Alkoxylation of *C*-chlorovinylsilanes

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The alkoxylation and isopropylideneiminoxylation of *C*-chlorovinylmethylchlorosilanes with various alcohols and acetone oxime were investigated. A series of new *C*-chlorovinylmethylalkoxy- and -isopropylideneiminoxysilanes was characterized by IR and ^{1}H NMR spectra. The effect of the number of chlorine atoms in *C*-chlorovinylmethylchlorosilanes on their reactivity in these reactions was determined.

Key words: *C*-chlorovinylmethylchlorosilanes, etherification; *C*-chlorovinylmethylalkoxysilanes, alcohols, IR spectra; ^{1}H NMR spectra.

A thorough study of the thermal interaction of hydrosilanes with chlorinated ethylenes[1,2] made it possible to obtain a series of known and novel *C*-chlorovinylmethylchlorosilanes differing in the numbers and positions of chlorine atoms in the vinyl group. Alkoxylation and isopropylideneiminoxylation of these compounds may result in new carbofunctional alkoxy- and isopropylideneiminoxysilanes that are of substantial practical interest. These compounds can be successfully used as dressings and catalysts of the cold vulcanization of silicone rubbers with terminal hydroxy groups.

In the present work we studied the interaction of the aforementioned *C*-chlorovinylmethylchlorosilanes with various alcohols in order to obtain and identify new carbofunctional alkoxysilanes. In addition, we tried to estimate an approximate relationship between the structure of the molecules (in particular, the number and position of chlorine atoms) and their reactivity.

We used the following reagents: MeOH (**1**), EtOH (**2**), ethyl cellosolve (**3**), acetone oxime (**4**), and α-naphthol (**5**). The first four compounds were selected because they are widely used in practice, and compound **5** was chosen for comparison as a representative of phenols. All reactions (except interactions with the oxime) were carried out in an inert solvent, CH_2Cl_2 (**6**), which was distilled off together with HCl formed in the reaction.

The reactions studied can be expressed as the general Scheme 1.

Scheme 1

$$Me_nCl_{3-n}SiR + (3-n)R'OH \rightarrow Me_n(OR')_{3-n}SiR + (3-n)HCl$$

$n = 0 \div 2$

$R = CCl{=}CH_2,\ CH{=}CHCl,\ CCl{=}CHCl,\ CH{=}CCl_2,\ CCl{=}CCl_2$

$R' = Me,\ Et,\ CH_2CH_2OEt,\ Me_2CNO,\ Nf$

In all cases (except interactions with the oxime), GLC analysis detected the formation of side products (the corresponding alkyl chlorides R'Cl, and high-boiling siloxane products), which were not analyzed quantitatively due to their low content. In addition, alkyl chlorides were continously removed from the reaction mixture together with compound **6**, which also hampered their quantitative determination. The primary attention was given to maintaining similar reaction conditions (see Experimental) and to determining the exact yields of the target products and their characteristics.

The results obtained are presented in Table 1. The compounds marked with asterisks are not new. However, these reactions were also carried out in order to determine the exact yields under these conditions.

It is evident from Table 1 that the alkoxylation of chlorodimethylvinylsilane with alcohols **1**, **2**, and **3** (see Table 1) is difficult to perform. The yields of the target alkoxydimethylvinylsilanes are as low as 42—47 %. Neither increasing the alcohol : chloride ratio, increasing the reaction temperature, or increasing the amount of compound **6** has much effect on the results.

