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Alkoxylation of 1,2-Bis(methylchlorosilyl)ethylenes and -Acetylenes

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Abstract—Reactions of a series of 1,2-bis(methylchlorosilyl)ethylenes and -acetylenes $Me_nCl_{3-n}Si–Z–SiCl_{3-n}Me_n$ (Z = CH=CH, C≡C; n = 0–2) with ethanol and acetoxime were studied. Novel alkoxy- and isopropylideneaminooxysilanes were obtained and characterized. A relation was found between the activity of Si–Cl bonds in the reactions studied and the structure of the carbon–carbon bridge.

In our previous studies on thermal reactions between hydrosilanes and chlorinated ethylenes [1, 2] we obtained a series of known and novel symmetrical 1,2-bis(methylchlrosilyl)ethylenes and -acetylenes. Replacement in such compounds of chlorine atoms by alkoxy and isopropylideneaminooxy groups may open the way to previously unknown carbofunctional alkoxy- and isopropylideneaminooxysilanes. These compounds are of practical interest as coupling agents, catalysts for cold curing of silicon rubbers, as well as chain-extending agents. Hydrolysis of such monomers may give novel polymeric materials with various degrees of branching and containing unsaturated fragments Si–Z–Si (Z = CH=CH; C≡C).

In the present work we studied reactions of 1,2-bis(methylchlorosilyl)ethylenes and -acetylenes with ethanol and acetoxime, with the aim to prepare and identify novel carbofunctional silanes. We also tried to correlate the structure of the molecules (in particular, the nature of the carbon–carbon bridge between the silicon atoms, the number of chlorine atoms) and their reactivity.

All the reactions studied can be described by the following general scheme:

$$Me_nCl_{3-n}Si–Z–SiCl_{3-n}Me_n + 2(3-n)ROH$$
$$\xrightarrow{CH_2Cl_2} Me_n(RO)_{3-n}Si–Z–Si(OR)_{3-n}Me_n$$
$$+ 2(3-n)HCl,$$

R = Et, $Me_2C=N$; Z = CH=CH, C≡C; n = 0–2.

The reactions with ethanol were performed in boiling methylene chloride with its simultaneous distillation, which allowed us to effectively remove the HCl formed. Gas-chromatographic analysis showed that the reactions give as by-products the corresponding alkyl chlorides RCl and high-boiling siloxane products; quantitative analysis of these by-products was not performed because of their very low contents. Moreover, alkyl chlorides were all the time removed from the reaction mixtures together with CH_2Cl_2, which complicated their quantitative analysis. Most emphasis was given to ensuring indentical reaction conditions (see Experimental) and determining exact yields and characterizing the target products.

To gain a better insight into the relationship between the nature of the carbon–carbon bridge between the silicon atoms and the activity of Si–Cl bonds, we studied reactions with ethanol of related symmetrical 1,2-bis(methylchlorosilyl)ethanes. The resulting data are listed in Table 1.

The data in Table 1 reveal two clearly defined regularities: (1) increasing activity of Si–Cl bonds in the monomers studied with increasing number of chlorine atoms in the molecules and decreasing number of methyl groups and (2) increasing activity of Si–Cl bonds with increasing electron density on the carbon–carbon bridge between the silicon atoms.

Oximation of 1,2-bis(methylchlorosilyl)ethylenes and -acetylenes was performed by another procedure [3]. These reactions were performed with a double excess of acetoxime which in this case acted both as reagent and as HCl acceptor. The resulting data are listed in Table 2.

It is readily seen from Table 2 that hexa- and tetraoxime derivatives **XI**, **XII**, **XIV**, and **XV** are formed in lower yields than dioxime derivatives **X** and **XIII**. However, the reactions went to completion, and the relative activities of Si–Cl bonds were impossible to compare. Moreover, the hexa- and tetraoxime derivatives proved crystalline substances. For isolation we had to recrystallize them from a toluene–hexane mixture, which produced inevitable losses. Therefore, the low yields of **XI**, **XII**, **XIV**, and **XV** may well be associated with this recrystallization. Here one can only note slightly better yields of acetylenic monomers compared with ethylenic.

Tables 3–5 list the physicochemical constants, elemental analyses, and ^{1}H NMR spectra of newly synthesized compounds.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Varian T-60A spectrometer for neat liquids or CCl_4 solutions. The internal references were TMS and cyclohexane.

Gas chromatography was performed on an LKhM-72 spectrometer with a thermal conductivity detector, column 2000±3 mm, packing 15% PMS-20000 on Chromaton N-AW, carrier gas helium, linear temperature programming at a rate of 12 deg/min.

Alkoxylations of 1,2-bis(methylchlorosilyl)ethanes, -ethylenes, and -acetylenes were performed in identical conditions: in a four-necked flask (50 ml) equipped with a stirrer, a thermometer, a dropping funnel, and a Vigreux column with a head for distillation of CH_2Cl_2. To a required amount of alcohol in 20–30 ml of CH_2Cl_2 we added dropwise at 50°C over the course of 30 min a solution of 0.1 mol of a chloride in

Table 1. Reaction of 1,2-bis(methylchlorosilyl)ethanes, -ethylenes, and -acetylenes with ethanol

Comp. no.[a]	Reaction product		Yield, %
	$Si(OR)_{3-n}Me_n$	*Z*	
I	$Si(OEt)Me_2$	CH_2CH_2	8
II	$Si(OEt)_2Me$	CH_2CH_2	67
III	$Si(OEt)_3$	CH_2CH_2	86
IV	$Si(OEt)Me_2$	CH=CH	32
V	$Si(OEt)_2Me$	CH=CH	74
VI	$Si(OEt)_3$	CH=CH	92
VII	$Si(OEt)Me_2$	C≡C	86
VIII*	$Si(OEt)_2Me$	C≡C	89
IX	$Si(OEt)_3$	C≡C	94

[a] Here and hereinafter, stars label newly synthesized compounds.

