

# Novel Synthesis of Cyclic Methylvinylsiloxanes by the Reaction of Methylvinyl Diethoxysilane with Phosphorous Pentachloride

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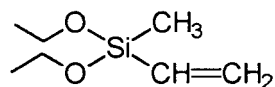
**ABSTRACT:** We report a novel synthesis of the cyclic oligomers  $[(\text{H}_2\text{C}=\text{CH})(\text{CH}_3)\text{SiO}]_n$  obtained by the reaction between phosphorous pentachloride and methylvinyl diethoxysilane. According to gas chromatography/mass spectrometry data, the reaction product consisted of a mixture of cyclic oligomers in which the most important fractions were composed of cycles with  $n = 5, 6,$  or  $7$ . The reaction product was also characterized by Fourier transform infrared and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Experimental results suggested a new kind of reaction between the phosphorous pentachloride and terminal olefins directly bonded to silicon, which was probably associated with sterical effects favoring C—O—Si bond cleavage of ethoxy groups instead of the conventional addition of phosphorous pentachloride to olefinic linkages. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 3182–3189, 2002

**Keywords:** methylvinyl diethoxysilane; cyclic methylvinylsiloxanes; phosphorous pentachloride; oligomers; synthesis; polysiloxanes

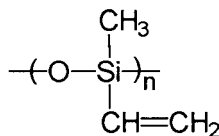
## INTRODUCTION

The addition of phosphorous pentachloride ( $\text{PCl}_5$ ) to nonsymmetrical olefins yields adducts of the type  $\text{RCHCl}-\text{CH}_2\text{PCl}_4$ ; treated with water or alcohols, these provide  $\alpha,\beta$ -unsaturated phosphonic acids or esters, respectively.<sup>1</sup>

Methylvinyl diethoxysilane ( $\text{C}_7\text{H}_{16}\text{O}_2\text{Si}$  or **1**) has a nonsymmetrical terminal double bond of the general type  $\text{RCH}=\text{CH}_2$ . Although styrene and 10-undecenoic acid have successfully led to the corresponding phosphonic derivatives,<sup>2,3</sup> the reaction between **1** and  $\text{PCl}_5$  has produced a mixture of cyclic methylvinylsiloxanes (**2**) instead of the expected unsaturated  $\alpha,\beta$ -phosphonic acids or esters.



**1**



**2**

$n = 5, 6, 7$

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Cyclic methylvinylsiloxanes are interesting compounds because they can be polymerized through vinyl groups and siloxane bond rearrangement. They can also be used to introduce unsaturation into a wide variety of organosiloxane materials.<sup>4</sup> The cyclic oligomers  $[(\text{CH}_2=\text{CH})(\text{CH}_3)\text{SiO}]_n$  ( $n = 3-7$ ) have been used as monomers to obtain poly(methylvinylsiloxane).<sup>5</sup>

The cyclic oligomers can be obtained from an appropriate haloorganosilane via refluxing with hydrochloric acid for 72 h. This reaction leads to a mixture of cyclic siloxanes, which can be fractionated under reduced pressure.<sup>6</sup> An alternative is the reaction between 1,3,5-trivinyl-1,3,5-trimethyl cyclotrisiloxane and vinylmethyl dichlorosilane at room temperature for 25 h in the presence of hydrochloric acid as a catalyst.<sup>7</sup>

The aforementioned methods produce cyclic siloxanes in variable yields and use haloorganosilanes, which are corrosive in nature and difficult to handle. On the contrary, the reaction of **1** and  $\text{PCl}_5$  takes place within 12 h at room temperature and provides **2** in an approximately 70% yield.

The results indicate that the cyclization process is aided by  $\text{PCl}_5$ , whereas the vinyl group remains unmodified during the reaction.

## EXPERIMENTAL

### Materials

**1** (molecular weight = 160.30 g/mol; Petrarch) and  $\text{PCl}_5$  (molecular weight = 208.25 g/mol; Merck) were used as received. Chromatographic water-free benzene (Riedel de Haen) was used as a reaction solvent. Methanol and ethanol (Merck) and dichloromethane (Riedel de Haen) were used without purification.