The introduction of chlorine to the vinyl group significantly increases the reactivity of the starting chlorosilanes. As a result, the yields of the corresponding alkoxysilanes reach 62—78 % (see Table 1). Judging

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Table 1. Yields and properties of *C*-chlorovinylalkoxymethylsilanes and alkoxy(vinyl)methylsilanes

Compound	Yield (%)	B.p./°C (p /Torr)	d_4^{20}	n_D^{20}	Ref.
$(MeO)Me_2SiCH{=}CH_2^*$ (**7**)	47	—	—	—	3
$(MeO)Me_2SiCCl{=}CH_2$ (**8**)	64	24—25(2)	0.973	1.4290	—
$(MeO)Me_2SiCH{=}CHCl^*$ (**9**)	65	—	—	—	4
$(MeO)Me_2SiCH{=}CCl_2$ (**10**)	70	25—26(2)	1.310	1.5580	—
$(MeO)Me_2SiCCl{=}CCl_2$ (**11**)	60	36—37(2)	1.416	1.5602	—
$(MeO)_2MeSiCH{=}CH_2^*$ (**12**)	62	—	—	—	3
$(MeO)_2MeSiCCl{=}CH_2$ (**13**)	68	27—28(5)	1.032	1.4257	—
$(MeO)_2MeSiCH{=}CHCl$ (**14**)	75	65(15)	1.044	1.4310	—
$(MeO)_2MeSiCCl{=}CHCl$ (**15**)	76	35(2—3)	1.191	1.4520	—
$(MeO)_2MeSiCH{=}CCl_2$ (**16**)	75	45—46(3)	1.166	1.4502	—
$(MeO)_2MeSiCCl{=}CCl_2$ (**17**)	70	58—60(3)	1.529	1.5739	—
$(MeO)_3SiCH{=}CH_2^*$ (**18**)	74	—	—	—	5
$(MeO)_3SiCCl{=}CH_2^*$ (**19**)	73	—	—	—	6
$(MeO)_3SiCH{=}CHCl^*$ (**20**)	72	—	—	—	6
$(MeO)_3SiCCl{=}CHCl^*$ (**21**)	75	—	—	—	7
$(MeO)_3SiCH{=}CCl_2^*$ (**22**)	83	—	—	—	7
$(MeO)_3SiCCl{=}CCl_2^*$ (**23**)	73	—	—	—	8
$(EtO)Me_2SiCH{=}CH_2^*$ (**24**)	46	—	—	—	9
$(EtO)Me_2SiCCl{=}CH_2$ (**25**)	62	23—24(2)	0.959	1.4291	—
$(EtO)Me_2SiCH{=}CHCl^*$ (**26**)	62	—	—	—	4
$(EtO)Me_2SiCH{=}CCl_2$ (**27**)	72	44—45(2)	1.068	1.4522	—
$(EtO)Me_2SiCCl{=}CCl_2$ (**28**)	52	66—67(2)	1.215	1.4767	—
$(EtO)_2MeSiCH{=}CH_2^*$ (**29**)	65	—	—	—	9
$(EtO)_2MeSiCCl{=}CH_2$ (**30**)	71	37—38(3)	0.989	1.4250	—
$(EtO)_2MeSiCH{=}CHCl^*$ (**31**)	77	—	—	—	4
$(EtO)_2MeSiCCl{=}CHCl$ (**32**)	85	93(14)	1.088	1.4480	—
$(EtO)_2MeSiCH{=}CCl_2^*$ (**33**)	89	—	—	—	4
$(EtO)_2MeSiCCl{=}CCl_2^*$ (**34**)	79	—	—	—	4
$(EtO)_3SiCH{=}CH_2^*$ (**35**)	78	—	—	—	5
$(EtO)_3SiCCl{=}CH_2^*$ (**36**)	77	—	—	—	6
