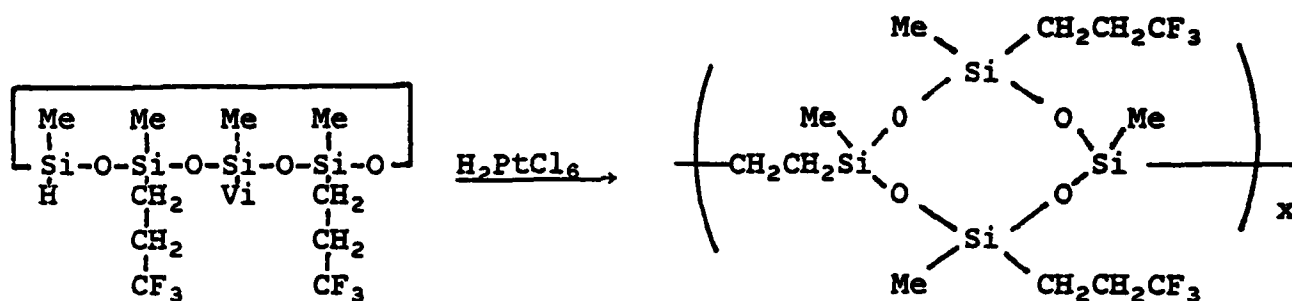
The feasibility of preparing and polymerizing reactive cyclic tetrasiloxanes was explored with mixed results. Examples of reactive cyclosiloxanes were synthesized but more work will be required to define polymerization conditions.

Several reactions were examined as potential routes to reactive cyclic tetrasiloxanes and their precursors. The reactions examined in some detail were cohydrolysis, siloxy - chloride exchange, hydrolysis of $\equiv\text{SiCl}$, $\equiv\text{SiOMe}$ and $\equiv\text{SiH}$ and acetoxy - silanol condensations. Using these reactions several intermediates were prepared and the new compounds were characterized (see tables). Six reactive cyclic tetrasiloxanes were prepared from the intermediates, and characterized:



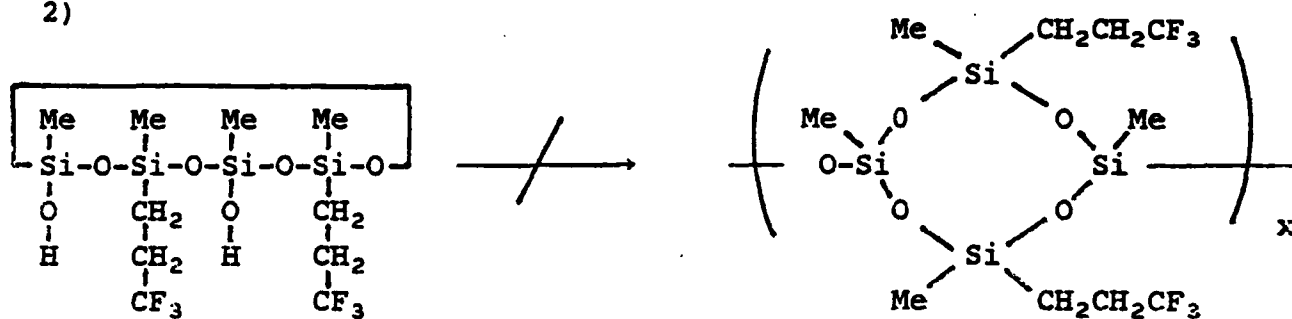
Two of these compounds were studied in polymerization reactions:

1)



Molecular weight of 43,300 was achieved; and .

2)



Polymerization was not achieved in this system.

CYCLIC POLYFLUOROSILOXANE POLYMERS AND COPOLYMERS

SECTION I

INTRODUCTION

All equilibrated polysiloxane systems contain cyclic



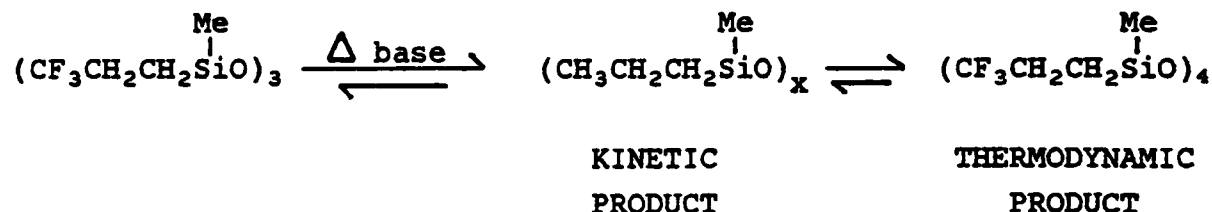
species, the level of which varies with the nature of the substituents on the silicon atom. The thermodynamic propensity toward cyclic configurations is intensified by bulky R groups and by dilution. Thus, Wright and Semlyen¹ found the following

¹ P. V. Wright and J.A. Semlyen, "Polymer" 11, 462 (1970).

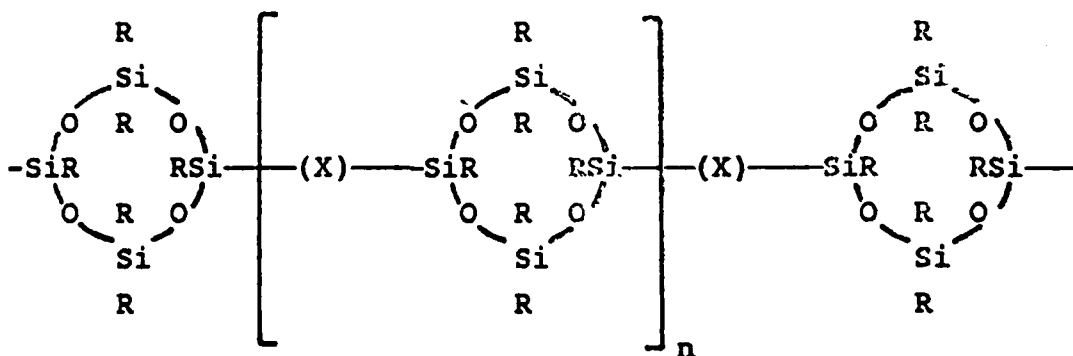
levels of cyclic species in equilibrated systems.

R	Wt. % of Cyclic Siloxanes at Equilibrium
H	8
Me	14
Et	22
Pr	34
CF ₃ CH ₂ CH ₂	80

Of particular interest is the poly(3,3,3-trifluoropropylmethyl) siloxane in which weight ratio at equilibrium was found to be ~80/20 respectively, i.e.,



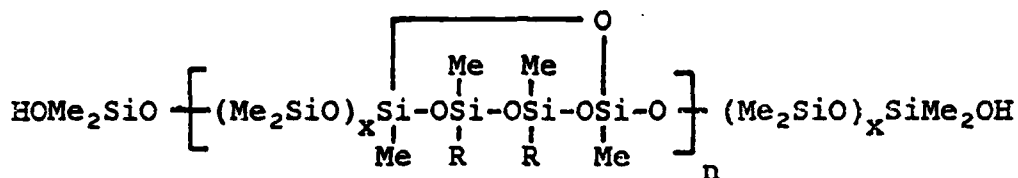
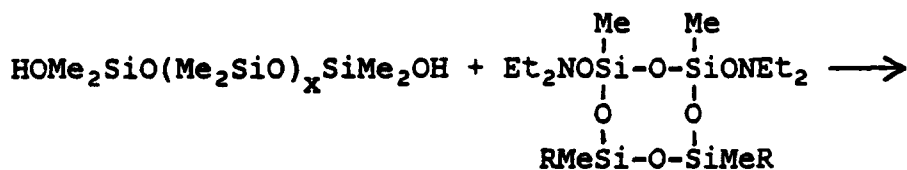
Work at Dow Corning has indicated that, depending on conditions, this ratio is in the range of 50-85% cyclic siloxanes and the remainder linear siloxanes. Products based on poly(3,3,3-trifluoropropylmethyl)siloxane possess excellent solvent resistance but have limited application in hot confined environments (450°F) where thermally induced depolymerization occurs with formation of cyclic tetramer. To satisfy this thermodynamic preference while maintaining the desirable properties of this system, we proposed to synthesize polymers and copolymers in which the repeating unit is a cyclic tetrasiloxane moiety.



The literature contain isolated examples of silicones containing cyclic moieties in the backbone of the polymer. Thus, Murphy² reported the preparation of polydimethylsiloxanes having

² R. A. Murphy, U. S. Patent 3, 296, 199 (1967).

