Chemistry

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Abstract

Full Text

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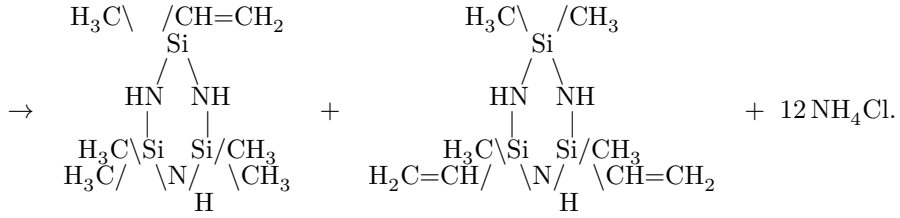
Unsaturated Derivatives of Cyclotrisilazane and Their Structure

Until now, unsaturated derivatives of the trisilazane heterocycle had not been described. We obtained* vinyl derivatives of cyclosilazanes by the ammonolysis reaction of methylvinyldichlorosilane or by co-ammonolysis of methylvinyldichlorosilane with dimethyldichlorosilane in benzene:

$$3(CH_3)_2SiCl_2 + 3(CH_3)(CH_2=CH)SiCl_2 + 18\,NH_3 \rightarrow$$



$$+\ 12\,NH_4Cl.$$

In the ammonolysis of methylvinyldichlorosilane, trimethyltrivinylcyclotrisilazane and tetramethyltetravinylcyclotetrasilazane were isolated. In the co-ammonolysis of dimethyldichlorosilane with methylvinyldichlorosilane, pentamethylvinylcyclotrisilazane and tetramethyldivinylcyclotrisilazane were isolated. The physical properties of the compounds obtained are given in Table 1.

Table 1

Compound	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calculated	MR found
Pentamethylvinylcyclotrisilazane $(CH_3)_5(CH_2=CH)Si_3N_3H_3$	54–56/3	1.4603	0.9414	67.20	67.51
Tetramethyldivinylcyclotrisilazane $(CH_3)_4(CH_2=CH)_2Si_3N_3H_3$	68–70/3	1.4703	0.9656	71.02	70.38

Figure 1. Infrared absorption spectra of organocyclosilazanes: 1 – $(CH_3)_3(CH_2=CH)_3Si_3N_3H_3$, 2 – $(CH_3)_5(CH_2=CH)Si_3N_3H_3$, 3 – $(CH_3)_6Si_3N_3H_3$

Figure 1: Figure 1. Infrared absorption spectra of organocyclosilazanes: 1 – $(CH_3)_3(CH_2=CH)_3Si_3N_3H_3$, 2 – $(CH_3)_5(CH_2=CH)Si_3N_3H_3$, 3 – $(CH_3)_6Si_3N_3H_3$

Compound	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR calculated	MR found
Trimethyltrivinylcyclotrisilazane $(CH_3)_3(CH_2=CH)_3Si_3N_3H_3$	100/7	1.4810	0.9673	75.00	75.20
Tetramethyltetravinylcyclotetrasilazane $(CH_3)_4(CH_2=CH)_4Si_4N_4H_4$	103–105/1	1.4980	0.9771	100.2	100.1

The composition of the compounds obtained was confirmed by elemental analysis and by determination of the molecular weights.

In order to obtain additional data on the structure of the unsaturated derivatives of cyclosilazane, the infrared and ultraviolet absorption spectra of the compounds obtained were studied. There are few works in the literature devoted to the IR spectra of cyclosilazanes, and there are no data at all on the absorption of such compounds in the UV region. The IR spectra were recorded on a UR-10 Karl Zeiss–Jena instrument** in a thin film, without solvent; the experimental data are given in Table 2. For comparison, there was also recorded and

* M. B. Lotarev took part in the synthetic part of the work.

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IR spectrum of hexamethylcyclotrisilazane. Figure 1 gives the intensities of the bands obtained. In the spectra of all the compounds studied, an absorption band was found in the region 928-930 cm^{-1}, corresponding to the asymmetric

Fig. 1. Infrared absorption spectra of organocyclosilazanes: 1 – $(CH_3)_3(CH_2=CH)_3Si_3N_3H_3$, 2 – $(CH_3)_5(CH_2=CH)Si_3N_3H_3$, 3 – $(CH_3)_6Si_3N_3H_3$

stretching vibration of the Si–N–Si bond in the six-membered ring ([1,2]), as well as a band at 618-620 cm^{-1}, corresponding to the symmetric stretching vibration of the Si–N–Si bond. Attention should be drawn to the fact