$(EtO)_3SiCH{=}CHCl^*$ (**37**)	81	—	—	—	10
$(EtO)_3SiCCl{=}CHCl$ (**38**)	77	60—61(1—2)	1.112	1.4350	—
$(EtO)_3SiCH{=}CCl_2$ (**39**)	84	72—74(2)	1.115	1.4361	—
$(EtO)_3SiCCl{=}CCl_2^*$ (**40**)	78	—	—	—	4
$(EtOCH_2CH_2O)Me_2SiCH{=}CH_2$ (**41**)	42	38—40(2)	0.853	1.4160	—
$(EtOCH_2CH_2O)Me_2SiCCl{=}CH_2$ (**42**)	78	42—43(1)	0.971	1.4378	—
$(EtOCH_2CH_2O)Me_2SiCH{=}CHCl$ (**43**)	75	75—77(2)	1.063	1.5750	—
$(EtOCH_2CH_2O)Me_2SiCH{=}CCl_2$ (**44**)	83	92—94(2)	1.079	1.4572	—
$(EtOCH_2CH_2O)Me_2SiCCl{=}CCl_2$ (**45**)	71	110—112(2)	1.178	1.4729	—
$(EtOCH_2CH_2O)_2MeSiCH{=}CH_2$ (**46**)	55	76—77(1)	0.931	1.4230	—
$(EtOCH_2CH_2O)_2MeSiCCl{=}CH_2$ (**47**)	66	80—81(1)	1.026	1.4399	—
$(EtOCH_2CH_2O)_2MeSiCH{=}CHCl$ (**48**)	65	85—86(1)	1.011	1.4400	—
$(EtOCH_2CH_2O)_2MeSiCCl{=}CHCl$ (**49**)	70	174(26)	1.111	1.4544	—
$(EtOCH_2CH_2O)_2MeSiCH{=}CCl_2$ (**50**)	68	108—110(1)	1.102	1.4506	—
$(EtOCH_2CH_2O)_2MeSiCCl{=}CCl_2$ (**51**)	66	127—128(2)	1.179	1.4664	—
$(EtOCH_2CH_2O)_3SiCH{=}CH_2^*$ (**52**)	77	—	—	—	11
$(EtOCH_2CH_2O)_3SiCCl{=}CH_2$ (**53**)	79	141—143(2)	1.049	1.4384	—
$(EtOCH_2CH_2O)_3SiCH{=}CHCl$ (**54**)	85	140—142(2)	1.047	1.4413	—
$(EtOCH_2CH_2O)_3SiCCl{=}CHCl$ (**55**)	92	210(20)	1.109	1.4502	—
$(EtOCH_2CH_2O)_3SiCH{=}CCl_2$ (**56**)	90	154—155(2)	1.108	1.4490	—
$(EtOCH_2CH_2O)_3SiCCl{=}CCl_2$ (**57**)	85	166—168(2)	1.170	1.4580	—
$(\alpha\text{-}C_{10}H_7O)Me_2SiCH{=}CH_2$ (**58**)	78	98—99(1)	1.081	1.5695	—
$(\alpha\text{–}C_{10}H_7O)Me_2SiCH{=}CHCl$ (**59**)	74	120—122(1)	1.169	1.5803	—
$(\alpha\text{-}C_{10}H_7O)Me_2SiCH{=}CCl_2$ (**60**)	75	155—156(1)	1.268	1.5860	—
$(\alpha\text{–}C_{10}H_7O)Me_2SiCCl{=}CCl_2$ (**61**)	74	166—170(1)	1.320	1.5870	—
$(Me_2C{=}NO)Me_2SiCH{=}CH_2$ (**62**)	55	54(24)	0.861	1.4330	—
$(Me_2C{=}NO)Me_2SiCCl{=}CH_2$ (**63**)	63	86(21)	0.995	1.4595	—
$(Me_2C{=}NO)Me_2SiCH{=}CHCl$ (**64**)	65	83(19)	0.995	1.4590	—
$(Me_2C{=}NO)Me_2SiCH{=}CCl_2$ (**65**)	63	138(114)	1.097	1.4725	—