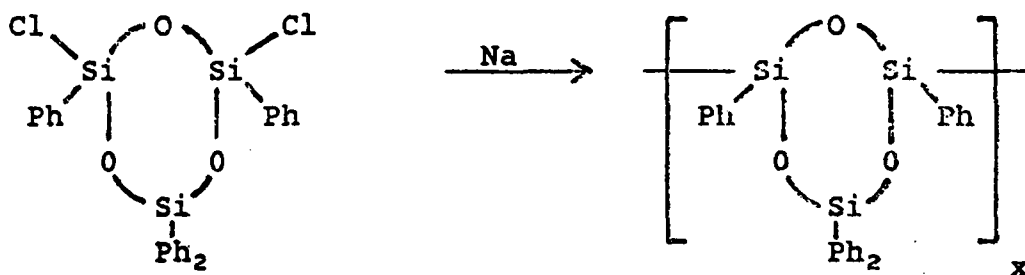
cyclic tetrasiloxane units:



where R = Me or C₅H₁₁

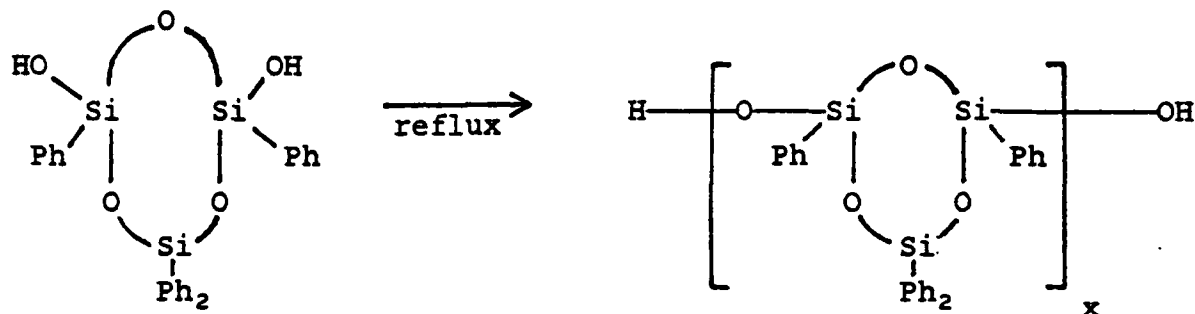
Perphenylated cyclotrisiloxanes which tend to be solids have been linked by sodium coupling of chlorosilanes³ and also

³ General Electric; British Patent 1,075,244 (1967).



by condensation of silanols⁴,

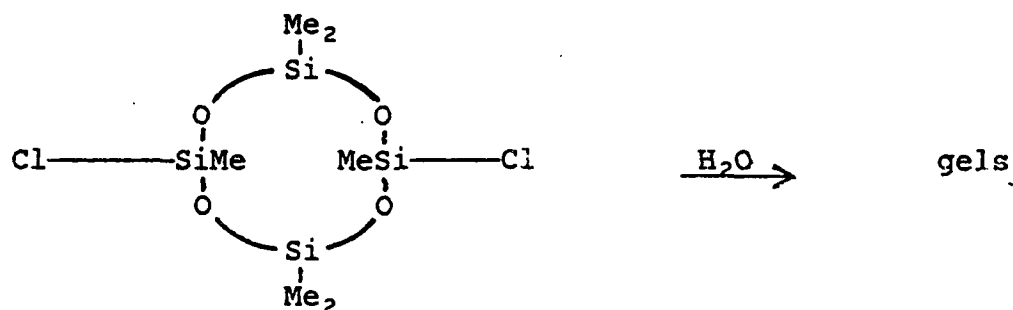
- ⁴ Tse C. Wu, U.S. Patent 3,400,145 (1968).
 Tse C. Wu, U.S. Patent 3,340,289 (1968).
 Tse C. Wu, U.S. Patent 3,354,119 (1967).
 Tse C. Wu, U.S. Patent 3,297,632 (1967).



These materials are claimed to have applications as dielectrics. Sokolov⁵ reacted a cyclic tetrasiloxane having two hydrolyzable

⁵ Sokolov, J. Gen. Chem., U.S.S.R. 29, 253 (1959).

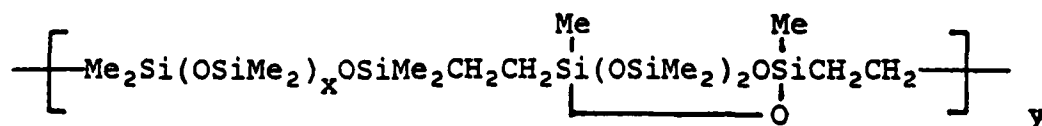
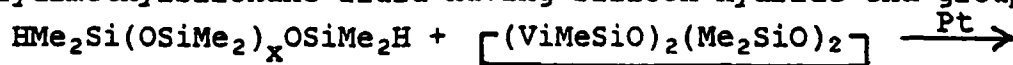
chlorines with water but no fluid products were isolated,



More to the point of our study is the work of Zhdanov⁶, in

⁶ Zhdanov, et.al., Dokl. Akad. Nauk SSSR, Ser. Kim. 211 (4-6), 1104-67 (1973).

which a vinyl functional cyclic tetrasiloxane was reacted with a polydimethylsiloxane fluid having silicon hydride end groups,



None of these systems has been exploited in a practical sense.

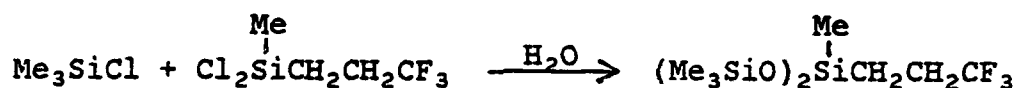
CYCLIC POLYFLUOROSILICONE POLYMERS AND COPOLYMERS

SECTION II

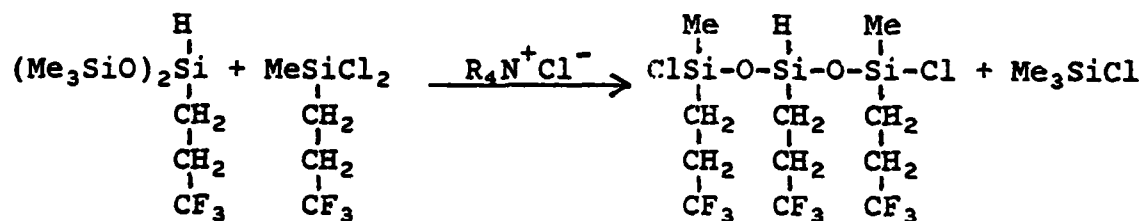
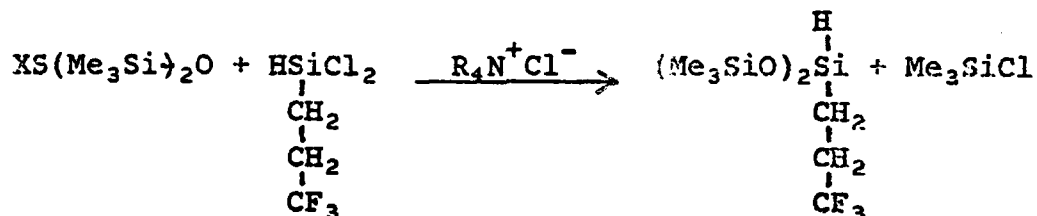
Discussion

This study required the synthesis of cyclic tetrasiloxanes bearing reactive groups. Earlier work at the Dow Corning Corporation indicated most of the desired intermediates could be obtained via cohydrolysis and siloxy/chloride exchange and considerable effort was expended trying to exploit these reactions.

Cohydrolysis is a straight forward reaction and the intermediates shown in Table I were prepared this way:

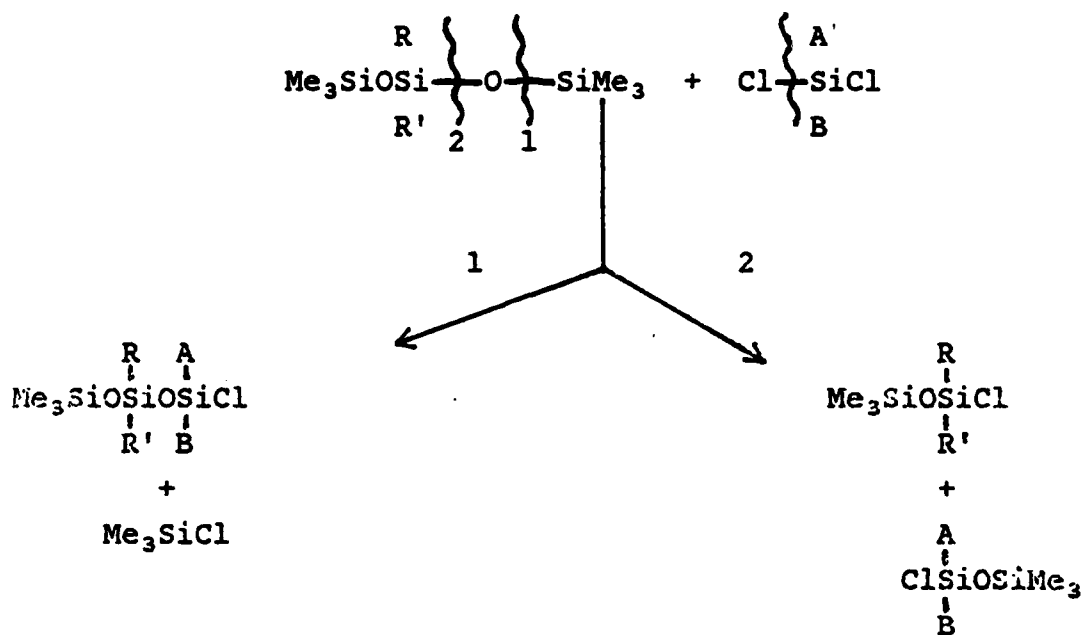


Siloxy/chloride exchanges catalyzed by quaternary salts,



are extremely versatile reactions in terms of the variety of unique materials one can produce, however, a lack of selectivity frequently limits their practical usefulness. Accordingly, a number of systems were screened to determine which ones were selective enough to be synthetically useful.

The method of screening siloxy/chloride exchange systems consisted of loading 1/4 ounce septum bottle with appropriate siloxane and chlorosilane, solvent, 5-20 weight percent catalyst and a stirring bar. The reactants were stirred at room temperatures ranging from 21° to 38°C and samples were withdrawn at intervals and analyzed by GLC. From the chromatographic data a judgment was made concerning the selectivity of the system. The two basic processes occurring are depicted below:



By GLC, process 1 gives higher boiling products and process 2 gives lower boiling products, relative to the starting siloxane. The occurrence of both processes to significant extents amounts to equilibration - randomization. A system was judged selective if process 1 was predominant, however, optimization was always required to make distillation effective.

Table II indicates the systems examined and those which were selective. Each example listed was run several times with variations in stoichiometry, concentration of catalyst and solvent, etc., thus the judgment concerning selectivity was not based on isolated cases.

