

# Reactions of chlorinated vinylsilanes with hydrogen chloride

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Catalytic hydrochlorination of a series of chloro(chlorovinyl)methylsilanes was studied. The course of the reaction depends on the number and position of the chlorine atoms in the initial monomers.

**Key words:** chloro(chlorovinyl)methylsilanes, hydrochlorination,  $\beta$ -elimination.

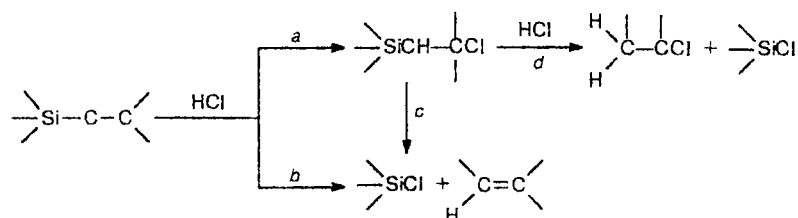
Hydrochlorination of chloro(chlorovinyl)methylsilanes is scarcely studied. It is only known that perchlorovinyltrichloro- and perchlorovinyltrimethylsilanes do not add hydrogen chloride under normal conditions.<sup>1</sup> If these reactions were successfully carried out, this would greatly extend the range of available chloroethylsilanes. It is of considerable interest to reveal a correlation between the structure of the monomers under study and their activity in hydrochlorination.

In the present work, we studied hydrochlorination of a series of chloro(chlorovinyl)methylsilanes  $\text{Me}_n\text{Cl}_{3-n}\text{SiR}$  (where  $n = 0-3$ ,  $\text{R} = \text{CH}=\text{CHCl}$ ,  $\text{CCl}=\text{CH}_2$ ,  $\text{CH}=\text{CCl}_2$ ,  $\text{CCl}=\text{CHCl}$ , and  $\text{CCl}=\text{CCl}_2$ ) (1–19, Table 1) in the presence of  $\text{FeCl}_3$  as a catalyst. The rate of reactions is strongly influenced by the temperature and the amount of the catalyst (the reactions do not occur without it at all). Our experiments showed that none of the (chlorovinyl)trichlorosilanes (1, 5, 9, 13, and 16) reacts with  $\text{HCl}$  even under rather drastic conditions (10 wt.%  $\text{FeCl}_3$ , 100 °C). It is necessary that at least one Cl atom be replaced by a Me group for hydrochlorination to occur.

The experimental results (Table 1) suggest a general scheme for the process that includes the addition of  $\text{HCl}$  to vinylsilane (Scheme 1, reaction *a*), cleavage of the  $\text{Si}-\text{C}$  bond in the initial vinylsilane (reaction *b*),  $\beta$ -elimination of the adduct (reaction *c*), and cleavage of the  $\text{Si}-\text{C}$  bond in the adduct (reaction *d*). The predominant reaction pathway depends on the structure of the initial chloro(chlorovinyl)methylsilane.

Thus  $\beta$ -chlorovinyl(methyl)dichlorosilane (2) gives both an adduct,  $\beta,\beta$ -dichloroethyl(methyl)dichlorosilane (20), and decomposition products, whereas compounds 3 and 4 afford only decomposition products.  $\alpha$ -Chlorovinylsilanes (6–8) form only adducts (21–23, respectively) independent of the structure of substituents at the Si atom. Chloro( $\beta,\beta$ - and  $\alpha,\beta$ -dichlorovinyl)-methylsilanes (10–12, 14, and 15) give only decomposition products (in the case of  $\beta,\beta$ -dichlorovinylsilanes 10 and 11, 1,1,1-trichloroethane in 20–30% yield was detected in the reaction mixture along with 1,1-dichloroethylene and chlorosilanes). Among perchlorovinylsilanes (16–19), only perchlorovinyltrimethylsilane 19 enters the reaction to give decomposition products.