Table 1. (Continued)

Compound	Yield (%)	B.p./°C (p /Torr)	d_4^{20}	n_D^{20}	Ref.
$(Me_2C{=}NO)Me_2SiCCl{=}CCl_2$ (**66**)	62	132(33)	1.224	1.4940	—
$(Me_2C{=}NO)_2MeSiCH{=}CH_2$ (**67**)	61	117(30)	0.956	1.4548	—
$(Me_2C{=}NO)_2MeSiCCl{=}CH_2$ (**68**)	67	98(2)	1.052	1.4678	—
$(Me_2C{=}NO)_2MeSiCH{=}CHCl$ (**69**)	63	84(1)	1.063	1.4710	—
$(Me_2C{=}NO)_2MeSiCCl{=}CHCl$ (**70**)	63	157(27)	1.134	1.4825	—
$(Me_2C{=}NO)_2MeSiCH{=}CCl_2$ (**71**)	71	92(1)	1.134	1.4812	—
$(Me_2C{=}NO)_2MeSiCCl{=}CCl_2$ (**72**)	67	105(1)	1.234	1.4973	—
$(Me_2C{=}NO)_3SiCH{=}CH_2$* (**73**)	70	—	—	—	12
$(Me_2C{=}NO)_3SiCCl{=}CH_2$ (**74**)	68	128—130(2)	1.107	1.4814	—
$(Me_2C{=}NO)_3SiCH{=}CHCl$* (**75**)	69	—	—	—	4
$(Me_2C{=}NO)_3SiCCl{=}CHCl$ (**76**)	70	330	—	—	—
$(Me_2C{=}NO)_3SiCH{=}CCl_2$* (**77**)	67	—	—	—	4
$(Me_2C{=}NO)_3SiCCl{=}CCl_2$* (**78**)	58	—	—	—	4

* The compounds have been synthesized previously.

Table 2. Vibration frequencies $\nu(C{=}C)/cm^{-1}$ for substituted vinylsilanes $X_nMe_{3-n}SiY$, n = 1—3

X	Y					
	$-CH{=}CH_2$	$-CCl{=}CH_2$	$-CH{=}CHCl$	$-CCl{=}CHCl$	$-CH{=}CCl_2$	$-CCl{=}CCl_2$
$C_2H_5OCH_2CH_2O$	1595—1600	1587—1593	1578—1582	1555—1556	1564—1570	1543—1547
C_2H_5O	1593—1600	1585—1593	1570—1575	1555—1556	1564—1566	1540—1547
MeO	1595	1589—1597	1575—1580	1555—1556	1566—1570	1543—1549
$Me_2C{=}NO$	1595—1597	1582—1595	1583—1585	1558	1568—1575	1545—1547

from the yields of the target products, the difference in the position of the chlorine atom in the vinyl group does not have much effect on the course of the reaction.

As the number of chlorine atoms in the vinyl group increases further, the activity of *C*-chloromethylvinylchlorosilanes continues to increase, but only slightly: the yields of dichlorovinylalkoxymethylsilanes (see Table 1) are somewhat higher than those of the corresponding monochlorovinylalkoxymethylsilanes.

The transition to perchlorovinylsilanes does not result in an increase in reactivity. Conversely, the yields of the corresponding perchlorovinylalkoxymethylsilanes decrease to some extent (see Table 1).

In the case of unsubstituted chloromethylvinylsilanes, the yields of the alkoxylation products increase on going from $Me_2ClSiCH{=}CH_2$ to $Cl_3SiCH{=}CH_2$. This suggests that the replacement of the methyl groups at the silicon atom by chlorine atoms facilitates alkoxylation.

When one compares Me_2ClSiR with $MeCl_2SiR$ and Cl_3SiR, the above difference in the reactivity of the Si—Cl bonds of the starting vinyl- and *C*-chlorovinylmethylchlorosilanes decreases significantly, which follows from the smaller difference in the yields of the target products (see Table 1).

The above regularities were not observed in similar reactions involving compound **5** (see Table 1), as the corresponding naphthoxy derivatives were obtained in approximately equal yields.

The interaction of vinyl- and *C*-chlorovinylmethylchlorosilanes with acetone oxime was carried out using a different procedure. In these reactions, we used a double excess of compound **4**, which served both as a reagent and as an acceptor of HCl under these conditions. Since the reactions were carried to completion, we did not manage to compare the reactivity of the Si—Cl bonds. The yields of the ultimate isopropylideneiminoxysilanes were rather similar (see Table 1).