**1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 0.05 (s, 3H), 1.00 (t,  $J = 6.9$  Hz, 6H,  $\text{CH}_3-\text{CH}_2$ ), 3.55 (q,  $J = 6.9$  Hz, 4H,  $\text{CH}_3-\text{CH}_2$ ), 5.5 (dd,  $J = 2.5$  and 9.5 Hz, 1H), 5.75 (dd,  $J = 2.5$  and 12.0 Hz, 1H), 6.1 (dd,  $J = 9.5$  and 12.0 Hz, 1H). IR: 3060, 2970, 2930, 1580, 1410, 1250, 1110, 1090, 1000, 970, 810, 770, 700  $\text{cm}^{-1}$ .

### Synthesis of Cyclic Methylvinylsiloxanes (**2**)

To a 50-mL, two-necked flask fitted with a dropping funnel, a drying tube, and a stirring bar,  $\text{PCl}_5$  (0.05 mol) and dry benzene (10 mL) were added. The flask was cooled in an ice-water bath,

and **1** (0.025 mol) in dry benzene (5 mL) was incorporated dropwise, under stirring, at such a rate (15 min) that the temperature was maintained at 20–25°C. The thick, white reaction mixture was stirred for an additional 30 min and allowed to stand overnight at room temperature.

The reaction product was then slowly added (for 20 min) to dry methanol (0.1 mol) cooled to 0°C, whereas the temperature was kept below 20°C. When the addition was complete, the resulting solution was concentrated to about 5 mL, washed with water, aqueous  $\text{NaHCO}_3$ , and more water, and then dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure to yield a product that was purified by chromatography on silica gel (1:1 chloroform/diethyl ether) and analyzed by NMR. The reaction also led to **2** when ethanol or water was used instead of methanol.

A total of 27.8 g of **2** was obtained from methanalysis; this corresponds to a 72% yield on the basis of the original weight of **1** added. Similar yields were attained from hydrolysis (69%) and ethanolysis (71%).

### Characterization

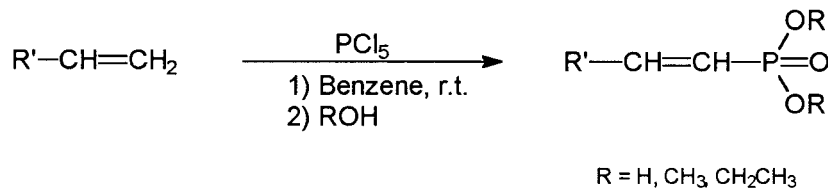
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz for  $^1\text{H}$  and 75.47 MHz for  $^{13}\text{C}$ ) in  $\text{CDCl}_3$ . The gas chromatography/mass spectrometry (GC-MS) work was carried out on a Hewlett-Packard GC HP 6890 (capillary-column) MS HP 5972 A, with lower injection port temperatures, 150–250 °C (10 °C/min), for minimal sample decomposition.<sup>8</sup> Fourier transform infrared spectra were obtained on a Nicolet Nexus 470.

### Cyclic Methylvinylsiloxane (**2**)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 0.00 (s, 3H), 5.63 (dd,  $J = 9.5$  and 12.1 Hz, 1H), 5.80 (dd,  $J = 2.5$  and 9.5 Hz, 1H), 5.99 (dd,  $J = 2.5$  and 12.1 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): -0.166, 133.65, 137.95).

$^{13}\text{C}$  NMR (distortionless enhancement by polarization transfer 135) showed two positive signals at -0.166 ( $\text{CH}_3-\text{Si}$ ) and 137.93 ( $-\text{HC}=\text{CH}_2$ ) and only one negative signal at 133.66 ( $\text{H}_2\text{C}=\text{CH}$ ).

IR: 3040, 2960, 1580, 1410, 1250, 1095, 1000, 970, 790, 700  $\text{cm}^{-1}$ . MS (relative intensity)  $m/z$ : 430 ( $\text{M}^+$ , 0.9%), 415 (100), 291 (55), 109 (50), 97 (82), 85 (45), 73 (42), 59 (33); 516 ( $\text{M}^+$ , 0.5%), 501 (82), 377 (90), 365 (73), 109 (48), 97 (100), 85 (55), 73 (41), 59 (30); 602 ( $\text{M}^+$ , 0.3%), 352 (52), 340 (49), 109 (35), 97 (100), 85 (72), 73 (51), 59 (38).



Scheme 1

## RESULTS AND DISCUSSION

The preparation of vinyl phosphonic acids and vinyl phosphonates can be accomplished by the addition of  $\text{PCl}_5$  to vinyl olefins. The direct hydrolysis of the addition complex affords phosphonic acid, whereas methanolysis or ethanolysis yields the corresponding diesters (Scheme 1).

