

## Liquid-phase chlorination of C-chlorovinylsilanes

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Liquid-phase chlorination of a number of chloro(chlorovinyl)methylsilanes was investigated. A number of novel C-chlorosilanes were characterized by IR and <sup>1</sup>H NMR spectra. Some regularities of these reactions were determined; correlations between the structure of chloro(chlorovinyl)methylsilanes and their reactivities were identified.

**Key words:** chloro(chlorovinyl)methylsilanes, chlorine, chlorination, chloroethylsilanes, C-chlorosilanes, IR spectra, <sup>1</sup>H NMR spectra.

Chlorination of trichloro( $\beta$ -chlorovinyl)silane, trichloro(perchlorovinyl)silane, perchlorovinyltrimethylsilane, and dichloro(perchlorovinyl)methylsilane has been considered in a number of papers.<sup>1–5</sup> It was reported that perchlorovinyltrimethylsilane is more active than trichloro(perchlorovinyl)silane and in one of these papers,<sup>5</sup> it has been noted that during chlorination of dichloro(perchlorovinyl)methylsilane, chlorine is added initially to the double bond and after that, the methyl group is chlorinated.

In the present work we attempted to study in detail chlorination of a number of chloro(chlorovinyl)methylsilanes Me<sub>n</sub>Cl<sub>3–n</sub>SiR (where  $n = 0–3$ ; R = –CCl=CH<sub>2</sub>, –CH=CHCl, –CCl=CHCl, –CH=CCl<sub>2</sub>, –CCl=CCl<sub>2</sub>), in order to evaluate the synthetic potential of these monomers in one of the most technologically efficient and industrially important reactions of preparation of carbochlorosilanes. On the other hand, it has been of interest to study the variation of activity of these compounds as a function of their structure, in particular, as a function of the number and positions of chlorine atoms in the molecule.

The reactions were carried out in the absence of solvents or catalysts. The obtained products and their yields are presented in Table 1.

Experimental data indicate that these reactions follow several pathways: (1) addition of chlorine to the double bond of silicon-containing chloroolefins yielding chloroethylsilanes; (2) replacement of hydrogen atoms in these chloroethylsilanes by chlorine; (3) formation of decomposition products; (4) substituting chlorination of the methyl groups attached to the silicon atoms.

Accumulation of methyl groups at the silicon atom facilitates all of these reactions. Below we consider each of them in more detail. Conditions in which the synthesis

was conducted and the properties of new carbochlorosilanes obtained in this study are presented in Table 2. Parameters of the <sup>1</sup>H NMR spectra are listed in Table 3. The  $\nu(\text{CCl})$  stretching vibrations in the IR spectra of chloroethylsilanes are exhibited at a frequency of 730–760 cm<sup>–1</sup>, *i.e.*, they are shifted to lower frequencies with respect to those of the starting chlorovinyl compounds. The  $\nu(\text{SiCl})$  stretching frequencies are retained irrespective of the structure of the alkyl substituents:  $\nu(\text{SiCl})$  460–490 cm<sup>–1</sup>;  $\nu(\text{SiCl}_2)$  480–490, 530–550 cm<sup>–1</sup>; and  $\nu(\text{SiCl}_3)$  460–480, 580–600 cm<sup>–1</sup>.

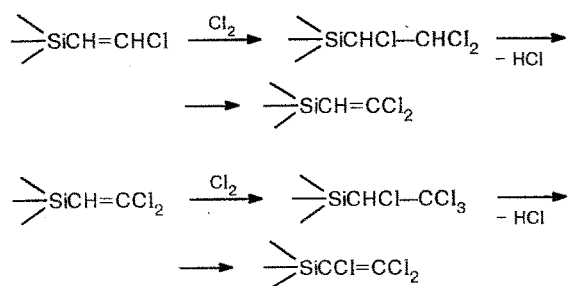
To evaluate relative activities of the double bonds in silicon-containing chloroolefins, we carried out a number of competing reactions in which gaseous chlorine was bubbled through an equimolar mixture of two compounds, and variation of the concentrations of the reactants was determined by GLC at regular intervals (Table 4).