Attempts to perform competitive reactions in order to determine more accurately the effect of the position of the chlorine atom in the vinyl moiety on the reactivity of Si—Cl bonds failed, since both GLC analysis and ^1H NMR spectral data showed that, even at room temperature, exchange reactions of chlorine atoms and alkoxy groups occur, *e.g.*:

$$Me_2(R'O)SiCH{=}CH_2 + Me_2ClSiCH{=}CHCl \rightleftharpoons$$

$$\rightleftharpoons Me_2ClSiCH{=}CH_2 + Me_2(R'O)SiCH{=}CH$$

R' = Me, Et, $EtOCH_2CH_2$

Table 3. ^1H NMR chemical shifts (δ)

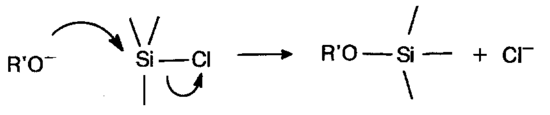
Compound	Vinyl group	$\geqslant$SiMe	Other groups (MeO; EtO; $EtOCH_2CH_2O$; α-$C_{10}H_7O$; $Me_2C=NO$)
7	5.45—6.48^a	0.12	3.48
8^b	5.70; 5.90	0.25	3.43
8	6.02; 6.39	0.13	3.36
9	5.83; 6.70	0.24	3.39
10	5.90	0.27	3.39
11	—	0.38	3.45
12	5.68—6.17^a	0.13	3.45
13^b	5.83; 5.97	0.21	3.48
13	5.87; 6.53	0.11	3.45
14	5.75; 6.75	0.24	3.48
15	6.68	0.25	3.50
16	5.85	0.23	3.48
17	—	0.34	3.53
19^b	5.88; 6.02	—	3.55
19	5.84; 6.63	—	3.51
20	5.72; 6.87	—	3.55
21	6.70	—	3.53
22	5.77	—	3.52
23	—	—	3.60
24	5.38—6.39^a	0.12	1.10(Me); 3.59(CH_2O)
25^b	5.70; 5.90	0.27	1.17(Me); 3.67(CH_2O)
25	6.03; 6.46	0.17	1.16(Me); 3.58(CH_2O)
26	5.90; 6.80	0.26	1.16(Me); 3.58(CH_2O)
27	5.93	0.26	1.17(Me); 3.67(CH_2O)
28	—	0.38	1.17(Me); 3.70(CH_2O)
29	5.65—6.15^a	0.10	1.17(Me); 3.70(CH_2O)
30^b	5.85; 5.95	0.22	1.20(Me); 3.79(CH_2O)
	5.87; 6.47	0.13	1.17(Me); 3.73(CH_2O)
31	5.77; 6.73	0.25	1.17(Me); 3.73(CH_2O)
32	6.72	0.25	1.20(Me); 3.80(CH_2O)
33	5.87	0.24	1.18(Me); 3.73(CH_2O)
34	—	0.33	1.21(Me); 3.82(CH_2O)
35	5.65—5.98^a	—	1.17(Me); 3.70(CH_2O)
36^b	5.87; 5.95	—	1.20(Me); 3.82(CH_2O)
	5.79; 6.57	—	1.18(Me); 3.75(CH_2O)
37	5.68; 6.74	—	1.18(Me); 3.79(CH_2O)
38	6.73	—	1.21(Me); 3.83(CH_2O)
39	5.79	—	1.23(Me); 3.83(CH_2O)
40	—	—	1.23(Me); 3.87(CH_2O)
41	5.46—6.47^a	0.18	1.15(Me); 3.23—3.80(CH_2O)^a
42^b	5.73; 5.87	0.27	1.13(Me); 3.40; 3.42; 3.73(CH_2O)
	6.02; 6.43	0.17	1.15(Me); 3.23—3.80(CH_2O)^a
43	5.90; 6.83	0.30	1.15(Me); 3.23—3.80(CH_2O)^a
44	5.97	0.27	1.14(Me); 3.23—3.81(CH_2O)^a
45	—	0.40	1.15(Me); 3.23—3.86(CH_2O)^a
46	5.66—6.16^a	0.13	1.13(Me); 3.23—3.89(CH_2O)^a
47^b	5.87; 5.90	0.28	1.16(Me); 3.24—3.93(CH_2O)^a
	5.93; 6.57	0.18	1.17(Me); 3.24—3.90(CH_2O)^a
48	5.83; 6.77	0.30	1.17(Me); 3.24—3.90(CH_2O)^a
49	6.87	0.28	1.15(Me); 3.38; 3.48; 3.82(CH_2O)
50	5.93	0.28	1.17(Me); 3.22—3.90(CH_2O)^a
51	—	0.41	1.14(Me); 3.28—3.97(CH_2O)^a
53	5.97	—	1.13(Me); 3.43; 3.47; 3.89(CH_2O)
54^c	5.87; 6.71	—	1.15(Me); 3.80—4.00(CH_2O)^a
55	7.01	—	1.17(Me); 3.46; 3.49; 3.95(CH_2O)
56	6.41	—	1.64(Me); 3.95; 3.97; 4.39(CH_2O)
57	—	—	1.56(Me); 3.87; 3.91; 4.37(CH_2O)
58^b	5.50—6.30^a	0.32	6.77—7.72^a; 8.20—8.38^a
	6.18; 6.45	0.17	6.65—7.70^a; 8.06—8.25^a
59	5.77; 6.60	0.50	6.65—7.70^a; 8.06—8.25^a
60	5.99	0.35	6.54—7.70^a; 8.03—8.28^a
61	—	0.47	6.67—7.70^a; 8.03—8.34^a
62	5.42—6.47^a	0.22	1.77
63^b	—	—	—
	6.03; 6.37	0.23	1.78
64	5.90; 6.60	0.35	1.78
65	6.00	0.35	1.82
66	—	0.47	1.80
67	5.86—6.16^a	0.33	1.82
68^b	5.91; 5.98	0.48	1.83; 1.88
	6.07; 6.57	0.35	1.80
69	5.95; 6.75	0.48	1.80
70	6.80	0.46	1.83
71	6.02	0.45	1.83
72	—	0.60	1.86; 1.90
74^b	6.07	—	1.87; 1.93
	6.03; 6.70	—	1.78; 1.85
75	5.90; 6.80	—	1.78; 1.85
76	6.89	—	1.90; 1.94
77	6.02	—	1.86; 1.88