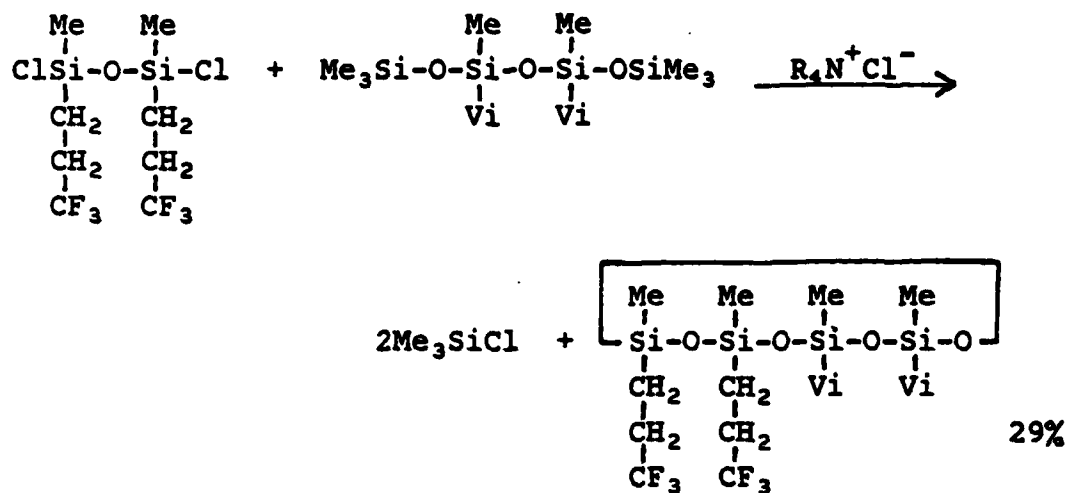
Some of the general characteristics of siloxy/chloride exchange reactions follow. The reactions are slow often requiring a week or longer to reach completion. The catalysts were Amberlyst® 26 and Amberlyst® 29 from Rohm and Haas which are quaternary ammonium chloride - functional resins which require drying for use in anhydrous systems. A-26 was the more selective and less active of the two catalysts. Freshly distilled chlorosilanes gave more selective reactions presumably because they contained less HCl which tends to give equilibration rather than selective exchange. The use of solvent usually slows the exchange and aids selectivity. Regulating the stoichiometry of the reagents seems to offer the best control of the selectivity. These systems are undoubtedly influenced by inductive effects of the groups on silicon but no systematic study has been made.

The desired products, which are chlorine endblocked siloxanes, are quite sensitive to equilibration by extraneous HCl and should be used as soon as possible. Equilibration was also observed during distillation with a monel spinning band. Occasionally an exchange reaction slows down or stops before reaching completion -- this behavior is not presently understood.

Several compounds were prepared via the exchange reactions, however, considerable difficulty was experienced in isolating highly pure materials. Eventually the time consuming nature of this chemistry demanded that this approach be abandoned.

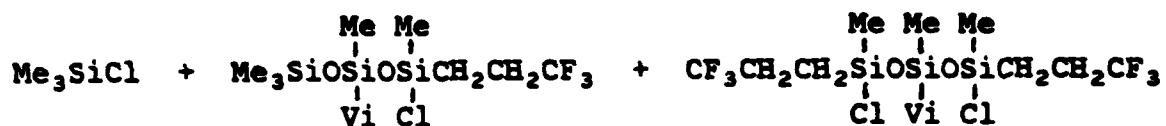
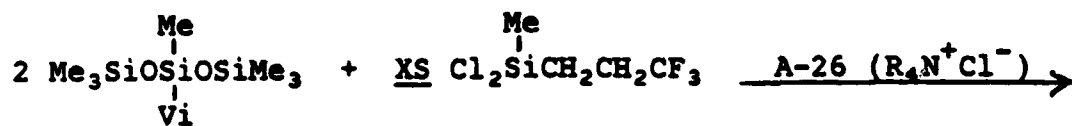
Of the materials appearing in Table I, II, and IV only compounds which were 99.9-100% pure by GLC were characterized in detail.

Siloxy/chloride exchange was employed to prepare a cyclic tetrasiloxane directly in one case:

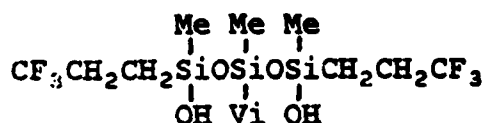


The system was not optimized because of long reaction times.

Siloxy/chloride exchange was also used in the system below:

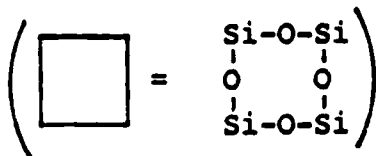
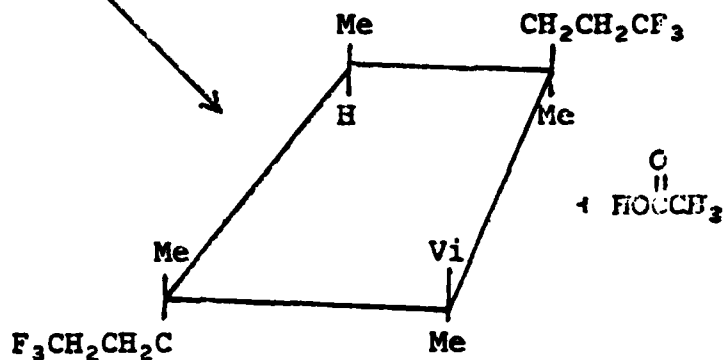


$\text{H}_2\text{O/NH}_4\text{OH}$

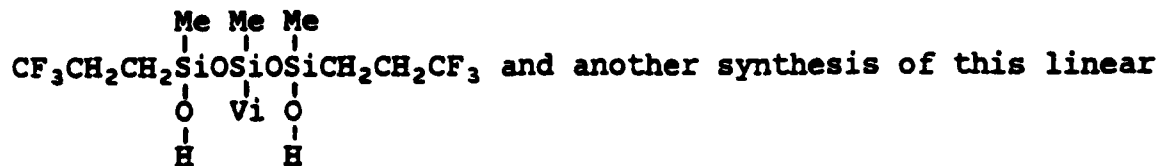


O Me
 $(\text{CH}_3\text{CO})_2\text{SiH}$

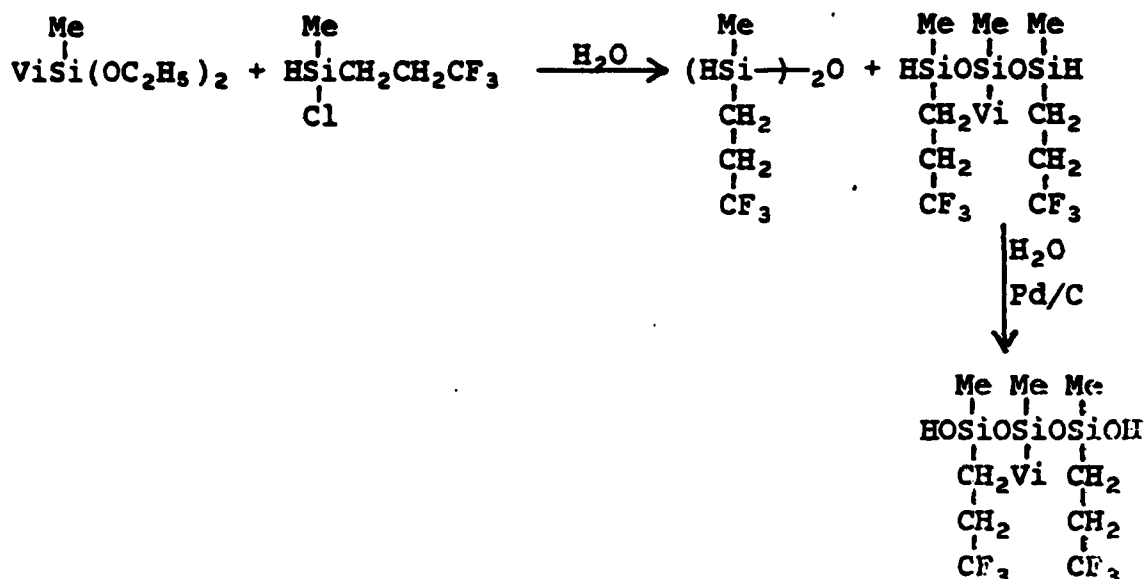
8 possible
isomers



This cyclic tetrasiloxane was a favored choice because it has a built in 1:1 concentration of reactive groups, i.e. $-\text{CH}=\text{CH}_2$ and SiH , and was easy to polymerize. The key intermediate in the preparation of this cyclic tetramer was



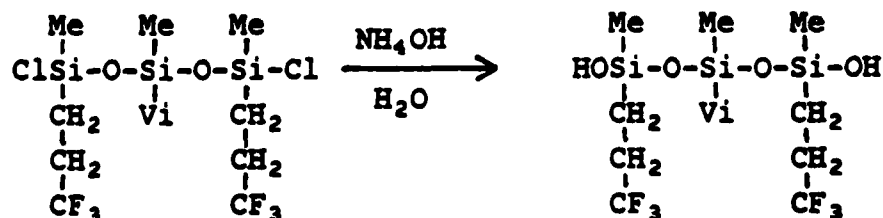
trimer was conceived:



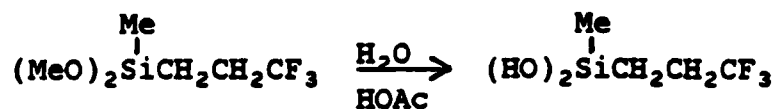
Unfortunately the palladium - catalyzed hydrolysis also led to reduction of the vinyl group and this approach was also abandoned. This side reaction is discussed later.

At several stages during this investigation silanols were important intermediates and they were prepared in various ways.