The competing reactions made it possible to identify the following general rules: (1) irrespective of the structure of the chloroolefin, replacement of a chlorine or hydrogen atom in it by the trichlorosilyl group deactivates the double bond in the reaction under consideration (Table 4, runs 1–5); (2) activity of the double bond in the chloro(C-chlorovinyl)silanes decreases as the number of chlorine atoms in the vinyl moiety increases (Table 4, runs 6–10); (3) with the numbers of chlorine atoms in the chloro(C-chlorovinyl)silane molecules being equal (Table 4, runs 6, 9), a chlorine atom in the  $\beta$ -position with respect to the silyl group exerts the greatest deactivating effect on the double bond, and with increase in the degree of chlorination the effect of the position of the chlorine atoms considerably decreases.

**Table 1.** Chlorination of C-chlorovinylsilanes

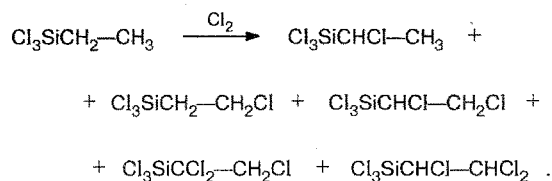
Starting chlorovinylsilane	Reaction products	Yield (% of the theoretical yield)	Starting chlorovinylsilane	Reaction products	Yield (% of the theoretical yield)
Cl <sub>3</sub> SiCH=CHCl	Cl <sub>3</sub> SiCHCl-CHCl <sub>2</sub>	95	Cl <sub>3</sub> SiCH=CCl <sub>2</sub>	Cl <sub>3</sub> SiCHCl-CCl <sub>3</sub>	95
	Cl <sub>3</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	2		Cl <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	2
	Cl <sub>3</sub> SiCHCl-CCl <sub>3</sub>	1	MeCl <sub>2</sub> SiCH=CCl <sub>2</sub>	MeCl <sub>2</sub> SiCHCl-CCl <sub>3</sub>	88
MeCl <sub>2</sub> SiCH=CHCl	MeCl <sub>2</sub> SiCHCl-CHCl <sub>2</sub>	95		MeCl <sub>2</sub> SiCCl=CCl <sub>2</sub>	2
	MeCl <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	2		MeCl <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	3
	MeCl <sub>2</sub> SiCHCl-CCl <sub>3</sub>	1	Me <sub>2</sub> ClSiCH=CCl <sub>2</sub>	Me <sub>2</sub> ClSiCHCl-CCl <sub>3</sub>	84
Me <sub>2</sub> ClSiCH=CHCl	Me <sub>2</sub> ClSiCHCl-CHCl <sub>2</sub>	70		Me <sub>2</sub> ClSiCCl=CCl <sub>2</sub>	3
	Me <sub>2</sub> ClSiCCl <sub>2</sub> -CHCl <sub>2</sub>	3		Me <sub>2</sub> ClSiCCl <sub>2</sub> -CCl <sub>3</sub>	5
	Me <sub>2</sub> ClSiCHCl-CCl <sub>3</sub>	2	Me <sub>3</sub> SiCH=CCl <sub>2</sub>	Me <sub>3</sub> SiCHCl-CCl <sub>3</sub>	30
	Me <sub>2</sub> ClSiCCl <sub>2</sub> -CCl <sub>3</sub>	2		Me <sub>3</sub> SiCCl=CCl <sub>2</sub>	2
	Me <sub>2</sub> SiCl <sub>2</sub>	6		Me <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	3
	CHCl=CHCl	5	Me <sub>3</sub> SiCl	7	
	CHCl <sub>2</sub> -CHCl <sub>2</sub>	2	CHCl=CCl <sub>2</sub>	5	
Me <sub>3</sub> SiCH=CHCl	Me <sub>3</sub> SiCHCl-CHCl <sub>2</sub>	45	CCl <sub>2</sub> =CCl <sub>2</sub>	1	
	Me <sub>3</sub> SiCH=CCl <sub>2</sub>	Traces	CHCl <sub>2</sub> -CCl <sub>3</sub>	2	
	Me <sub>3</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	2	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCHCl-CCl <sub>3</sub>	33	
	Me <sub>3</sub> SiCHCl-CCl <sub>3</sub>	1	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	6	