[a] The limits of a common multiplet for several signals with similar chemical shifts are given.

[b] A mixture of *cis* and *trans* isomers. The first value corresponds to the *trans* isomer and the second one to the *cis* isomer.

[c] A *trans* isomer.

According to the literature data,[13] the nucleophilic substitution at the silicon atom involves the S_N2 mechanism.



The presence of electronegative substituents decreases the electron density at the silicon atom and hence favors the approach of a nucleophilic reagent to this atom. This probably explains why etherification occurs more readily when electron-donating methyl groups are replaced by chlorine atoms or alkoxy groups.

The increased reactivity of the Si—Cl bonds in vinylsilanes due to the introduction of a chlorine atom to the vinyl group can be explained similarly. The vinyl group has electron-donating properties with respect to silicon.[14] When a chlorine atom is introduced, additional electronic effects come into force. First, they include the $-I$-effect of the C—Cl σ-bond, and second, the mesomeric effect due to the p_π—p_π interaction involving the free electron pairs of the halogen atom and the electrons of the double bond. The directions of the above two effects are opposite.[15] Most likely, the overall electron effect is directed to the chlorine atom. This in turn weakens the effect of the d_π—p_π interaction and renders the chlorovinyl group electron-withdrawing or, at least, decreases its electron-donating properties with respect to the silicon atom. Probably, the second chlorine atom introduced to the vinyl group has a similar effect. It is likely that the third chlorine atom does not increase the electronegativity of the chlorovinyl group as significantly; in addition, the yields of the target products decrease for some other reasons.