In connection with our interest in the chemistry of  $\alpha,\beta$ -unsaturated phosphonic systems, we tried to synthesize the aforementioned phosphonic derivatives from **1** (Scheme 2).

However, instead of the phosphonic derivatives, in all cases the same product was obtained (**2**).

Therefore, obtaining **2** was serendipitous.<sup>9</sup> In fact, the spectroscopic characteristics of the isolated product did not conform to those of the expected vinyl phosphonic acid or the corresponding esters (**3a-c**).

The reaction between **1** and  $\text{PCl}_5$  resulted in the formation of a methylvinylsiloxane oil without the loss of vinyl unsaturation.

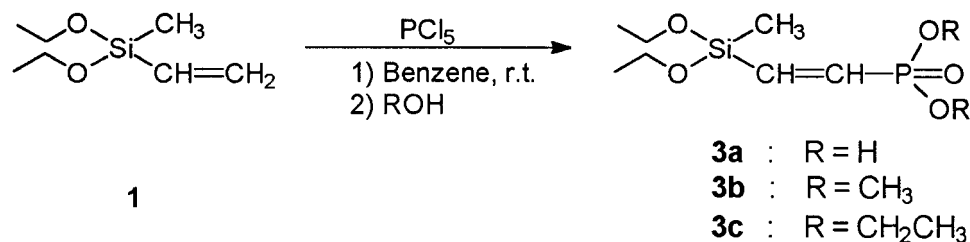
The absence of the ethoxy groups signals in the  $^1\text{H}$  NMR spectra indicated the complete conversion of the starting material (**1**) into the cyclic methylvinylsiloxane (**2**), as shown in Figure 1.

The NMR spectra only show the methyl group and the vinyl group, and this agrees with the cyclic structure of the siloxanes because of the equivalent environments for the silicon substituents [Fig. 1(b,c)].

The IR spectra of the reactive end product show the  $\text{Si-CH}_3$  bond as a strong, sharp band at  $1250\text{ cm}^{-1}$ . The unsaturation was easily recognized in the form of two medium bands corresponding to the stretching carbon-hydrogen bond at  $3040\text{ cm}^{-1}$  and the stretching carbon-carbon double bond at  $1595\text{ cm}^{-1}$ . The sharp absorption at  $1410\text{ cm}^{-1}$  and the strong double band between  $960$  and  $1000\text{ cm}^{-1}$  due to the out-of-plane bending hydrogen-carbon vibration confirmed the presence of vinyl groups.

Although the stretching vibrations of  $\text{O-CH}_2\text{CH}_3$  and  $\text{Si-OCH}_2\text{CH}_3$ , defined as two strong doublets at  $2870\text{-}2980$  and  $1080\text{-}1110\text{ cm}^{-1}$ , respectively,<sup>11</sup> helped us to identify the ethoxy groups in the starting material, in **2**, a widening of the last band confirmed the stretching of the  $\text{Si-O}$  bond in the cyclic oligomer.<sup>12</sup> Additional evidence that the ethoxy groups were not present in **2** is the medium single band due to the methyl at  $2960\text{ cm}^{-1}$ .

The reaction product was also analyzed by GC and proved to be a mixture of mainly cyclic pentamer (49%) and cyclic hexamer (39%), with some cyclic heptamer (12%).



Scheme 2

Current Data Parameters  
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 EXPNO 30  
 PROCNO 1

F2 - Acquisition Parameters  
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 INSTRUM spect  
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 PULPROG zg30  
 TO 69536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6250.000 Hz  
 FIDRES 0.095387 Hz  
 AQ 5.242299 sec  
 RG 45  
 DW 80.000 usec  
 DE 114.28 usec  
 TE 300.0 K  
 DI 1.00000000 sec  
 P1 10.00 usec  
 SF01 300.1351798 MHz  
 NUCLEUS <sup>1</sup>H

F2 - Processing parameters  
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 SF 300.1334052 MHz  
 NQW EN  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

ID NMR plot parameters  
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 FIP 11.000 ppm  
 FJ 3301.47 Hz  
 FZP -1.000 ppm  
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 PPMCH 0.60000 ppm/cm  
 NTCN 180.00005 Hz/cm