	Me <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	14	Cl <sub>3</sub> SiCCl=CHCl	Cl <sub>3</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	94
	Me <sub>3</sub> SiCl	10		Cl <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	2
	CHCl=CHCl	7	MeCl <sub>2</sub> SiCCl=CHCl	MeCl <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	93
	CHCl <sub>2</sub> -CHCl <sub>2</sub>	3		MeCl <sub>2</sub> SiCCl=CCl <sub>2</sub>	1
	CHCl=CCl <sub>2</sub>	Traces		MeCl <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	3
	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCHCl-CHCl <sub>2</sub>	4	Me <sub>3</sub> SiCCl=CHCl	Me <sub>3</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	45
(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	3	Me <sub>3</sub> SiCCl=CCl <sub>2</sub>		2	
(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	3	Me <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>		4	
Cl <sub>3</sub> SiCCl=CH <sub>2</sub>	Cl <sub>3</sub> SiCCl <sub>2</sub> -CH <sub>2</sub> Cl	97	Me <sub>3</sub> SiCl	Traces	
	MeCl <sub>2</sub> SiCCl=CH <sub>2</sub>	MeCl <sub>2</sub> SiCCl <sub>2</sub> -CH <sub>2</sub> Cl	96	CHCl=CCl <sub>2</sub>	Traces
MeCl <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>		1	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	34	
Me <sub>2</sub> ClSiCCl=CH <sub>2</sub>	Me <sub>2</sub> ClSiCCl <sub>2</sub> -CH <sub>2</sub> Cl	95	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	5	
	Me <sub>2</sub> ClSiCCl <sub>2</sub> -CHCl <sub>2</sub>	2	Cl <sub>3</sub> SiCCl=CCl <sub>2</sub>	Cl <sub>3</sub> SiCCl <sub>2</sub> -Cl <sub>3</sub>	96
Me <sub>3</sub> SiCCl=CH <sub>2</sub>	Me <sub>3</sub> SiCCl <sub>2</sub> -CH <sub>2</sub> Cl	62		MeCl <sub>2</sub> SiCCl=CCl <sub>2</sub>	95
	Me <sub>3</sub> SiCCl=CHCl	Traces	(CH <sub>2</sub> Cl)Cl <sub>2</sub> SiCCl <sub>2</sub> -Cl <sub>3</sub>	Traces	
	Me <sub>3</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	7	Me <sub>2</sub> ClSiCCl=CCl <sub>2</sub>	Me <sub>2</sub> ClSiCCl <sub>2</sub> -Cl <sub>3</sub>	72
	Me <sub>3</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	4		(CH <sub>2</sub> Cl)MeClSiCCl <sub>2</sub> -CCl <sub>3</sub>	17
	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CH <sub>2</sub> Cl	19	Me <sub>3</sub> SiCCl=CCl <sub>2</sub>	Me <sub>3</sub> SiCCl <sub>2</sub> -Cl <sub>3</sub>	35
	(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CHCl <sub>2</sub>	1		(CH <sub>2</sub> Cl)Me <sub>2</sub> SiCCl <sub>2</sub> -CCl <sub>3</sub>	53

Not only chloroethylsilanes resulting from substituting chlorination of chloroethyl radicals B, but also C-chlorovinylsilanes containing more chlorine atoms in the vinylic group than the starting compounds were detected in the reaction products (Table 1). It may be suggested that these compounds are formed *via* dehydrochlorination of the initially formed chloroethylsilanes:



Therefore, this direction of the process may occur by two routes: substituting chlorination of chloroethyl radicals (a); or their successive dehydrochlorination and chlorination (b), for example see Scheme 1.

