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Liquid-Phase Chlorination of Chlorosilyl-substituted Ethylenes and Acetylenes

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Abstract—The liquid-phase chlorination of bis(chloromethylsilyl)ethylenes and -acetylenes $Me_nCl_{3-n}SiZ \cdot SiMe_nCl_{3-n}$ (n = 0–3; Z = CH=CH, C≡C) was studied. Novel carbochlorosilanes were obtained and characterized. The effect of substituents on the activity of the multiple bond of chlorosilylolefins in the reaction studied was determined.

Earlier [1] we studied the liquid-phase chlorination of C-chlorovinylsilanes to show that the reaction occurs unselectively as (a) chlorine addition at the multiple bonds of chlorosilylolefins to form dichloroethylsilanes, (b) chlorination of methyl groups, (c) substitutive chlorination of the dichloroethyl groups formed, and (d) decomposition of chlorine-substituted silanes.

Proceeding with these studies we performed an analogous liquid-phase chlorination reaction with bis(chloromethylsilyl)ethylenes and -acetylenes $Me_nCl_{3-n} \cdot SiZSiMe_nCl_{3-n}$ (n = 0–3; Z = CH=CH, C≡C) in the absence of catalysts and solvents. It was found that in these reactions, too, chlorine addition to the multiple bonds occurs, followed by substitutive chlorination of the chloroethyl and methyl substituents at silicon and decomposition. Accumulation of more methyl groups at the silicon atom facilitates all the mentioned reactions.

Bis(trichlorosilyl)- and bis(dichloromethylsilyl)acetylene derivatives take up only one or two chlorine molecules at the multiple bonds. With bis(chlorodimethylsilyl) and bis(trimethylsilyl) derivatives, profound alkylation of the methyl groups occurs (10–18%) along with adduct formation.

Bis(chloromethyl)ethylenes are alkylated even less selectively. Here only $Cl_3SiCH=CHSiCl_3$ forms an adduct in high yield (Table 1). Beginning with the $MeCl_2Si$ derivative, vigorous substitutive chlorination of the chloroethyl bridge between the silicon atoms occurs along with chlorine addition by the double bond, whereas in the Me_2ClSi and Me_3Si derivatives, two more processes, chlorination of the methyl groups and decomposition. The reaction conditions and adduct yields are listed in Table 1.

By competitive chlorination of chlorosilylethylenes and chloroethylenes [1] we earlier found that the Cl_3Si group stronger, compared with chlorine, deactivates the olefin double bond. In the present work we tried to estimate the effect of substitution of the chlorine atoms in the trichlorosilyl group on the relative

Table 1. Chlorination conditions and adduct yields[a]

Compound	Synthesis conditions		Yield, %
	Δ*t*, °C	time, h	
$Cl_3SiCCl=CClSiCl_3$ (**I**)	22–87	5.5	52
$Cl_3SiCCl_2–CCl_2SiCl_3$ (**II**)	22–87	5.5	43
$MeCl_2SiCCl=CClSiMeCl_2$ (**III**)[b]	22–115	3.5	58
$MeCl_2SiCCl_2–CCl_2SiMeCl_2$ (**IV**)[b]	22–115	3.5	39
$Me_2ClSiCCl=CClSiMe_2Cl$ (**V**)[b]	22–94	3.5	47
$Me_2ClSiCCl_2–CCl_2SiMe_2Cl$ (**VI**)[c]	22–94	3.5	28
$Me_3SiCCl=CClSiMe_3$ (**VII**)	22–68	3.0	38
$Me_3SiCCl_2–CCl_2SiMe_3$ (**VIII**)	22–68	3.0	17
$Cl_3SiCHCl–CHClSiCl_3$ (**IX**)	22–84	6.0	82
$MeCl_2SiCHCl–CHClSiMeCl_2$ (**X**)[c]	22–75	4.5	43

[a] Substitutive chlorination products were not isolated because of the low yields and close boiling points. [b] Compounds **III, IV**, and **V** are prepared for the first time. [c] Compounds **VI** and could not be isolated and characterized because of the presence of closely boiling admixtures. Their contents in the reaction mixtures and yields were estimated by GLC.

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Table 2. Competitive chlorination of equimolar mixtures of chlorosilylolefins

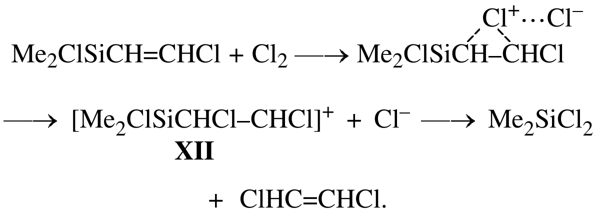
Run no.	Initial mixture	Reagent molar ratios during reaction					
		0.2 h	0.5 h	1.0 h	1.2 h	1.5 h	2 h
1	$ClHC=CHCl/Cl_3SiCH=CHCl$	–	0.98	0.78	–	0.71	0.55
2	$ClHC=CHCl/MeCl_2SiCH=CHCl$	0.98	0.99	0.95	0.92	0.89	0.90
3	$ClHC=CHCl/Me_2ClSiCH=CHCl$	1.15	1.50	1.82	1.95	2.11	–
4	$ClHC=CHCl/Me_3SiCH=CHCl$	1.31	1.84	2.15	2.58	–	–
5	$Cl_3SiCH=CHCl/Cl_3SiCH=CHSiCl_3$	–	0.99	0.87	–	0.82	0.75
6	$MeCl_2SiCH=CHCl/MeCl_2SiCH=CHSiMeCl_2$	–	0.98	0.97	–	0.94	0.93
7	$Me_2ClSiCH=CHCl/Me_2ClSiCH=CHSiMe_2Cl$	1.10	1.15	1.24	1.28	–	–
8	$Me_3SiCH=CHCl/Me_3SiCH=CHSiMe_3$	1.15	1.28	1.30	1.46	–	–