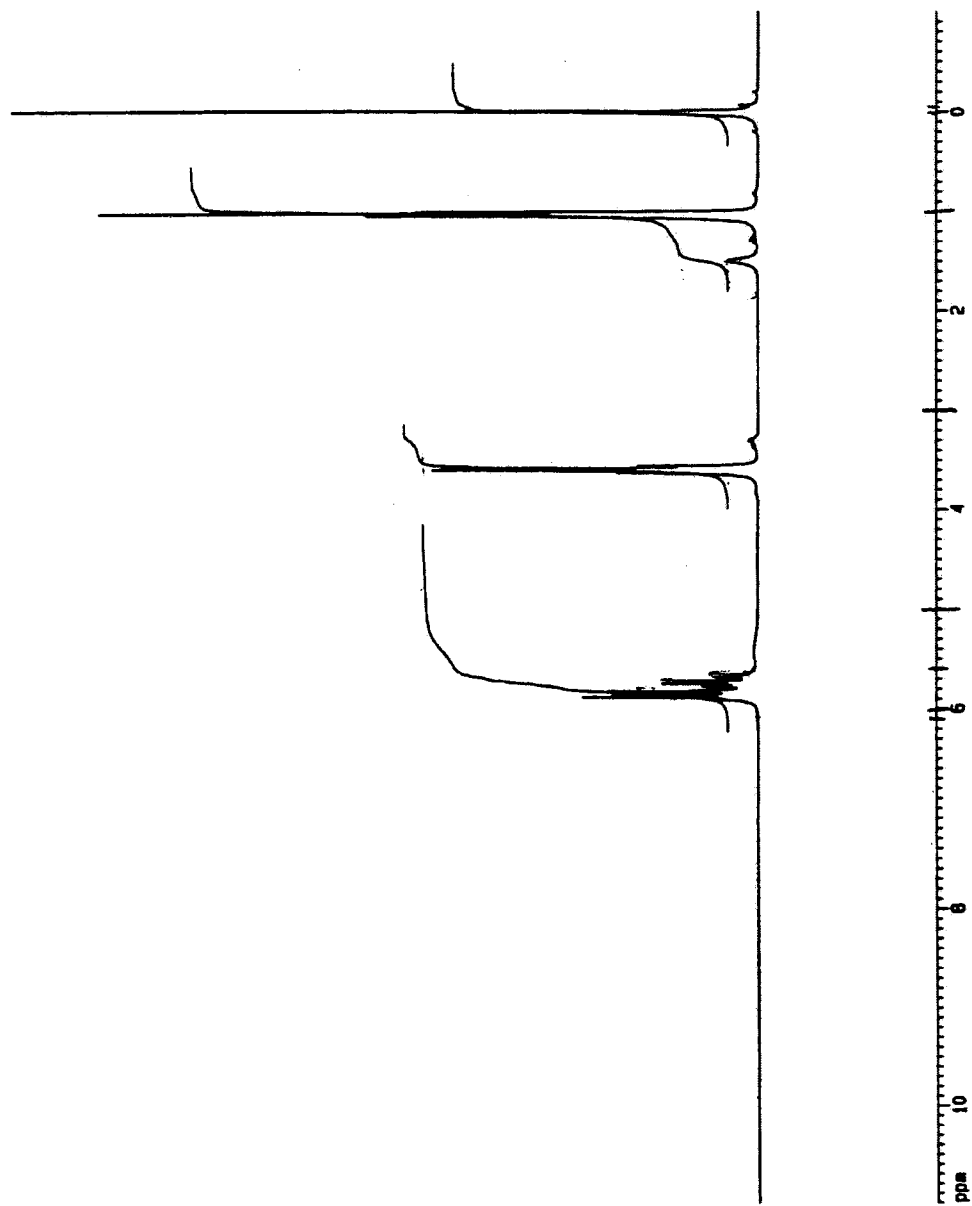


Figure 1. <sup>1</sup>H NMR spectra of (a) **1** and (b,c) **2** obtained by the hydrolysis and methanolysis, respectively, of compound **4**.

```

Current Data Parameters
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EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
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Time     10.05
INSTRUM spect
PROBHD   5 mm BBO BB-1
PULPROG zg30
TD       65536
SOLVENT CDCl3
NS       16
DS       2
SWH      6250.000 Hz
FIDRES   0.095367 Hz
AQ       5.2429295 sec
RG       90
DM       80.000 usec
DE       114.29 usec
TE       300.0 K
D1       1.0000000 sec
P1       10.00 usec
SFO1     300.1351790 MHz
NUCLEUS  1H

F2 - Processing parameters
SI       32768
SF       300.1334162 MHz
MDN      EN
SSB      0
LB       0.30 Hz
GB       0
PC       1.00

1D NMR plot parameters
CX       20.00 cm
F1P      11.000 ppm
F1       3301.47 Hz
F2P      -1.000 ppm
F2       -300.13 Hz
PPMCH    0.60000 ppm/cm
HZCM     180.08005 Hz/cm
    
```