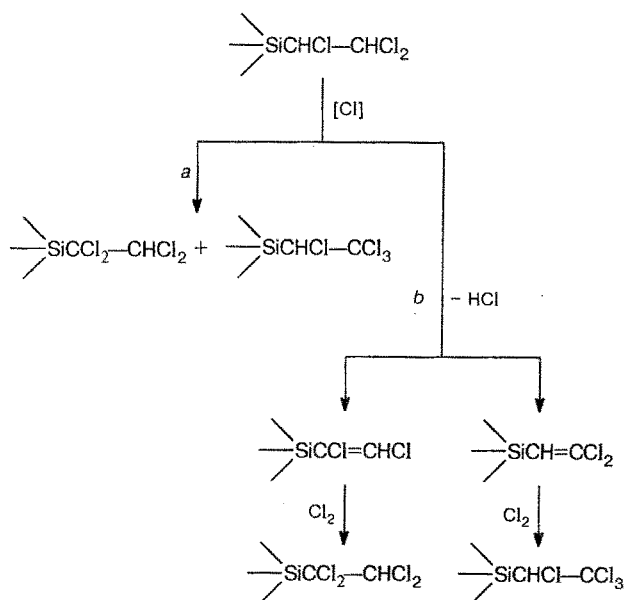
Chlorination of trichloroethylsilane under similar conditions gave chloroethylsilanes:



No trichlorovinylsilane or trichloro(monochlorovinyl)silane were detected in the reaction products. However, this does not rule out the possibility that the

**Table 2.** Chlorination conditions and properties of the products obtained

Compound	Synthesis conditions		B.p./°C (p/Torr)	M.p./°C	d <sub>4</sub> <sup>20</sup>	n <sub>d</sub> <sup>20</sup>
	ΔT/°C	Duration/h				
Cl <sub>3</sub> SiCHCl—CHCl <sub>2</sub> ( <b>1</b> )	22—93	6.0	63(3)	—	1.635	1.5049
CH <sub>3</sub> Cl <sub>2</sub> SiCHCl—CHCl <sub>2</sub> ( <b>2</b> )	22—103	6.0	75(10)	—	1.473	1.4988
(CH <sub>3</sub> ) <sub>2</sub> ClSiCHCl—CHCl <sub>2</sub> ( <b>3</b> )	22—83	5.0	52(2)	—	1.329	1.4918
(CH <sub>3</sub> ) <sub>3</sub> SiCHCl—CHCl <sub>2</sub> ( <b>4</b> )	22—55	5.0	37(1.5)	—	1.196	1.4828
Cl <sub>3</sub> SiCCl <sub>2</sub> —CH <sub>2</sub> Cl ( <b>5</b> )	22—30	4.0	50(1)	58	—	—
CH <sub>3</sub> Cl <sub>2</sub> SiCCl <sub>2</sub> —CH <sub>2</sub> Cl ( <b>6</b> )	24—64	2.5	56(3)	54—56	—	—
(CH <sub>3</sub> ) <sub>2</sub> ClSiCCl <sub>2</sub> —CH <sub>2</sub> Cl ( <b>7</b> )	24—50	2.5	60(5)	53	—	—
(CH <sub>3</sub> ) <sub>3</sub> SiCCl <sub>2</sub> —CH <sub>2</sub> Cl ( <b>8</b> )	17—37	2.5	80(30)	48—50	—	—
(ClCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCCl <sub>2</sub> —CH <sub>2</sub> Cl ( <b>9</b> )	17—37	2.5	68(3)	36—38	—	—
Cl <sub>3</sub> SiCHCl—CCl <sub>3</sub> ( <b>10</b> )	22—45	4.0	53(1)	—	1.710	1.5169
CH <sub>3</sub> Cl <sub>2</sub> SiCHCl—CCl <sub>3</sub> ( <b>11</b> )	22—34	4.0	39—40(1)	—	1.565	1.5121
(CH <sub>3</sub> ) <sub>2</sub> ClSiCHCl—CCl <sub>3</sub> ( <b>12</b> )	22—54	4.0	46(1.5)	—	1.443	1.5060
(CH <sub>3</sub> ) <sub>3</sub> SiCHCl—CCl <sub>3</sub> ( <b>13</b> )	22—40	3.0	33(1)	—	1.288	1.4954
(ClCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCHCl—CCl <sub>3</sub> ( <b>14</b> )	22—40	3.0	71(1.5)	—	1.414	1.5180
Cl <sub>3</sub> SiCCl <sub>2</sub> —CHCl <sub>2</sub> ( <b>15</b> )	24—42	7.0	53—54(1)	—	1.713	1.5175
CH <sub>3</sub> Cl <sub>2</sub> SiCCl <sub>2</sub> —CHCl <sub>2</sub> ( <b>16</b> )	22—53	5.0	66—67(2)	—	1.586	1.5157
(CH <sub>3</sub> ) <sub>3</sub> SiCCl <sub>2</sub> —CHCl <sub>2</sub> ( <b>17</b> )	19—38	7.5	46—48(1)	—	1.308	1.5015
(ClCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCCl <sub>2</sub> —CHCl <sub>2</sub> ( <b>18</b> )	19—38	7.5	72—73(1)	—	1.424	1.5234
Cl <sub>3</sub> SiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>19</b> )	70—75	12.0	56(1)	—	1.796	1.5329
CH <sub>3</sub> Cl <sub>2</sub> SiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>20</b> )	65—70	6.0	54(1)	—	—	—
(CH <sub>3</sub> ) <sub>2</sub> ClSiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>21</b> )	65—70	5.5	51(1)	—	1.539	1.5244
(ClCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>22</b> )	65—70	5.5	76(1)	—	1.614	1.5368
(CH <sub>3</sub> ) <sub>3</sub> SiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>23</b> )	22—30	4.5	63(2)	—	1.394	1.5133
(ClCH <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCCl <sub>2</sub> —CCl <sub>3</sub> ( <b>24</b> )	22—30	4.5	88(2)	—	1.514	1.5360