Scheme 1



**Table 1.** The reaction of chloro(chlorovinyl)methylsilanes with HCl in the presence of FeCl<sub>3</sub>

Initial vinylsilane	FeCl <sub>3</sub> (wt.%)	Reaction time/h	T/°C	Reaction products	Yield (%)	Conversion of the initial vinylsilane (%)
Cl <sub>3</sub> SiCH=CHCl (1)	10	4	100	—	—	—
MeCl <sub>2</sub> SiCH=CHCl (2)	5	4	25–31*	Me(Cl <sub>2</sub> CHCH <sub>2</sub> )SiCl <sub>2</sub> (20)	89	93
				MeSiCl <sub>3</sub>		74
				CH <sub>2</sub> =CHCl		
Me <sub>2</sub> ClSiCH=CHCl (3)	1	3	25–35*	MeCHCl <sub>2</sub>		74
				CH <sub>2</sub> =CHCl <sub>2</sub>		
Me <sub>3</sub> SiCH=CHCl (4)	1	2	25–35*	Me <sub>2</sub> SiCl <sub>2</sub>		85
				CH <sub>2</sub> =CHCl		
				Me <sub>3</sub> SiCl		
Cl <sub>3</sub> SiCCl=CH <sub>2</sub> (5)	10	4	100	—	—	—
MeCl <sub>2</sub> SiCCl=CH <sub>2</sub> (6)	3	5	18–20*	MeCl <sub>2</sub> SiCCl <sub>2</sub> Me (21)	9	9
Me <sub>2</sub> ClSiCCl=CH <sub>2</sub> (7)	3	5	20–24*	Me <sub>2</sub> ClSiCCl <sub>2</sub> Me (22)	42	42
Me <sub>3</sub> SiCCl=CH <sub>2</sub> (8)	3	5	20–25*	Me <sub>3</sub> SiCCl <sub>2</sub> Me (23)	72	73
Cl <sub>3</sub> SiCH=CCl <sub>2</sub> (9)	10	4	100	—	—	—
MeCl <sub>2</sub> SiCH=CCl <sub>2</sub> (10)	5	4	70	CH <sub>2</sub> =CCl <sub>2</sub>		66
				MeSiCl <sub>3</sub>		
				MeCCl <sub>3</sub>		
Me <sub>2</sub> ClSiCH=CCl <sub>2</sub> (11)	2	5	25–30*	CH <sub>2</sub> =CCl <sub>2</sub>		98
				Me <sub>2</sub> SiCl <sub>2</sub>		
				MeCCl <sub>3</sub>		
Me <sub>3</sub> SiCH=CCl <sub>2</sub> (12)	1	3	25–32*	CH <sub>2</sub> =CCl <sub>2</sub>		98
				Me <sub>3</sub> SiCl		
Cl <sub>3</sub> SiCCl=CHCl (13)	10	4	100	—	—	—
MeCl <sub>2</sub> SiCCl=CHCl (14)	5	4	80	CHCl=CHCl		3
				MeSiCl <sub>3</sub>		
Me <sub>3</sub> SiCCl=CHCl (15)	2	4	25–35*	CHCl=CHCl		92
				Me <sub>3</sub> SiCl		
				CH <sub>2</sub> ClCHCl <sub>2</sub>		
Cl <sub>3</sub> SiCCl=CCl <sub>2</sub> (16)	10	4	100	—	—	—
MeCl <sub>2</sub> SiCCl=CCl <sub>2</sub> (17)	5	4	100	—	—	—
Me <sub>2</sub> ClSiCCl=CCl <sub>2</sub> (18)	5	4	100	—	—	—
Me <sub>3</sub> SiCCl=CCl <sub>2</sub> (19)	2	4	70	CHCl=CCl <sub>2</sub>		70
				Me <sub>3</sub> SiCl		

\* The temperature increases spontaneously to the upper limit of the indicated range.