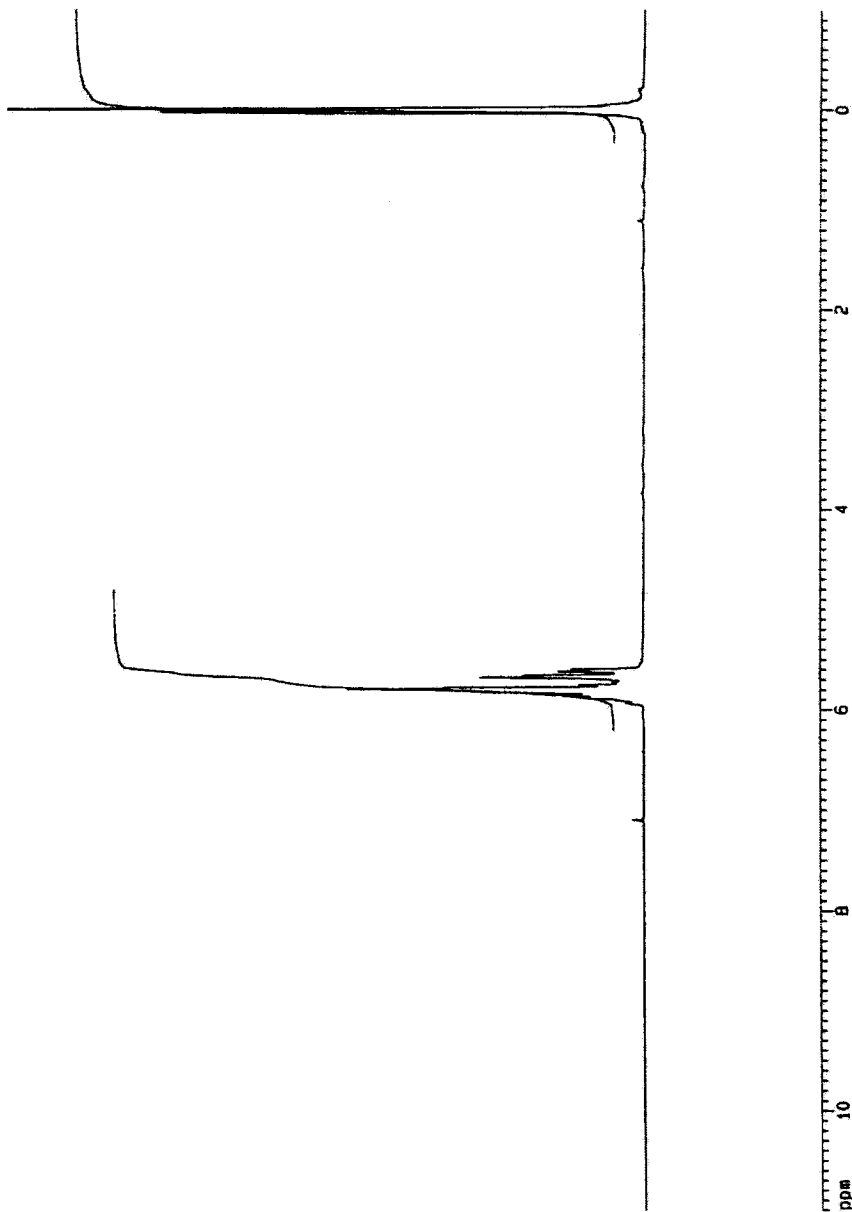


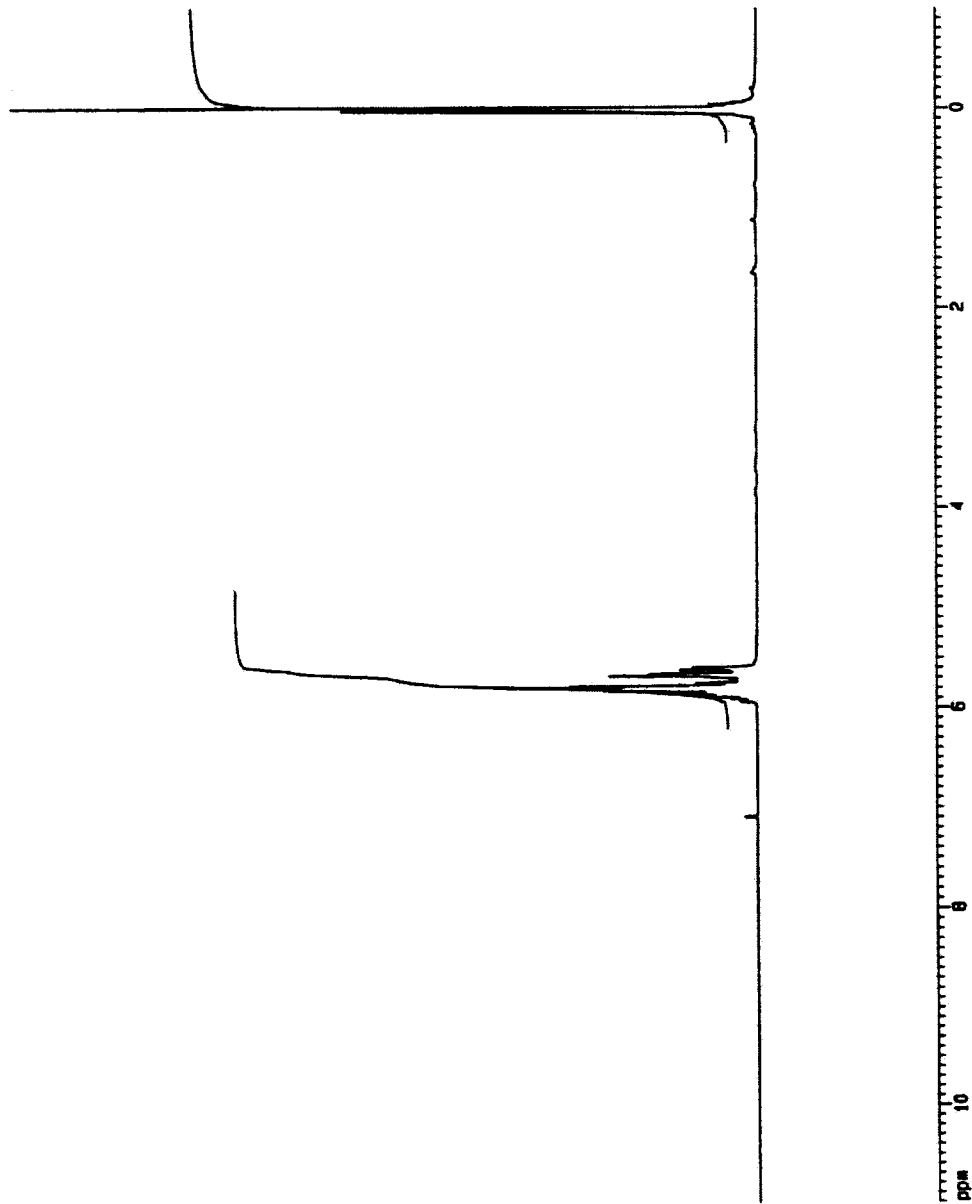
Figure 1. (Continued from the previous page)

Current Data Parameters  
 NAME storifemmed  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
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 INSTRUM spect  
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 PULPROG zg30  
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 AQ 5.242626 sec  
 RB 90  
 CW 80.000 usec  
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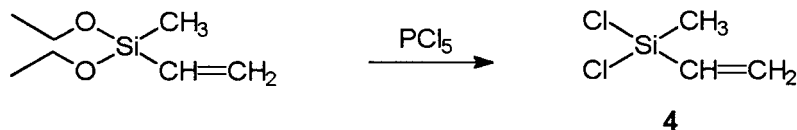
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 PC - 1.00

10 MHz plot parameters  
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 FIP 11.000 ppm  
 F1 3301.47 Hz  
 F2 -1.000 ppm  
 FZ -300.13 Hz  
 PRNCH 0.00000 ppm/cm  
 MICH 180.00005 Hz/cm



(c)