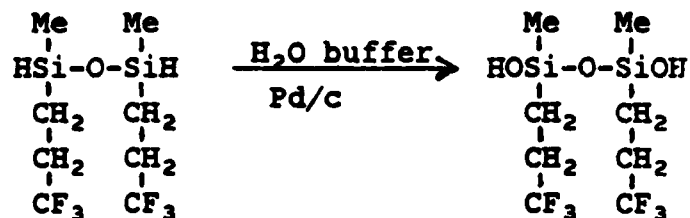
Hydrolysis of SiCl :



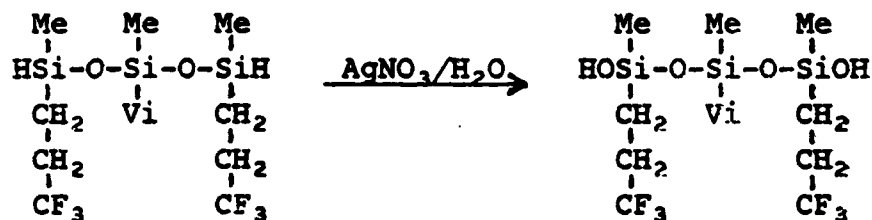
Hydrolysis of SiOMe:



Hydrolysis of SiH:

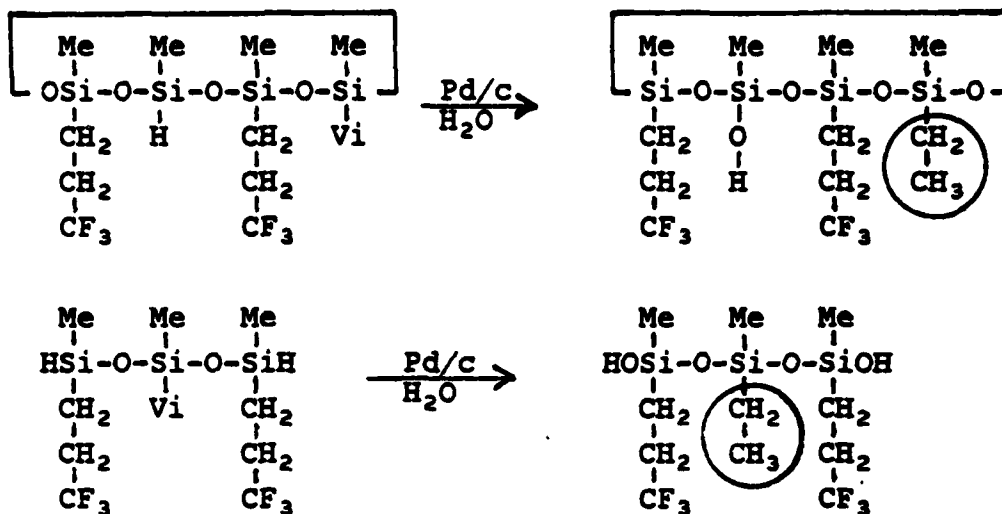


Oxidation of SiH:

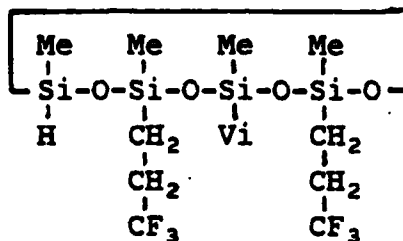


The major side reaction in the preparation of silanols is condensation to form linear or cyclic siloxanes.

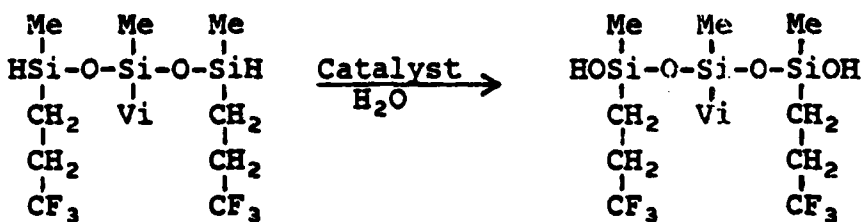
In general it is advantageous to keep the various systems close to neutrality and to work up the products as quickly as possible. The groups on silicon affect the reactivity and the tolerance of the silanol to changes in pH. With $-\text{CH}_2\text{CH}_2\text{CF}_3$ groups on silicon, weakly acidic or neutral hydrolysis schemes gave the best results. The hydrolysis of SiH in the presence of Pd/C is a most convenient reaction to carry out and usually gave high yields and purity, however, in two instances it also effected the reduction of vinyl as alluded above.



Since the above linear trisiloxane diol containing vinyl was vital in the preparation of



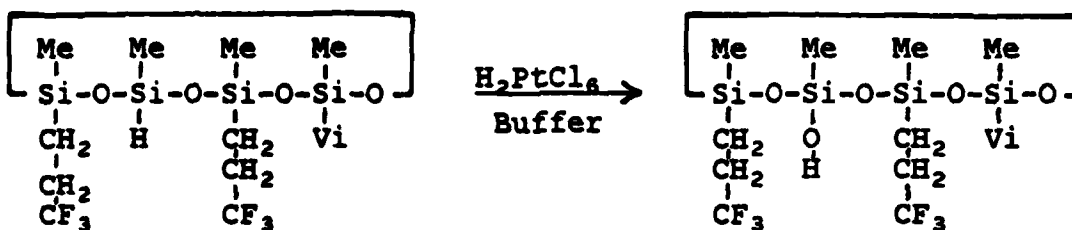
several attempts were made to hydrolyze the trisiloxane dihydride cleanly.



The potential catalysts tried in this reaction were Ag (very slow), H₂PtCl₆ (mixed results, some reduction) and pyridine (slow -induced condensation).

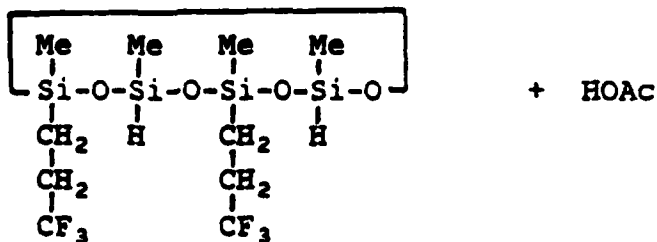
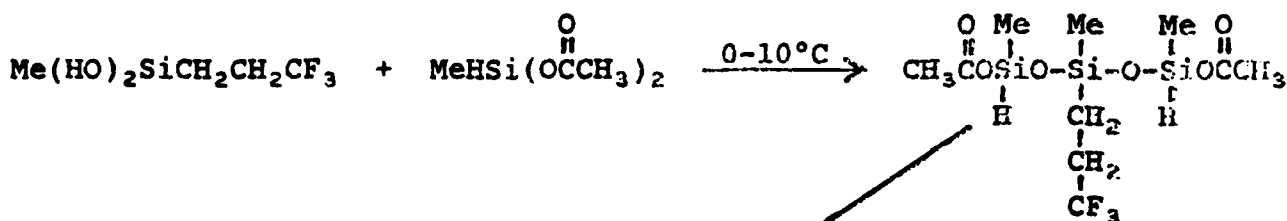
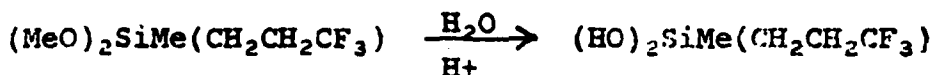
Silver nitrate was employed to oxidize the SiH groups but the resulting disilanol was colored yellow, had poor stability and quickly formed other compounds and polymer. A satisfactory method for making this trisiloxane diol was not devised.

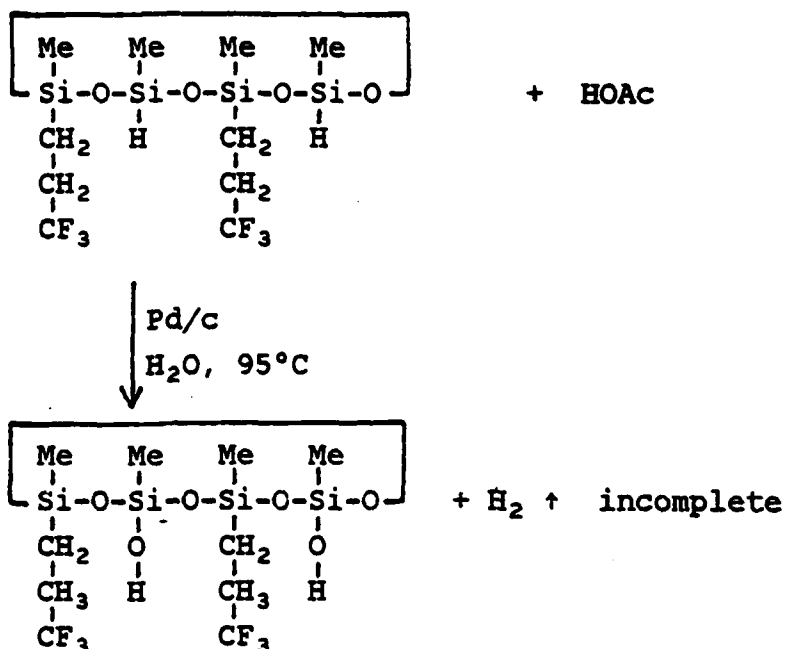
Small scale hydrolysis of the cyclic tetrasiloxane



was achieved without reduction of vinyl, allowing isolation and identification of the silanol but work was stopped on this system because of the difficulties in making intermediates to the cyclic hydride, as explained above.