**Table 2.** Hydrochlorination of β-chlorovinyl(methyl)dichlorosilane 2 under different conditions

FeCl <sub>3</sub> (wt.%)	Reaction time/h	T/°C	Content in the reaction mixture (wt.%)			Conversion 2 (%)
			MeCHCl <sub>2</sub>	MeSiCl <sub>3</sub>	Me(Cl <sub>2</sub> CHCH <sub>2</sub> )SiCl <sub>2</sub>	
0.5	1.5	25	—	0.2	1.9	2.5
0.5	4	25	—	0.3	3.5	4.4
0.5	4	55	0.2	0.6	16.3	17.6
0.5	7	55	0.4	1.1	20.9	25.1
3.0	7	55	3.2	20.8	49.5	84.2
5.0	7	25	0.4	3.1	89.0	93.0
5.0	7	55	5.9	26.3	58.1	91.2

**Table 3.** The reaction of silane 2 with FeCl<sub>3</sub> (50–60 °C)

FeCl <sub>3</sub> (wt.%)	Time of exposure of FeCl <sub>3</sub> to air /min	Reaction time /h	Content in the reaction mixture (wt.%)			Conversion of 2 (%)
			MeCHCl <sub>2</sub>	MeSiCl <sub>3</sub>	Me(Cl <sub>2</sub> CHCH <sub>2</sub> )SiCl <sub>2</sub>	
2	—	14	Traces	0.2	1.0	1.4
5	—	14	0.4	0.8	1.7	3.5
10	—	14	1.2	1.9	3.4	7.7
15	—	14	1.5	2.2	3.8	8.2
5	—	27	0.6	1.3	1.8	4.0
5	4	27	0.9	2.2	2.5	6.4
5	8	27	2.3	3.1	3.1	9.3
5	12	27	2.6	3.6	3.5	10.5

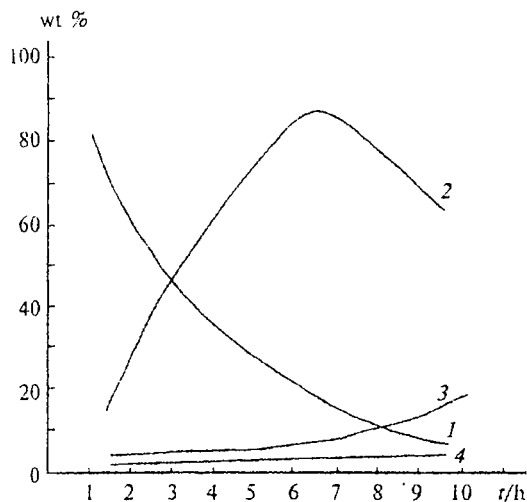


Fig. 1. The dependence of the mass content of the initial compound and the products of hydrochlorination of silane **2** on time (the reaction was carried out without heating, 5 wt. %  $\text{FeCl}_3$ ). Curve (1) refers to the initial silane **2**; (2) refers to the adduct; (3) refers to  $\text{MeSiCl}_3$ ; and (4) refers to  $\text{MeCHCl}_2$ .

To explain the results obtained, we studied in more detail the reaction of silane **2** with  $\text{HCl}$ . This reaction is the most informative because it is the sole reaction that yields both the addition and decomposition products. The results of the hydrochlorination of silane **2** under different conditions are given in Table 2.

The initial silane **2** is a mixture of *cis*- and *trans*-isomers (in the ratio 1 : 3). GLC analysis showed that the stereoisomeric composition of nonconsumed silane **2** is virtually independent of the hydrochlorination conditions.

It follows from Table 2 that an increase in the amount of  $\text{FeCl}_3$  favors conversion of the initial compound **2**, while elevation of the temperature results, to a larger extent, in the formation of decomposition products.

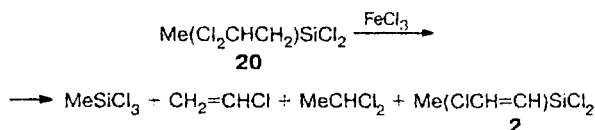
Figure 1 illustrates the time dependence of the mass content of silane **2** and the final products of the reaction carried out in the presence of 5 wt. %  $\text{FeCl}_3$  at 25 °C.