Table 2. Reaction of 1,2-bis(methylchlorosilyl)ethylenes and -acetylenes with acetoxime

Comp. no.	Reaction product		Yield, %
	$Si(ONCMe_2)_{3-n}Me_n$	*Z*	
X*	$Si(ONCMe_2)Me_2$	CH=CH	73
XI*	$Si(ONCMe_2)_2Me$	CH=CH	57
XII*	$Si(ONCMe_2)_3$	CH=CH	52
XIII*	$Si(ONCMe_2)Me_2$	C≡C	81
XIV*	$Si(ONCMe_2)_2Me$	C≡C	63
XV*	$Si(ONCMe_2)_3$	C≡C	60

Table 3. Formulas, names, and physicochemical constants of the newly synthesized compounds **VIII**–**XV**

Comp. no.	Formula	Name	bp, °C (*p*, mm)	mp, °C[a]
VIII[b]	$Me(EtO)_2SiC{\equiv}CSi(OEt)_2Me$	1,2-Bis(diethoxymethylsilyl)acetylene	54 (3)	–
X[c]	$Me_2(Me_2CNO)SiCH{=}CHSi(ONCMe_2)Me_2$	1,2-Bis[(isopropylideneaminooxy)dimethylsilyl]ethylene	92 (1–2)	–
XI	$Me(Me_2CNO)_2SiCH{=}CHSi(ONCMe_2)_2Me$	1,2-Bis[bis(isopropylideneaminooxy)methylsilyl]ethylene	–	69–71
XII	$(Me_2CNO)_3SiCH{=}CHSi(ONCMe_2)_3$	1,2-Bis[tris(isopropylideneaminooxy)silyl]ethylene	–	95–97
XIII	$Me_2(Me_2CNO)SiC{\equiv}CSi(ONCMe_2)Me_2$	1,2-Bis[isopropylideneaminooxy)dimethylsilyl]acetylene	101 (1–2)	50–52
XIV	$Me(Me_2CNO)_2SiC{\equiv}CSi(ONCMe_2)_2Me$	1,2-Bis[bis(isopropylideneaminooxy)methylsilyl]acetylene	–	73–75
XV	$(Me_2CNO)_3SiC{\equiv}CSi(ONCMe_2)_3$	1,2-Bis[tris(isopropylideneaminooxy)silyl]acetylene	–	93–94

[a] Solvent for crystallization: toluene–hexane, 1 : 1. [b] d_4^{20} 0.9401, n_D^{20} 1.4220, MR_D: found 78.39, calculated 78.48. [c] d_4^{20} 0.9364, n_D^{20} 1.4610, MR_D: found 83.80, calculated 83.87.

Table 4. Elemental analyses of the newly synthesized compounds **VIII**–**XV**

Comp. no.	Found, %					Formula	Calculated, %				
	C	H	N	O	Si		C	H	N	O	Si
VIII	49.60	8.88	–	22.23	19.45	$C_{12}H_{26}O_4Si_2$	49.66	8.96	–	22.07	19.31
X	50.38	9.12	9.80	11.16	19.54	$C_{12}H_{26}N_2O_2Si_2$	50.35	9.09	9.79	11.19	19.58
XI	49.10	7.95	14.47	12.70	14.26	$C_{16}H_{32}N_4O_4Si_2$	50.00	8.33	14.58	12.50	14.58
XII	46.39	7.51	16.10	18.31	10.65	$C_{20}H_{38}N_6O_6Si_2$	46.69	7.39	16.34	18.67	10.89
XIII	49.82	8.38	9.65	11.57	19.58	$C_{12}H_{24}N_2O_2Si_2$	50.70	8.45	9.86	11.27	19.72
XIV	47.29	7.48	14.36	15.77	14.10	$C_{16}H_{30}N_4O_4Si_2$	48.24	7.54	14.07	16.08	14.07
XV	46.70	7.11	16.55	18.96	10.68	$C_{20}H_{36}N_6O_6Si_2$	46.87	7.03	16.40	18.75	10.93

Table 5. ^1H NMR chemical shifts (δ, ppm) of compounds **VIII** and **X**–**XV**[a]

Comp. no.	CH=	$Me_2CN=O$	MeSi
X	6.74	1.78	0.21
XI	6.68	1.83	0.33
XII	6.75	1.83, 1.87	–
XIII	–	1.87	0.30
XIV	–	1.87	0.40
XV	–	1.83	–

[a] Compound **VIII**, δ, ppm: 3.65 (CH_2O), 1.04 (Me), 0.03 (MeSi).

10–15 ml of CH_2Cl_2. The solvent was simultaneously distilled off. The reaction mixture was fractionated to isolate the final products.

Oximation of 1,2-bis(methylchlorosilyl)ethylenes and -acetylenes with acetoxime was performed by the following procedure. To a mixture of a required amount of acetoxime (double excess) and 50–100 ml of toluene we added at 55–60°C a solution of 0.1 mol of chlorosilane in 10–20 ml of toluene. The reaction mixture was left to stand for 2 h at that temperature, and the precipitate of acetoxime hydrochloride was filtered off. Gaseous ammonia was barboted through the filtrate to alkaline reaction. The mixture was filtered, and the fitrate was fractionated to isolate the final products. Compounds **XI**–**XV** were obtained by recrystallization from a 1:1 toluene–hexane mixture.

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