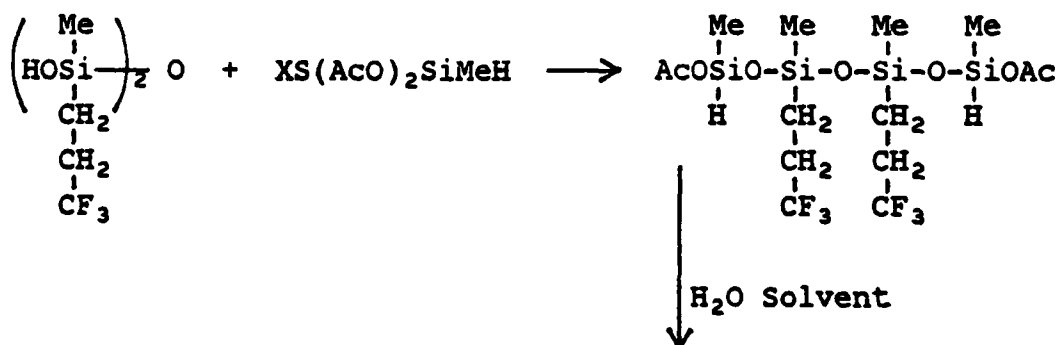
In view of these difficulties an alternate chemical system was examined and these reactions apparently have broad applicability for the preparation of reactive cyclic tetrasiloxanes. Unfortunately, this was discovered late in the program.

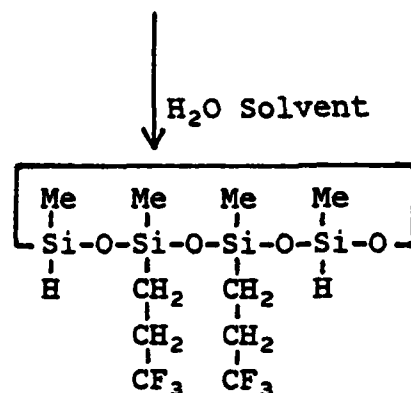




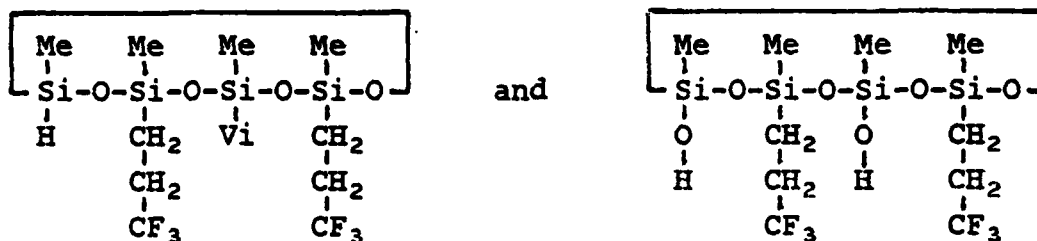
This system appears to be the most workable of those examined. The difference in reactivity of the acetoxy groups in $\text{MeHSi}(\text{OAc})_2$ allows the formation of acetoxy-ended trisiloxane in high yield. The subsequent cyclization has given low yields but should respond to optimization studies. The presence of isomeric structures in the cyclic dihydride was shown in the hydrolysis where differences in reactivity were seen. Thus, part of the SiH hydrolyzed readily at room temperature while warming to 95°C for several hours failed to completely hydrolyze the cyclic dihydride.

Similar chemistry was employed in the preparation of a reactive cyclic dihydride isomeric with the one above:

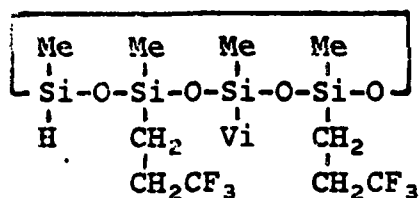




Only two materials were available in quantities sufficient for preliminary polymerization studies,



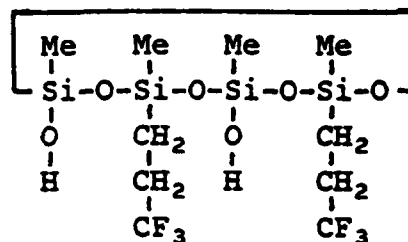
Polymerizations of small samples (0.3 to 1.0 g) of



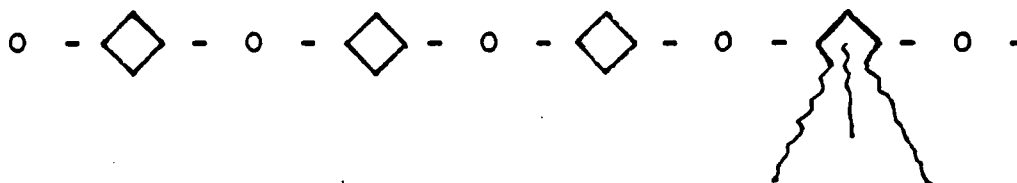
via catalysis by chloroplatinic acid were carried out in tetrahydrofuran and cyclohexane and met with variable results. The potential for gelation exists in these systems so polymer quality was determined by dissolution in acetone. All the polymerizations occurred concurrent with the disappearance of $\equiv\text{SiH}$ and $\equiv\text{SiVi}$ as shown by infrared analyses. The neat system is strongly exothermic and gave a product which was partially insoluble, i.e. contained some gel. Characterization by GPC gave uninterpretable traces but Membrane Osmometry gave satisfactory molecular weight data. Molecular weights ranging from 23,500 to 91,000 were observed.

Synthetic difficulties in the preparation of this cyclic monomer precluded a more extensive evaluation.

Condensation polymerization of



to produce polymer was not achieved. As in the hydrolysis of the corresponding hydride, a spectrum of reactivity was observed during attempts at polymerization. Partial condensation was accomplished at room temperature but only low molecular weights could be produced this way. Further heating to 90° gave gelation - apparent ring opening which renders each cyclic unit essentially tetrafunctional.



Time constraints precluded further evaluation.

CYCLIC POLYFLUOROSILICONE POLYMERS AND COPOLYMERS

SECTION III

Experimental

The following are typical of the procedures used.

A. COHYDROLYSIS

1. Preparation of $\text{Me}_3\text{Si}(\text{OSiCH}_2\text{CH}_2\text{CF}_3\text{Me})_n\text{OSiMe}_3$, where $n = 1, 2$,

A 2-liter, 3-necked flask equipped with a stirrer, condenser, thermometer and addition funnel, was charged with 404.5 g (2.0 mol) of 3,3,3 trifluoropropylmethyldimethoxysilane and 761.4 mL (6.0 mol) of trimethylchlorosilane. A cold solution of 54 g of water in 100 mL of isopropanol was added slowly over a period of 10 minutes. Then 400 mL of cold water was added and the products were agitated for thirty minutes. The phases were separated and the organic layer was washed twice with 300 mL of distilled water and finally with 200 mL of 5% aqueous sodium bicarbonate. The products were dried over calcium sulfate, filtered and distilled to give 389.2 g (1.22 mol; 61%) of 3,3,3 trifluoropropylmethyl-bis(trimethylsiloxy)silane, $n_D^{25} 1.3779$, b.p. 82° (22 mm), $^1\text{H-NMR}$ (CCl_4) [δ 0.11 (s, CH_3) + δ 0.06 (s, $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}^*\text{CH}_3$) 21H], [δ 0.67 (m, SiCH_2-) + δ 2.05 (m, CH_2CF_3) 4H] and 115.7 g (0.24 mol, 24%) of 3,5 bis(3,3,3trifluoropropyl)permethyltetrasiloxane, $n_D^{25} 1.3789$, b.p. $55-57^\circ$ (0.14 mm), $^1\text{H-NMR}$ (CCl_4) δ 0.13 (s, CH_3 , 24H), δ 0.73 (m, SiCH_2) + δ 2.06 (m, CF_3CH_2) 8H.

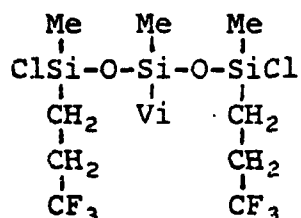
2. Preparation of $[\text{HMeSi}(\text{CH}_2\text{CH}_2\text{CF}_3)]_2\text{O}$ and $[\text{HMeSi}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{O}]_2\text{Si}(\text{Me})\text{Vi}$

In a 500 mL, 3 necked flask equipped with a stirrer, condenser, and thermometer, 5.4 g (0.3 mol) of distilled water was added dropwise

to a mixture of 105.9 g (0.6 mol) of 3,3,3 trifluoropropylmethylchlorosilane and 32.1 g (0.2 mol) of vinylmethyldiethoxysilane. The system was kept below room temperature with an ice bath. Water (100 mL) was added and the organic layer was separated and washed with 30 mL of saturated aqueous sodium bicarbonate. The organic layer was dried over sodium sulfate, filtered, and distilled to give the following: 0.134 mol of $[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{O}]_n$, b 45° (4.5 mm), n_D^{25} 1.3558 (Reported $n_D^{25}/1.3569$); $[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}]_n\text{SiMeVi}$; 0.138 mol (69%), b 56° (4 mm), Sp. Gr. 1.083, Rd(Calc'd) 0.2125, Rd(Found) 0.2114.

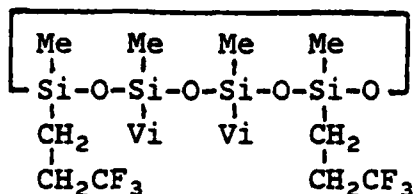
B. SILOXY/CHLORIDE EXCHANGE

1. Preparation of 1,5-dichloro-3-vinyl-1,5-bis(3,3,3 trifluoropropyl)-1,3,5-trimethyltrisiloxane,



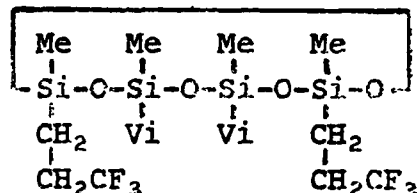
A 500 mL, 3 necked flask equipped with a condenser, thermometer, and magnetic stirrer was charged with 59.4 g (0.2 mol) of $(\text{Me}_3\text{SiO})_2\text{SiMeVi}$, 211.1 g (1.0 mol) of $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiMeCl}_2$, 100 mL of cyclohexane and 30 g of dry Amberlyst® 26. The reactants were stirred at room temperature and monitored by GLC. After five days the catalyst was removed by filtration and the products were fractionated to give 38.4 g (0.085 mol; 42.5%) of $[\text{ClMe}(\text{CF}_2\text{CH}_2\text{CH}_2)\text{SiO}]_n\text{SiMeVi}$; b.p. 100° (15 mm); n_D^{25} 1.3895; $^1\text{H-NMR}$ (CCL_4), δ 6.1 (m, 3H, $-\text{CH}=\text{CH}_2$), $[\delta$ 2.5 (m, CF_3CH_2-) + δ 1.06 (m, SiCH_2) 8H], δ 0.52 (s, 6H, CH_3SiCl), δ 0.30 (s, 3H, CH_3SiVi).