activity of the chlorosilylolefin double bond. Table 2 lists the results of competitive chlorination of 1,2-dichloroethylene and 1-silyl-2-chloroethylenes, as well as 1-silyl-2-chloro- and 1,2-disilylethylenes. As seen from the table, substitution by methyl of even one chlorine atom at silicon much affects the relative activities of chloro- and silyl-substituted olefins and almost equalizes the effects of the silyl group and chlorine atom (Table 2, run no. 2). Further methyl substitution for chlorine renders silyl-substituted chloroolefins much more reactive than 1,2-dichloroethylene (Table 2, run nos. 3 and 4). The same pattern, while less pronounced, is observed for the 1-silyl-2-chloro- and 1,2-disilylethylene pairs (Table 2, run nos. 5–8).

To find out decomposition pathways, we studied in more detail chlorination of $Me_2ClSiCH=CHCl$. As shown earlier [1], the reaction gives decomposition products along with adduct **XI**.

$$Me_2ClSiCH=CHCl \xrightarrow{Cl_2} \underset{\textbf{XI}}{Me_2ClSiCHCl–CHCl_2} + Me_2SiCl_2 + ClHC=CHCl.$$

It proved that individual adduct **XI** withstands prolonged heating (130–140°C). On this basis one can assume that decomposition accompanies formation of this compound, most likely, from intermediate carbocation **XII**.



$$Me_2ClSiCH=CHCl + Cl_2 \longrightarrow Me_2ClSi\overset{Cl^+\cdots Cl^-}{CH–CHCl} \longrightarrow \underset{\textbf{XII}}{[Me_2ClSiCHCl–CHCl]^+} + Cl^- \longrightarrow Me_2SiCl_2 + ClHC=CHCl.$$

At the same time, we found that chlorination of adduct **XI** yields, along with expected substitutive chlorination products, much decomposition products.

$$\underset{\textbf{XI}}{Me_2ClSiCHCl–CHCl_2} \xrightarrow{Cl_2} \underset{9\%}{Me_2SiCl_2} + \underset{8\%}{ClHC=CHCl} + \underset{14\%}{Me_2ClSiCCl_2–CHCl_2} + \underset{15\%}{Me_2ClSiCHCl–CCl_3} + \underset{6\%}{Me_2ClSiCCl_2–CCl_3}.$$

Obviously, further reaction of adduct **XI** with chlorine occurs by two directions: (a) more profound (substitutive) chlorination and (b) Si–C bond fission to give the above decomposition products.

EXPERIMENTAL

The ^1H NMR spectra were obtained on a Varian T-60A instrument for neat liquids and CCl_4 solutions. The internal reference was benzene. Gas chromatography was performed on an LKhM-72 chromatograph with a thermal conductivity detector, column 2000 × 3 mm, packing 15% of PMS-20000 on Chromaton N-AW, carrier gas helium, linear oven temperature programming at 12 deg/min.

Chlorination of chlorosilylolefins. Gaseous chlorine was barboted through 0.1–0.2 mol of unsaturated compound at a rate of 3–4 g/h. In most cases, the temperature of the reaction mixtures rose jumpwise. The reaction completeness was controlled by GLC. Chlorine was barboted until complete (or almost complete) consumption of the starting chlorosilylolefins. The products were isolated by vacuum distillation.

1,2-Bis(dichloromethylsilyl)dichloroethylene (III). bp 91°C (2 mm), n_D^{20} 1.5200, d_4^{20} 1.4785. The ^{1}H NMR spectrum contains two singlets at 0.95 and 0.97 ppm (5 : 3), characteristic of methyl groups at silicon. These signals were assigned to the *trans* and *cis* isomers. Found, %: C 14.95; H 1.77; Cl 66.14; Si 17.17. $C_4H_6Cl_2Si_2$. Calculated, %: C 14.86; H 1.86; Cl 65.94; Si 17.34.

1,2-Bis(dichloromethylsilyl)perchloroethane (IV). mp 33–35°C. The ^{1}H NMR spectrum contains a signal at 1.44 ppm, which is consistent with the proposed structure. Found, %: C 12.33; H 1.57; Cl 71.79; Si 14.35. $C_4H_6Cl_8Si_2$. Calculated, %: C 12.18; H 1.52; Cl 72.08; Si 14.21.

1,2-Bis(chlorodimethylsilyl)dichloroethylene (V). bp 122°C (20 mm), n_D^{20} 1.5025, d_4^{20} 1.2383. The ^{1}H NMR spectrum contains two singlets at 1.12 and 1.10 ppm (5:4), characteristic of methyl groups at silicon. These signals were assigned to the *trans* and *cis* isomers. Found, %: C 25.84; H 4.15; Cl 51.04; Si 19.67. $C_6H_{12}Cl_9Si_2$. Calculated, %: C 25.53; H 4.26; Cl 50.35; Si 19.86.

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