**Scheme 1**

reaction occurs by route *b*, because, as has been shown by the competing reactions (Table 4, run 11), chlorovinylsilanes react with chlorine much more rapidly than chloroethylsilanes.

The tendency of chloro(chlorovinyl)methylsilanes to form decomposition products is determined by both the

**Table 3.** Parameters of the <sup>1</sup>H NMR spectra of C-chlorosilanes

Compound	Chemical shifts, δ		
	α-H	β-H	Other groups
<b>1</b>	3.97	6.02	—
<b>2</b>	3.81	6.06	0.91(Me)
<b>3</b>	3.80	6.13	0.63(Me); 0.56(Me)
<b>4</b>	3.56	5.89	0.2(Me)
<b>5</b>	—	4.09	—
<b>6</b>	—	4.07	1.07(Me)
<b>7</b>	—	4.07	0.73(Me)
<b>8</b>	—	3.95	0.31(Me)
<b>9</b>	—	4.00	0.43(Me); 3.02(CH <sub>2</sub> Cl)
<b>10</b>	4.33	—	—
<b>11</b>	4.27	—	1.0(Me)
<b>12</b>	4.17	—	0.73(Me); 0.68(Me)
<b>13</b>	3.97	—	0.29(Me)
<b>14</b>	4.13	—	0.46(Me); 0.40(Me); 2.95(CH <sub>2</sub> Cl)
<b>15</b>	—	6.00	—
<b>16</b>	—	6.10	1.13(Me)
<b>17</b>	—	5.87	0.33(Me)
<b>18</b>	—	5.85	0.43(Me); 3.02(CH <sub>2</sub> Cl)
<b>19</b>	—	—	—
<b>20</b>	—	—	1.17(Me)
<b>21</b>	—	—	0.78(Me)
<b>22</b>	—	—	0.92(Me); 3.24(CH <sub>2</sub> Cl)
<b>23</b>	—	—	0.30(Me)
<b>24</b>	—	—	0.60(Me); 3.13(CH <sub>2</sub> Cl)