2. Preparation of 1,3 Bis(3,3,3-trifluoropropyl)-5,7-divinyl
1,3,5,7-tetramethyltetrasiloxane,



A 100 mL flask equipped with a magnetic stirrer, condenser and vented through a drying tube, was loaded with 10.05 g (0.03 mol) of $\text{Me}_3\text{Si}(\text{OSiMeVi})_2\text{OSiMe}_3$, 11.01 g (0.03 mol) of $[\text{ClMe}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{Si}]_2\text{O}$, 5 g of Amberlyst 26 (quaternary salt-functional resin from Rohm and Haas) and 50 mL of cyclohexane. These were stirred, heated at 60-65°C and monitored by GLC. After four days the major product (68% by GLC) stopped increasing.

Distillation gave 4.2 g (29%) of

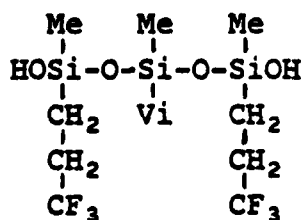


properties and analyses appear in Table II. A non-volatile residue was also obtained.

C. PREPARATION OF SILANOL

1. Hydrolysis of SiCl

Preparation of 1,5-Dihydroxy-1,5-bis(3,3,3 trifluoropropyl)-3-vinyl-1,3,5-trimethyltrisiloxane,



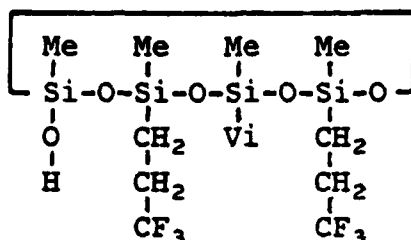
Into a 200 mL separatory funnel 20 mL of diethylether, 15 g of ice and 0.3 mL of conc. NH_4OH (0.004 mol) were introduced. These were stirred while a solution of 0.453 g (0.001 mol) of $(\text{ClMe}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO})_2\text{SiMeVi}$ in 10 mL of diethylether was added dropwise over a period of 2 min. After separation, the aqueous layer was discarded and the siloxane layer was diluted with 20 mL of hexane and washed with distilled water until free of chloride ion (AgNO_3 test). The product was dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum to give 0.23 g (0.00055 mol; 55% of $[(\text{HO})\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}]_2\text{SiMeVi}$, n_D^{25} 1.3925, $^1\text{H NMR}$ (d_6 DMSO), δ 6.4 (s, 2H, OH), δ 5.9 (m, 3H, $-\text{CH}=\text{CH}_2$), [δ 0.066 (s, CH_3SiOH) + δ 0.16 (s, CH_3SiVi) 9H], [δ 1.7-2.7 (m, CF_3CH_2) + δ 0.65 (m, SiCH_2) (8H)].

2. Preparation of Silanols via Hydrolysis of SiH

Hydrolysis of $[\text{HSiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)]_2\text{O}$ Catalyzed by Palladium on Carbon.

In a 500 mL flask the following were combined in the order indicated: 1.0 g of 5% Pd/C, 200 mLs of dioxane, 20 mL of aqueous phosphaste buffer (~ 1.1 mol of H_2O) and 29.8 g (0.1 mol) of symmetrical bis(3,3,3-trifluoropropyl)dimethyldisiloxane. After 2 hours the evolution of gas had subsided and the product was concentrated under vacuum. Analysis by IR indicated the complete reaction of SiH. The concentrate was dissolved in 100 mL of diethylether, dried over anhydrous calcium sulfate, filtered, and devolatized to give a viscous liquid, n_D^{25} 1.3798. After standing overnight the disilanol crystallized.

3. Preparation of 1,5 Bis(3,3,3-trifluoropropyl)-3-vinyl-7-hydroxy-1,3,5,7,-tetramethyltetrasiloxane,



To 10 mL of 95/5 dioxane/water 0.53 g (0.0012 mol) of 1,5 bis (3,3,3-trifluoropropyl)-3-vinyl-1,3,5,7-tetramethyltetrasiloxane was added followed by 4 μ l of 5% chloroplatinic acid in isopropanol. Analysis by GLC indicated the clean formation of a new compound of longer retention time. When the starting hydride was consumed the mixture was washed once with distilled water, dissolved in methylene chloride, dried over anhydrous CaSO_4 , filtered and concentrated under vacuum. The concentrate showed only methylene chloride and the new compound by GLC. ^1H NMR (DMSO), δ 6.6 (s, 1H, SiOH), 5.6-6.3 (m, 3H, Vi), 0.7 (m, 4H, SiCH₂), 0.190, 0.175 (2s, $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiMe}^*$) + 0.139, 0.126 (2s, ViSiMe^*) + 0.066, 0.055 (2s, HOSiMe^*)₃12H.

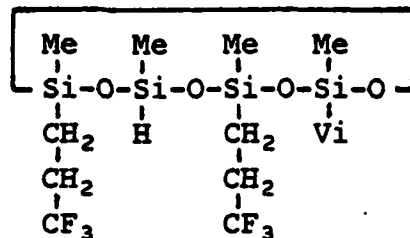
4. Hydrolysis of $\equiv\text{SiOMe}$

Preparation of 3,3,3 Trifluoropropylmethoxysilanediol

A 16 oz. bottle was charged with 360 mL of distilled water, 100 μ l of acetic acid, and 40.50 g (0.2 mol) of 3,3,3 trifluoropropylmethoxydimethoxysilane. The bottle was capped and agitated. After 30 minutes a clear homogenous solution had formed. The solution stood at room temperature for 1 hour and then was extracted with diethylether (4 x 50 mL). The ethereal extracts were diluted with 100 mL of methylene chloride, dried over anhydrous calcium sulfate, filtered, and concentrated to give 20.3 g (58%) of white flakes, m.p. 86-7°. ^1H , NMR (DMSO), δ 5.97 (s, 2H, SiOH), 0.57 (m, 2H, SiCH₂), 0.0 (s, 3H, SiMe).

D. CYCLIZATION

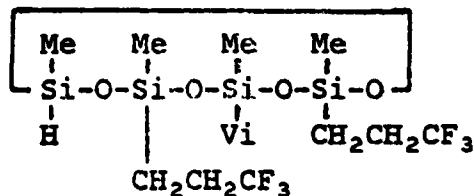
Preparation of 1,5-bis(3,3,3 trifluoropropyl)7-vinyl-3-hydrido-1,3,5,7-tetramethyltetrasiloxane,



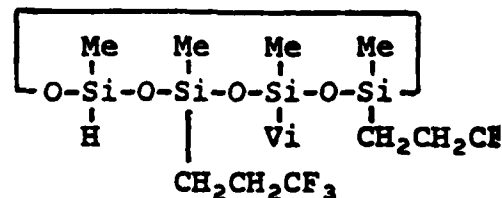
A solution of 0.208 g (0.005 mole) of $[(\text{HO})\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}]_2\text{SiMeVi}$ in 10 ml of dry hexane was made up in a 1 ounce polyethylene bottle. This was stirred while a solution of 0.0005 mole of $\text{MeHSi}(\text{OAc})_2$ in 10 mL of dry hexane was added over a period of ten minutes. The products were stirred for 1 hour and analysis by GLC indicated one major peak (60 area %) and several smaller ones. A sample of the major product was separated by preparative GLC; ^1H NMR (CCl_4), δ 4.8 (m, 3H, Vi), δ 6.0 (s, 1H, SiH) [δ 2.1 (m, CH_2CF_3) δ 0.82 (m, SiCH_2) (8H)], δ 0.20 (s, 12H, MeSi); IR (neat film) 3070 cm^{-1} .

E. POLYMERIZATION

1. Polymerization of



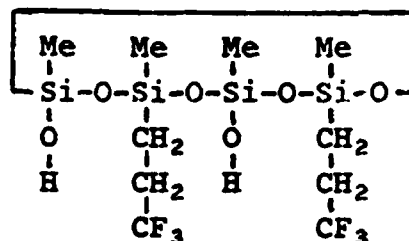
In a 0.25 ounce vial 0.9 g (0.002 mole) of



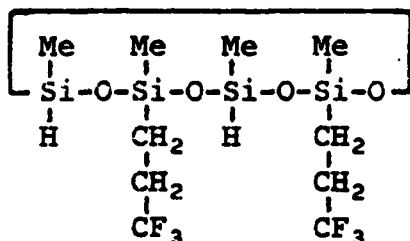
was dissolved in 0.9 g of THF, 1 μl of 5 wt. % chloroplatinic acid in isopropanol was added, and the vial was capped. The

solution was warmed to 35° and a rapid increase in viscosity was noted. These conditions were maintained for four hours. The polymer was devolatilized at <1 mm Hg. but the odor of tetrahydrofuran persisted. The vial was opened and kept at 38° over night - a non-flowing polymer was left. IR indicated a complete loss of SiH (2170 cm^{-1}) and $-\text{CH}=\text{CH}_2$ (3070 cm^{-1}). Characterization by GPC failed. Molecular weight (Membrane Osmometry) 43,300. The polymer was completely soluble in acetone or THF.