Obviously, the overall effect of all of the chlorine atoms on the donor-acceptor properties of a vinyl group is not just the arithmetic sum of the contributions of the electrons of each of the chlorine atoms, but is more complicated. This is confirmed by the data obtained from the IR spectra of the compounds synthesized. Table 2 presents the vibration frequencies of the double bond in the vinyl and chlorovinyl groups of the compounds. The following relation between the vibration intensities was obtained:

$$CH{=}CH_2 < CCl{=}CH_2 < CH{=}CHCl < CCl{=}CHCl < CH{=}CCl_2 > CCl{=}CCl_2$$

It can be seen from Table 2 that the type of substituent at the silicon atom has only a slight effect on the ν(C=C) frequency. On the other hand, the accumulation of chlorine atoms in the vinyl group results in a considerable decrease in the ν(C=C) frequency. As shown above, the vibration intensity increases simultaneously.

It is known[16] that the introduction of electronegative substituents at an sp^2 carbon atom in an olefinic group causes a shift of the absorption bands toward lower frequencies. Generally, this also results in an increase in band intensities.

Hence, based on literature data,[16] we can also conclude that in our case the electron-withdrawing properties of the vinyl group increase as it accumulates chlorine atoms. However, when β,β-dichlorovinyl substituents are replaced by perchlorovinyl groups, the intensity of the ν(C=C) vibrations decreases. This is probably because the electron-withdrawing properties of the perchlorovinyl group are weaker than those of the β,β-dichlorovinyl group. This in turn leads to the lower reactivity of perchlorovinylmethylchlorosilanes in alkoxylation, and, hence, to decreased yields of the corresponding perchlorovinylmethylalkoxysilanes.

The ^1H NMR spectral data are presented in Table 3. The integral intensities in the spectra of all of the samples studied correspond to the theoretical ratio of the proton signals of the various substituents at the silicon atom. The β-chlorovinylsilanes were mixtures of *cis* and *trans* isomers in which the latter predominate, therefore the spectra of these samples contained a double set of signals. The assignment of the latter was based on the vicinal coupling constants in the ethylene moiety: $^3J_{cis\text{-}CH=CHCl}$ = 9.0—9.8 Hz, $^3J_{trans\text{-}CH=CHCl}$ = 14.9—15.5 Hz.

The only exception in the series of β-chlorovinylsilanes was $(EtOCH_2CH_2O)_3SiCH{=}CHCl$, whose sample contained only the *trans* isomer.

Experimental

^1H NMR spectra of the compounds studied were obtained on a Varian T-60A spectrometer for pure liquids or solutions in CCl_4. $SiMe_4$, HMDS, cyclohexane, and benzene were used as internal standards.

IR spectra were recorded in the 200—4000 cm^{-1} region on a Bruker IFS-113v IR Fourier spectrophotometer using cells with capillary thickness layers and CsI optics.

All experiments involving the alkoxylation of *C*-chlorovinylmethylchlorosilanes were carried out under identical conditions, namely, in a four-necked flask (50 mL) equipped with a stirrer, thermometer, dropping funnel, and a dephlegmator with an attachment for separation of compound **6**. A solution of a *C*-chlorovinylmethylchlorosilane (0.1 mol) in compound **6** (10—15 mL) was added dropwise over a period of 30 min at 50 °C to a calculated amount of alcohol and **6** (20—30 mL). Simultaneously, **6** was distilled off. The reaction mixture was then distilled to isolate the target products.

Reactions of *C*-chlorovinylmethylchlorosilanes **4** with acetone oxime were carried out according to the following procedure. A solution of a chlorosilane (0.1 mol) in toluene (10—20 mL) was added at 55—60 °C to a mixture of a calculated amount of **4** (a twofold excess) and toluene (50—100 mL). The mixture was kept for 2 h at the same temperature, and the precipitate of acetone oxime hydrochloride was filtered off. Gaseous ammonia was passed through the filtrate until the solution became alkaline. The solution was again filtered, and the filtrate was distilled to isolate the target products.

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