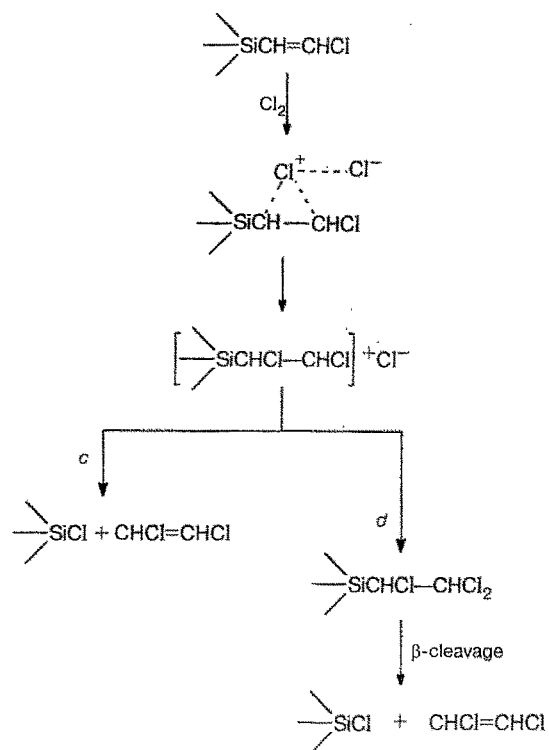
**Table 4.** Competing chlorination of equimolar mixtures of silicon-containing chloroolefins

Run	Starting mixture	Ratio between the molar concentrations of the reactants in the course of the reaction					
		0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
1	ClHC=CHCl Cl <sub>3</sub> SiCH=CHCl	0.98	0.78	0.71	0.55	—	—
2	ClHC=CCl <sub>2</sub> Cl <sub>3</sub> SiCH=CCl <sub>2</sub>	0.68	0.33	0.20	—	—	—
3	Cl <sub>2</sub> C=CCl <sub>2</sub> Cl <sub>3</sub> SiCCl=CCl <sub>2</sub>	0.90	0.87	0.85	0.82	0.70	0.64
4	ClHC=CHCl Cl <sub>3</sub> SiCCl=CHCl	0.43	0.33	0.30	—	—	—
5	ClHC=CCl <sub>2</sub> Cl <sub>3</sub> SiCCl=CCl <sub>2</sub>	0.88	0.76	0.70	0.52	0.39	0.37
6	Cl <sub>3</sub> SiCCl=CH <sub>2</sub> Cl <sub>3</sub> SiCH=CHCl	0.96	0.95	0.84	0.73	0.76	0.72
7	Cl <sub>3</sub> SiCH=CHCl Cl <sub>3</sub> SiCH=CCl <sub>2</sub>	0.97	0.92	0.80	0.75	0.79	—
8	Cl <sub>3</sub> SiCH=CHCl Cl <sub>3</sub> SiCCl=CHCl	0.81	0.79	0.77	0.75	0.67	—
9	Cl <sub>3</sub> SiCCl=CHCl Cl <sub>3</sub> SiCH=CCl <sub>2</sub>	—	0.96	0.95	0.94	0.94	—
10	Cl <sub>3</sub> SiCH=CCl <sub>2</sub> Cl <sub>3</sub> SiCCl=CCl <sub>2</sub>	0.92	0.90	0.89	0.79	0.75	—
11	Cl <sub>3</sub> SiCH=CH <sub>2</sub> Cl <sub>3</sub> SiCH <sub>2</sub> -CH <sub>3</sub>	0.397	0.05	—	—	—	—