2. Preparation and Attempted Polymerization of



To 20 mL of dioxane containing 2 ml of aqueous NaOH/NaH₂PO₄ buffer solution and 0.01 g of 5% Pd/c, 5.24 g (0.012 mol) of



was added. Evolution of hydrogen began immediately and subsided after 2 hours. The mixture was heated to ~35°C and reaction began again. After two days infrared analysis indicated the presence of SiH (4.7 microns). The temperature was raised to ~95°C and held for 5 hours. A small amount of SiH still remained. Several drops of saturated aqueous silver nitrate were added. Various colors appeared and some evolution of gas was noted. The products were filtered, washed with distilled water and taken up in methylene chloride and filtered again. Devolatilization gave a yellow oil which was dissolved in THF and heated at 40°C with carbon black for 3 hours. Filtration and concentration gave 5 g of a faintly yellow oil; n_D^{25} 1.3910, no SiH left by IR. ^1H , NMR (DMSO), δ 5.9-6.8 (several singlets, 2H, SiOH), δ 0.7 (m, 4H, SiCH₂), 0.11, 0.13,

0.18, 0.53 (singlets, 12H, SiMe). Samples of the disilanol were heated with condensation catalysts; tetramethylguanidine octoate and tetramethylguanidine trifluoroacetate both led to gelation, calcium oxide effected condensation but a low molecular weight oil was produced.

F. MISCELLANEOUS

1. Preparation of Methyldiacetoxysilane

Into a 500 mL, 3 neck flask equipped with a paddle stirrer, thermometer, condenser vented through a drying tube, inlet for nitrogen, Dean Stark trap, and addition funnel, sodium acetate (98.4 g; 1.1 mol) and 500 ml of toluene were transferred. The system was blanketed with nitrogen and methyldichlorosilane (57.2 g; 0.5 mol) was added to the addition funnel. The slurry of sodium acetate was azeotroped free of water, cooled to room temperature and the addition of methyldichlorosilane was started keeping the temperature below 50°C. After the addition was completed the products were stirred for one hour, filtered under nitrogen and distilled to give 38.8 g of methyldiacetoxysilane (50%); n_D^{25} 1.3960, b.p. 54° (8 mm), 99% purity by GLC.

2. Preparation of Methylbis(methylacetoxysiloxy)-3,3,3-trifluoropropylsilane

To 33.9 g (0.2 mol) of methyldiacetoxysilane, which was stirred magnetically and cooled in a ice bath, a solution of 17.8 g (0.09 mol) of 3,3,3 trifluoropropylmethylsilanediol in 50 mL of dry THF was added over a period of 20 minutes. Distillation at reduced pressure gave 26.6 g (0.07 mol, 78%) of

$$[\text{MeH}(\overset{\text{O}}{\parallel}\text{CH}_3\text{CO})\text{SiO}]_2\text{SiMeCH}_2\text{CH}_2\text{CF}_3$$
: n_D^{25} 1.3856, purity 99.97% by GLC, b 73° (0.1 mm); H^1 , NMR (CCL_4), δ 0.18 (s, 3H, SiMe*), 0.50 (s, 6H, SiHMe*), 0.78 (m, 2H, SiCH₂), 2.0-2.1 (m, 8H, CH₃ $\overset{\text{O}}{\parallel}\text{C}$ + CF₂CH₂) 4.73 (s, 1H, SiH).

GLB3/E

TABLE II
CYCLIC SILOXANES
CHARACTERIZATION

COMPOUND	Method	b.p. (mm)	n_D^{25}	Sp.Gr.	Calcd	Rd Found
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{H} & \text{CH}_2 & \text{Vi} & \text{CH}_2 \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	D	52 (0.73)	1.3814	1.1579	0.2007	0.2002
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{CH}_2 & \text{Vi} & \text{Vi} & \text{CH}_2 \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	B-2	79 (4.2)	1.3906	1.140	0.2071	0.2082
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{H} & \text{H} & \text{CH}_2 & \text{CH}_2 \\ & & \text{CH}_2 & \text{CH}_2 \\ & & \text{CF}_3 & \text{CF}_3 \end{array}$	D	68 (0.43)	1.3722			
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{H} & \text{CH}_2 & \text{H} & \text{CH}_2 \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	D	44 (0.07)	1.3732	1.1766	0.1925	0.1936
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{O} & \text{CH}_2 & \text{O} & \text{CH}_2 \\ & & & \\ \text{H} & & \text{H} & \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	C-2	mushy solid ¹	1.3910			
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ & & & \\ \text{---Si-O-Si-O-Si-O-Si-O---} \\ & & & \\ \text{O} & \text{CH}_2 & \text{Vi} & \text{CH}_2 \\ & & & \\ \text{H} & \text{CH}_2 & & \text{CH}_2 \\ & \text{CF}_3 & & \text{CF}_3 \end{array}$	C-3					
$\begin{array}{ccc} \text{Me} & \text{Me} & \text{Me} \\ & & \\ \text{---Si-O-Si-O-Si-O---} \\ & & \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ & & \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ & & \\ \text{CF}_3 & & \text{CF}_3 \end{array}$	D		1.3735	1.1613	0.1947	0.1964

¹ These cyclic siloxanes are mixtures of isomers

TABLE II (continued)

CYCLIC SILOXANES
CHARACTERIZATION

COMPOUND	H' NMR (CCl ₄)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{H} & \text{CH}_2 & \text{Vi} & \text{CH}_2 \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	δ 4.8 (m, 3H, Vi), 6.0 (s, 1H, SiH) [2.1 (m, CFCH ₂) + 0.82 (m, CH ₂ Si)(8H)]. 0.2 (s, 12H, CH ₃ Si)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{CH}_2 & \text{Vi} & \text{Vi} & \text{CH}_2 \\ \text{CH}_2\text{CF}_3 & & & \text{CH}_2\text{CF}_3 \end{array}$	δ 5.43-6.3 (m, 6H, Vi), 2.03 (m, 4H, CH ₂) 0.78 (m, 4H, SiCH ₂), 0.39, 0.37 (2s, 6H, ViSiCH ₃), 0.31 (s, 6H, SiCH ₃)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{H} & \text{H} & \text{CH}_2 & \text{CH}_2 \\ & & \text{CH}_2 & \text{CH}_2 \\ & & \text{CF}_3 & \text{CF}_3 \end{array}$	δ 4.72 (s, 2H, SiH), 2.2 (m, 4H, CF ₃ CH ₂), 0.87 (m, 4H, SiCH ₂), 0.24 (s, 12H, SiMe)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{H} & \text{CH}_2 & \text{H} & \text{CH}_2 \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	δ 4.68 (s, 2H, SiH), 2.0 (m, 4H, CH ₂ CF ₃), 0.8 (m, 4H, SiCH ₂), 0.22 (s, 12H, SiMe)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{O} & \text{CH}_2 & \text{O} & \text{CH}_2 \\ \text{H} & & \text{H} & \\ & \text{CH}_2\text{CF}_3 & & \text{CH}_2\text{CF}_3 \end{array}$	(DMSO) δ 6.7 (s, 2H, SiOH), .034-.16 (several singlets, 20H, SiMe)
$\begin{array}{cccc} \text{Me} & \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O-Si-O} \\ \text{O} & \text{CH}_2 & \text{Vi} & \text{CH}_2 \\ \text{H} & \text{CH}_2 & & \text{CH}_2 \\ & \text{CF}_3 & & \text{CF}_3 \end{array}$	DMSO δ 6.6 (s, 1H, SiOH), 5.6-6.3 (m, 3H, SiVi), 0.7 (m, 4H, SiCH ₂), 0.19-0.055 (6s, 12H, SiMe)
$\begin{array}{ccc} \text{Me} & \text{Me} & \text{Me} \\ \text{Si-O-Si-O-Si-O} \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ \text{CF}_3 & & \text{CF}_3 \end{array}$	δ 2.5-1.8 (m, 4H, CF ₃ CH ₂), 1.05-0.4 (m, 9H, SiCH + CH ₂ CH ₃), 0.02, 0.012 (2s, 9H, SiMe)

TABLE I

COMPOUNDS PREPARED BY COHYDROLYSIS

CHARACTERIZATION DATA

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COMPOUND	b.p. (mm)	n_D^{25}	Sp.Gr. ²⁵	NMR
$(\text{Me}, \text{SiO})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_2$	82 (22)	1.3779	0.9480	δ 0.67(m, SiCH ₂) + 2.05(m, CF ₃ CH ₂) (4H) δ 0.11(s, SiCH ₃) + δ 0.06(s, CH ₃ SiCH ₂ CH ₂ CF ₃) (21H)
$(\text{Me}, \text{SiO})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_2$	56 (0.14)	1.3789	1.0396	δ 0.73(m, SiCH ₂) + δ 2.06(m, CF ₃ CH ₂) (8H), δ 0.13(s, 24H, SiCH ₃)
$(\text{Me}, \text{SiO})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_2$	61 (10)	1.3696	--	δ 4.56(s, 1H, SiH), δ 2.0(m, 2H, CF ₃ CH ₂), δ 0.73(m, 2H, CH ₂ Si), δ 0.11(s, 18H, SiCH ₃)
$(\text{Me}, \text{SiO})_2\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)_2$	103 (10)	1.3694	--	δ 4.65(s, 2H, SiH), δ 2.2(m, 4H, CF ₃ CH ₂) δ 0.81(m, 4H, SiCH ₂), δ 0.16(s, 17H, SiCH ₃)
$(\text{Me}, \text{SiO})_2\text{SiMeVi}$ (reported ¹ , 70 (25), n_D^{25} 1.3947)	80 (40)	1.3947		
$(\text{Me}, \text{SiO})_2\text{SiMeVi}$ (reported ¹ , 99 (13), n_D^{25} 1.4069)	89 (7)	1.4067		
$[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2\text{Si})_2\text{SiO}]_2\text{SiMeVi}$	56 (4)	1.3747		δ 0.17(s, 3H, ViSiMe), 0.24 (s, 6H, HSiMe) 1.7(m, 4H, SiCH ₂), 2.1(m, 4H, CF ₃ CH ₂), 4.7(s, 2H, SiH), 5.9(m, 3H, Vi)
$[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2\text{Si})_2\text{O}]_2\text{SiMe}$ (reported ² 63 (12), n_D^{25} 1.3569)	79 (25)	1.3559		
$[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2\text{Si})_2\text{O}]_2\text{SiMe}$ CH ₂ CH ₂ CF ₃	57 (0.06)	1.3620	1.1847	(CCl ₄) δ 2.2-.25(2s, 9H, SiMe), 0.73 (m, 6H, SiCH ₂), 1.97(m, 6H, CF ₃ CH ₂), 4.63(s, 2H, SiH)

¹Private communication, D. R. Weyenberg, Dow Corning Corp.²Private communication, D. R. Weyenberg, Dow Corning Corp.