It can be seen from the figure that initially adduct **20** is mainly formed (curve 2), and decomposition products are present in minor amounts. However, as the reaction mixture is depleted of silane **2** (curve 1), the content of adduct **20** begins to decrease, while that of  $\text{MeSiCl}_3$  (curve 3) increases. Then, the adduct decomposes to give  $\text{MeSiCl}_3$  and vinyl chloride (this is confirmed by further experiments). It should be noted that curves 3 and 4 (the content of  $\text{MeCHCl}_2$ ) significantly differ at this period of time. The percentage of  $\text{MeSiCl}_3$  begins to increase sharply, while that of  $\text{MeCHCl}_2$  is increased much more slowly, *i.e.*, the character of curve 4 remains virtually unchanged over all the reaction time. Attempts at performing hydrochlorination of vinyl chloride under these conditions to obtain  $\text{MeCHCl}_2$  failed. In our opinion, the results obtained suggest that initially the reaction follows mainly pathway *a* (see Scheme 1) and then pathways *c* and *d*.

It turned out that the reaction of silane **2** with  $\text{FeCl}_3$  in the absence of  $\text{HCl}$  gives the same products, though in lower yields.

It was found that the content of products is directly proportional to the concentration of the catalyst and to the degree of its hydrolysis. The latter was concluded after special experiments where  $\text{FeCl}_3$  had been preliminarily exposed to air (Table 3.)

It is also noteworthy that extension of the period of exposure favors to a larger extent the formation of decomposition products rather than adduct **20**. The latter, when in contact with  $\text{FeCl}_3$  (in the absence of  $\text{HCl}$ ), gives silane **2** and the same decomposition products



However, if  $\text{HCl}$  is introduced into the reaction mixture, adduct **20** undergoes no chemical transformation. Apparently, it is moisture in combination with the catalyst that favors cleavage of the  $\text{Si}-\text{C}$  bond of adduct **20**.

Hence, one can assume that the hydrochlorination of chloro(chlorovinyl)methylsilanes proceeds *via* an in-

Scheme 2

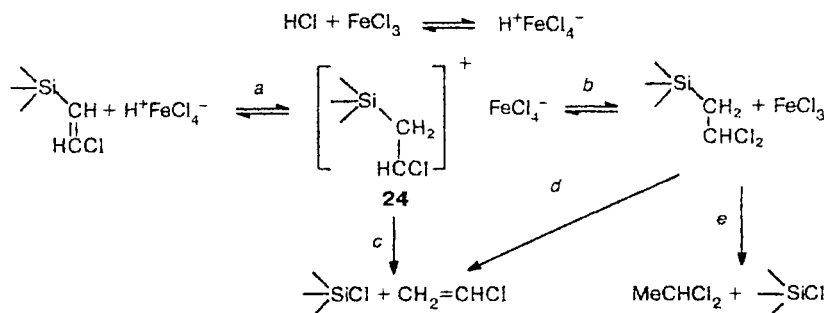


Table 4. The properties of adducts 20–23

Adduct	B.p./°C (p/Torr)	M.p. /°C	$\delta$	
			MeSi	Other protons
20	40 (1)	*	0.94	2.41 (CH <sub>2</sub> ) 6.04 (CH)
21	75 (70)	56–60	0.97	2.17 (CH <sub>3</sub> )
22	25 (5)	45–46	0.6	2.10 (CH <sub>3</sub> )
23	50 (30)	40–41	0.26	2.03 (CH <sub>3</sub> )

\*  $n_D^{20}$  1.4740,  $d_4^{20}$  1.3940.

intermediate (24) (Scheme 2), which can either dissociate reversibly into the initial compounds (pathway *a*), give hydrochlorination products with recovery of FeCl<sub>3</sub> in the catalytic cycle (pathway *b*), or decompose at the Si—C bond to form decomposition products (pathway *c*), as shown in Scheme 2 (with  $\beta$ -chlorovinylsilanes as the examples).

The direction of decomposition of intermediate 24 depends on the structure of the initial chlorovinyl-(methyl)silane, in particular, on the nature of substituents at the Si atom. As the number of chlorine atoms at silicon increases, the attack on the Si atom becomes less probable, which may be due to a higher degree of electrostatic repulsion between the silyl group and FeCl<sub>4</sub><sup>−</sup>.