nature of the substituents at the silicon atoms and the structure of the vinylic radical. In both cases, accumulation of chlorine atoms reduces the tendency of these compounds to form decomposition products. In fact, decomposition during chlorination of chloro( $\beta$ -chlorovinyl)methylsilanes is observed in the case of Me<sub>2</sub>ClSiCH=CHCl and Me<sub>3</sub>SiCH=CHCl, and during chlorination of chloro( $\beta$ , $\beta$ -dichlorovinyl)methylsilanes, it is observed only in the case of Me<sub>3</sub>SiCH=CCl<sub>2</sub>. Chloro(perchlorovinyl)methylsilanes do not undergo decomposition at all, even in the case of Me<sub>3</sub>SiCCl=CCl<sub>2</sub> (see Table 1). It should also be noted that not only the number of chlorine atoms, but also their arrangement in the vinylic group has a substantial effect on the occurrence of the reaction under consideration by this pathway. The data given in Table 1 indicate that virtually no decomposition products are formed when the starting chloro(chlorovinyl)methylsilane contains a chlorine atom in the  $\alpha$ -position with respect to the silyl group, irrespective of both the number of chlorine atoms in the vinyl radical and the nearest environment of the silicon atom.

Formation of decomposition products may result from either nucleophilic cleavage of the  $\equiv\text{Si}-\text{C}\equiv$  bond

(pathway *c*) or  $\beta$ -cleavage typical of this type of compounds<sup>6</sup> (pathway *d*):



In both cases, accumulation of electronegative chlorine atoms at the silicon atom would hamper cleavage of the  $\equiv\text{Si}-\text{C}\equiv$  bond owing to both steric and inductive factors, arising due to electrostatic repulsion between the Cl<sup>-</sup> ion (pathway *c*) or the  $\beta$ -chlorine atom (pathway *d*) and the silyl group. Chlorine located at the  $\alpha$ -carbon atom of chloro(chlorovinyl)methylsilane exerts a similar shielding effect on the  $\equiv\text{Si}-\text{C}\equiv$  bond. It has been reported in a monograph<sup>6</sup> that  $\alpha$ , $\beta$ -dichloroalkylsilanes are more stable toward  $\beta$ -cleavage than other chloroalkylsilanes containing no chlorine atoms in the  $\alpha$ -position. The combination of the above-mentioned factors determines susceptibilities of the monomers under study to the formation of decomposition products.

As regards substituting chlorination of the methyl groups attached to silicon, the experimental data obtained by us confirm the previous conclusion<sup>5</sup> concerning the order in which the reactions take place, *viz.*, that chlorine adds initially to the double bond, and the hydrogen atoms of methyl groups are replaced thereafter, since in none of the experiments, formation of chlorovinyl(chloromethyl)silanes was detected. Substituting chlorination of the methyl groups becomes noticeable if the molecule incorporates a Me<sub>3</sub>Si group and three chlorine atoms in the ethyl group. It is one of the predominating processes when chloro(tetrachloroethyl)- and chloro(perchloroethyl)methylsilanes form, and in the latter case, even two methyl groups at the

silicon atom are sufficient for this reaction to proceed (Table 1).

### Experimental

<sup>1</sup>H NMR spectra were obtained on a Varian T-60A spectrometer operating at 60 MHz with neat liquids or CCl<sub>4</sub> solutions. Benzene was used as the internal standard. IR spectra in the 200–4000 cm<sup>-1</sup> region were recorded on a Bruker IFS-113v Fourier spectrometer in cells with a capillary thick layer and windows of CsI crystals.

**Chlorination of chloro(chlorovinyl)methylsilanes.** Gaseous chlorine was passed through a bubbler into 0.1–0.2 mol of chlorovinylsilane at a rate of 3–4 g h<sup>-1</sup>. In most cases, the temperature of the reaction mixture increased jumpwise. Completion of the reactions was checked by GLC. Bubbling of chlorine was continued until the starting chlorovinylsilane was entirely (or almost entirely) consumed. The products were isolated by vacuum distillation.

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Received December 16, 1994;  
in revised form May 3, 1995