TABLE I (con't.)

COMPOUNDS PREPARED BY COHYDROLYSIS
CHARACTERIZATION DATA

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COMPOUND	Rd		%C		%H		%Si		%F	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Me $(\text{Me}_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{CF}_3$	0.2392	0.2401	37.7	38.3	7.9	8.1	25.1	26.5	17.9	17.2
Me $[\text{Me}_3\text{SiOSi}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{O}]_2$	0.2180	0.2193	35.4	36.0	6.8	7.0	23.7	21.9	24.0	24.9
H $(\text{Me}_3\text{SiO})_2\text{SiCH}_2\text{CH}_2\text{CF}_3$	--	--	35.5	35.6	7.6	7.7	27.7	26.3	18.7	18.5
H $[\text{Me}_3\text{SiOSi}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{O}]_2$	--	--	32.3	32.7	6.3	6.3	25.2	24.3	25.5	26.4
SiMeVi $[\text{HMe}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{SiO}]_2$	0.2125	0.2114								
SiMe $[\text{HMe}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}]_2$ $\text{SiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)$	0.1872	0.1853								

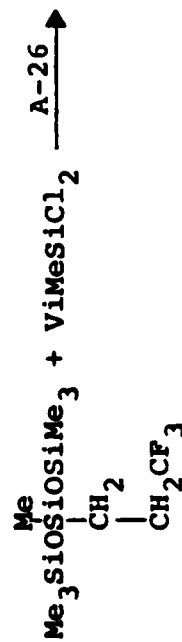
TABLE III

SILOXY/CHLORIDE EXCHANGE SYSTEMS SCREENED

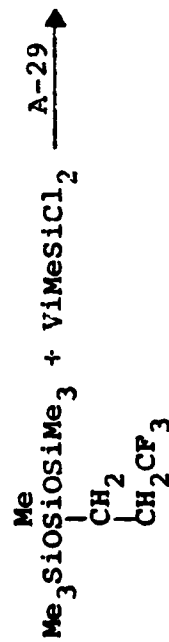
TRIMER REACTIONS



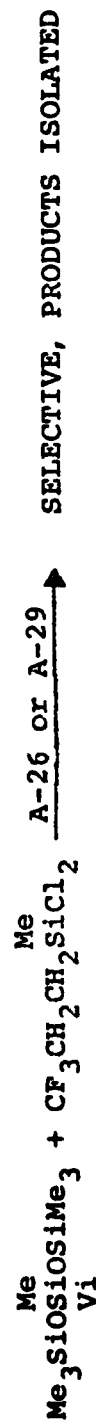
VERY SLOW, SELECTIVE, OPTIMIZATION ATTEMPTED



SELECTIVE, PRODUCTS ISOLATED



LESS SELECTIVE THAN A-26



SELECTIVE, PRODUCTS ISOLATED

TABLE III (continued)

TETRAMER REACTIONS

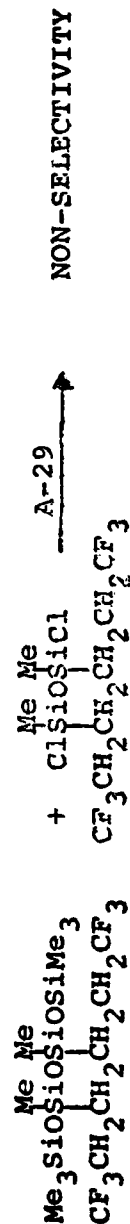
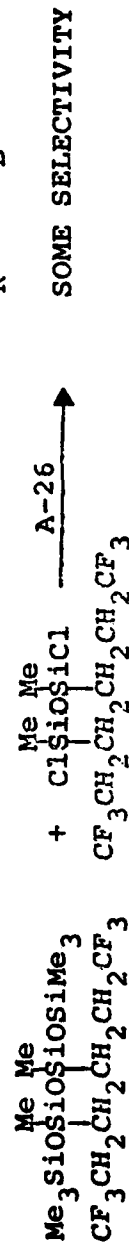
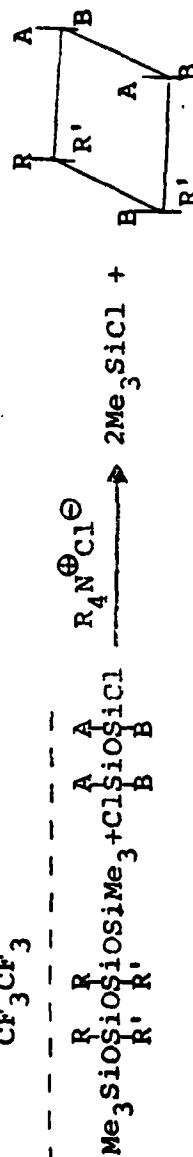
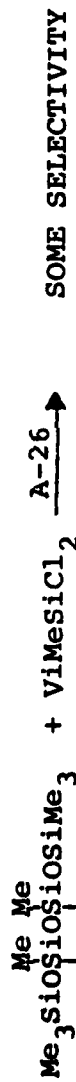
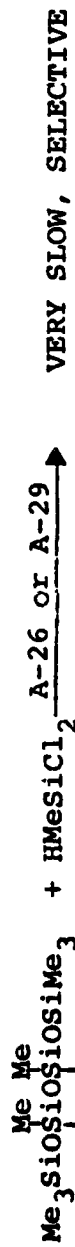


TABLE IV
COMPOUNDS PREPARED BY SILOXY/CHLORIDE EXCHANGE

COMPOUND	b.p.	Other	H' NMR (CCl ₄)
$\begin{array}{c} \text{H} \\ \\ \text{Me}_3\text{SiOSiCH}_2\text{CH}_2\text{CF}_3 \\ \\ \text{Cl} \end{array}$	75 (70mm)	—	δ 5.11 (s, 1H, SiH), δ 0.2 (s, 9H, SiMe) $[\delta$ 2.14 (m, CF ₃ CH ₂) + δ 1.06 (m, CH ₂ Si) (4H)]
$\begin{array}{c} \text{H} \\ \\ \text{Me}_3\text{Si(OSi} \cdots \text{)}_2\text{Cl} \\ \\ \text{CH}_2\text{CH}_2\text{CF}_3 \end{array}$	76 (5 mm)	—	δ 5.21 (s, 1H, ClSiH), δ 4.67 (s, 1H, SiH), δ 0.16 (s, 9H, SiMe), $[\delta$ 2.13 (m, CH ₂ CF ₃) + δ 1.02 (m, SiCH ₂) (8H)]
$\begin{array}{c} \text{Me Me} \\ \\ \text{Me}_3\text{SiOSiSiCl} \\ \\ \text{Pr Vi} \end{array}$	72 (6 mm)	NEUT. EQUIV. FD. 358 CALC'D. 351	δ 6.0 (m, 3H, Vi), δ (m, 4H, CH ₂ CH ₂ CF ₃), δ 0.51 (s, 3H, CH ₃ SiCl) δ 0.13 (s, 9H, Me ₃ Si), $[\delta$ 2.10 (m, CFCH ₂ + δ 0.76 (m, SiCH ₂) (4H)]
$\begin{array}{c} \text{Me Me} \\ \\ (\text{ClSiO})_2\text{SiCH}_2\text{CH}_2\text{CF}_3 \\ \\ \text{Vi} \end{array}$	88 (6 mm)	NEUT. EQUIV. FD. 197 CALC'D. 191.7	δ 6.1 (m, 3H, Vi), δ 0.5 + (s, 6H, CH ₃ SiCl), δ 0.25 (s, 3H, CH ₃ Si), $[\delta$ 2.13 (m, CH ₂ CF ₃) + δ 0.85 (m, SiCH ₂) (4H)]
$\begin{array}{c} \text{Me} \\ \\ (\text{ClSiO} \cdots \text{)}_2\text{SiMeVi} \\ \\ \text{CH}_2\text{CH}_2\text{CF}_3 \end{array}$	100 (15 mm)	—	δ 6.1 (m, 3H, Vi), $[\delta$ 2.15 (m, CH ₂ CF ₃) + δ 1.06 (m, SiCH ₂) (4H)], δ 0.52 (s, 6H, MeSiCl) δ 0.36 (s, 3H, CH ₃ SiVi)
$\begin{array}{c} \text{Me} \\ \\ (\text{HOSiO} \cdots \text{)}_2\text{SiMe} \\ \\ \text{CH}_2\text{CH}_2\text{CF}_3 \end{array}$	DERIVATIVE	δ 6.42 (s, 2H, SiOH), δ 5.9 (m, 3H, Vi), $[\delta$ 2.2 (m, CH ₂ CF ₃) + δ 0.65 (m, CH ₂ Si) (8H)], δ 0.66 (s, 6H, CH ₃ Si), δ 0.16 (s, 3H, CH ₃ SiVi)	²⁵ n _D 1.3925

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