In the absence of HCl, FeCl<sub>3</sub> is hydrolyzed under the action of atmospheric moisture to give HCl and, in the end, the acid H<sup>+</sup>FeCl<sub>4</sub><sup>−</sup>.<sup>2,3</sup>

As mentioned above, the reaction of silane 2 with HCl yields not only vinyl chloride and MeSiCl<sub>3</sub> but also MeCHCl<sub>2</sub>. It could be assumed that 1,1-dichloroethane results from the hydrochlorination of CH<sub>2</sub>=CHCl. However, a special experiment gave no evidence for this. It should also be noted that CH<sub>2</sub>=CHCl was detected in all series of reactions with chloro( $\beta$ -chlorovinyl)methylsilanes (see Table 1, compounds 2–4), while 1,1-dichloroethane was detected only upon hydrochlorination of silane 2, i.e., in the case of formation of adduct 20. Hence, one can assume that MeCHCl<sub>2</sub> is formed as a result of cleavage of the Si—C bond of this adduct (see Scheme 2, pathway *e*).

The formation of MeCHCl<sub>2</sub> in the hydrochlorination of silane 2 suggests that pathway *b* (see Scheme 2) occurs only in this reaction, whereas, in the case of silanes 3 and 4, the reaction follows pathway *a* and then *c* (see Scheme 2). Another possible direction of the process is the formation of the adduct with subsequent  $\beta$ -elimination (characteristic of similar compounds)<sup>4</sup> resulting in CH<sub>2</sub>=CHCl and the corresponding chlorosilanes (Scheme 2, pathway *d*). As the number of the Me groups at the Si atom increases, the  $\beta$ -elimination becomes more favorable. It is quite probable that silanes 3 and 4 give adducts that immediately decompose and do not undergo the slower cleavage of the Si—C bond (pathway *e*). Apparently, in the case of

chloro( $\beta$ , $\beta$ -dichlorovinyl)methylsilanes 10 and 11, the adducts formed not only undergo  $\beta$ -elimination easily but also have the more labile Si—C bond, which favors their partial decomposition to give 1,1,1-trichloroethane (pathway *e*).

In the case of chloro( $\alpha$ -chlorovinyl)methylsilanes 6–8, the proton adds only to the  $\beta$ -C atom, and a further attack of the FeCl<sub>4</sub><sup>−</sup> ion at the  $\alpha$ -C atom results in adducts 21–23. Here, reaction *c* (Scheme 2) does not occur at all. However, hydrochlorination of chloro( $\alpha$ , $\beta$ -dichlorovinyl)- and -(perchlorovinyl)silanes (14, 15, and 19) give decomposition products, though under more severe conditions and in lower yields.

## Experimental

NMR spectra of the compounds under study were recorded on a Varian T-60A spectrometer (pure liquids and solutions in CCl<sub>4</sub>) with cyclohexane or benzene as the internal standard. GLC analysis was performed on an LKhM-72 chromatograph equipped with a katharometer (detector temperature 260 °C, column length 2 m, 15% PMS-20000 phase on Chromaton N-AW, column temperature 0–280 °C, helium as the carrier gas at a rate of 40 mL min<sup>−1</sup>, evaporator temperature 300 °C).

Commercial FeCl<sub>3</sub> and commercial HCl (from a cylinder) were used without additional purification.

The procedure for synthesis and spectral characteristics of the initial compounds are given in Ref. 5.

**Reaction of chloro(chlorovinyl)methylsilanes with HCl (general procedure).** HCl was passed at a rate of 0.1–0.2 L h<sup>−1</sup> through a continuously stirred mixture of the initial compound (0.2 mol) and 1–10 wt. % FeCl<sub>3</sub>. If the reaction did not occur, the reaction mixture was heated on an oil bath. The reaction mixture was periodically analyzed by GLC. The reaction products were isolated by distillation. The properties of adducts 20–23 are summarized in Table 4.

**The reaction of vinyl chloride with HCl.** HCl and CH<sub>2</sub>=CHCl were passed through a continuously stirred mixture of MeSiCl<sub>3</sub> (0.2 mol) (it simulates the conditions of hydrochlorination of chloro(chlorovinyl)methylsilanes) and 2–5% FeCl<sub>3</sub> at a rate of 0.1–0.2 L h<sup>−1</sup>. GLC analysis of the reaction mixture did not detect MeCHCl<sub>2</sub>. The reaction did not occur on heating either.

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