Figure 1. (Continued from the previous page)



Scheme 3

The most significant fragments in the three cyclic siloxanes were found in the lower mass region. All of them arose from a direct cleavage and rearrangement combined process that is known to take place in this kind of silicon compound.<sup>13</sup>

They can be assigned as follows: 59,  $[\text{HO}-\text{Si}=\text{CH}_2]^+$ ; 73,  $[(\text{CH}_2)_3-\text{Si}]^+$ ; 85,  $[(\text{CH}_3)_2-\text{Si}-\text{CH}=\text{CH}_2]^+$ ; 97,  $[(\text{CH}_2=\text{CH})_2-\text{Si}-\text{CH}_3]^+$ ; and 109,  $[\text{Si}(\text{CH}=\text{CH}_2)_3]^+$ .

Except for the pentamer, in which the base peak was observed at  $m/z = 415$  for the  $\text{M}^+-\text{CH}_3$  fragment, in both the hexamer and heptamer, the 100% relative intensity peak was found at  $m/z = 97$ . In this rearrangement cation, the positive charge on the silicon atom is adjacent to the  $\pi$ -electron system of the vinyl group, which leads to a highly resonant stabilized ion.

Even though the reaction mixture in the first step was kept under anhydrous conditions, in the second step, water or water-miscible solvents were used. The highly acidic reaction media due to  $\text{PCl}_5$  could favor  $\text{Si}-\text{O}-\text{C}$  bond scission, leading to the chlorinated adduct **4** (Scheme 3), which was easily hydrolyzed to give the alcohol **5**.

The halogen acid was liberated, and the reaction was reversible, but the equilibrium lay far to the right ( $K \cong 10^{14}$  for chlorosilanes).<sup>14</sup> The  $\text{SiOH}$  groups were so sensitive that traces of acids promoted their condensation, and  $\text{Si}-\text{O}-\text{Si}$  linkages could be formed to give oli-

gomeric and polymeric methylvinylsiloxanes (**2**; Scheme 4).<sup>15</sup>

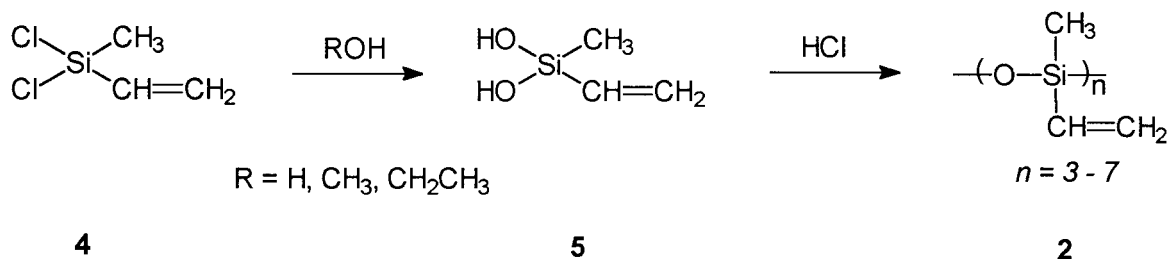
Although remarkably stable under thermal and oxidative degradation, the  $\text{Si}-\text{O}-\text{Si}$  bond was subject to chemical attack and subsequent rearrangement to form siloxane structures of various molecular sizes.<sup>16</sup>

It seems reasonable to assume that  $\text{PCl}_5$  was consumed because the  $\text{Si}-\text{O}-\text{C}$  bonds were easily broken. This stage proceeded smoothly, and the reaction involving electrophilic attack by the reagent on the double bond could not take place.

Another experiment allowed us to verify this observation: when a mixture of the cyclic methylvinylsiloxanes was reacted with  $\text{PCl}_5$  under the same reaction conditions used for **1**, **2** was recovered as the major product (82%) along with minor amounts of an unidentified byproduct. The addition of  $\text{PCl}_5$  to vinyl groups in the cyclic oligomer was again not observed.

All these experimental results suggest a new kind of reaction between  $\text{PCl}_5$  and vinyl groups directly bonded to silicon atoms. We still have no explanation, but an investigation into the chemical behaviors of  $\text{Si}-\text{CH}=\text{CH}_2$  and their analogues ( $\text{C}-\text{CH}=\text{CH}_2$ ) is on the way.

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Scheme 4

nicas, and the Universidad Nacional del Sur of Argentina for their financial support.

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