Table 2

$(CH_3)_6Si_3N_3H_3$	$(CH_2=CH)(CH_3)_5\cdot Si_3N_3H_3$	$(CH_2=CH)_2(CH_3)_4\cdot Si_3N_3H_3$	$(CH_2=CH)_3(CH_3)_3\cdot Si_3N_3H_3$	Assignment
–	530	530	530	ν'_{sym} SiNSi
618	620	620	620	ν_{sym} SiC
678	679	677	680	
–	730	730	730	
790	791	791	789	ν_{asym} SiC
818	817	810	838	ρCH_3
867	859	853		ρCH_3
928	928	930	928	ν_{asym} SiNSi
–	1010	1010	1010	$\delta' = C—H$
1167	1168	1171	1168	γNH
1254	1254	1253	1253	δ_{sym} CH_3
1400	1403	1403	1403	δ_{asym} CH_3
–	1593	1592	1590	$\nu C=C$
2892	2890	2890	2895	ν_{sym} CH_3
			2940	
2950	2951	2951	2956	ν_{asym} CH_3
–	–	3005	3002	
–	–	3042	3042	
3402	3402	3402	3395	νNH

that the stretching vibration of the C=C double bond is observed in the region 1590-1593 cm^{-1}, characteristic of vibrations of conjugated double bonds. This apparently should be explained by conjugation of the π-electrons of the double bond with the free 3*d*-orbitals of silicon.

Table 3

$(CH_3)_3(CH_2=CH)_3Si_3N_3H_3$		$(CH_3)_3(CH_2=CH)_3Si_3N_3H_3CH)_3Si_3N_3H_3$		$(CH_3)_4(CH_2=CH)_2Si_3N_3H_3CH)_2Si_3N_3H_3$	
λ_{max}, Å	ε	λ_{max}, Å	ε	λ_{max}, Å	ε
2540	4.38	2550	0.65	2480	2.03
2620	4.16	2610	0.49	2540	1.24
2650	2.70	2650	0.47	2600	0.84
2680	3.32	2680	0.45	2640	0.40
				2680	0.32

$(CH_3)_4(CH_2=CH)Si_3N_3H_3$		$(CH_3)_5(CH_2=CH)Si_3N_3H_3$	
λ_{max}, Å	ε	λ_{max}, Å	ε
2540	4.38	2550	0.65
2620	4.16	2610	0.49
2650	2.70	2650	0.47
2680	3.32	2680	0.45

In triallyltrimethylcyclotrisilazane, in comparison with vinylmethylcyclosilazanes, the shifts of the vibration frequencies toward lower frequencies

Fig. 2. UV spectrum of hexamethylcyclotrisilazane and methylvinylcyclosilazanes. 1—trimethyltrivinylcyclotrisilazane; 2—pentamethylvinylcyclotrisilazane; 3—hexamethylcyclotrisilazane

Figure 2: Fig. 2. UV spectrum of hexamethylcyclotrisilazane and methylvinylcyclosilazanes. 1—trimethyltrivinylcyclotrisilazane; 2—pentamethylvinylcyclotrisilazane; 3—hexamethylcyclotrisilazane

is not observed. In triallyltrimethylcyclotrisilazane, for the $C = C$ bond an absorption band is observed at 1632 cm^{-1}, which corresponds, as was to be expected, to a nonconjugated double bond.

This fact is also observed in the IR spectra of vinyl- and allylchlorosilanes ([3]). There are data ([4]) according to which the bond order of Si—N—Si is 1.18, i.e., the unshared electron pairs of nitrogen are partially delocalized with participation of the 3*d* orbitals of silicon. It was therefore of interest to determine whether the conjugation

$$\text{Si—C} = \text{C}$$

is transmitted through the inorganic ring from one vinyl group to another. In order to obtain data making it possible to judge this, we measured the absorption spectra of the compounds obtained in the UV region with a VSU-1 Carl Zeiss—Jena spectrophotometer. In the spectrum of hexamethylcyclotrisilazane we found no absorption maxima. Hexamethylcyclotrisilazane without solvent (layer thickness 0.5 cm) is transparent to UV rays with wavelength $\lambda > 3200$ Å (Fig. 2). In the spectra of vinyl derivatives of cyclotrisilazane, in the region 2400-2700 Å, several absorption maxima appear because of the presence of double bonds in the molecule of the compounds studied. Figure 2 gives the UV spectra of trimethyltrivinylcyclotrisilazane and pentamethylvinylcyclotrisilazane in *n*-hexane. Table 3 lists the wavelengths at which maxima appear (λ_{max}) and the corresponding molar absorption coefficients (ε).

Fig. 2. UV spectrum of hexamethylcyclotrisilazane and methylvinylcyclosilazanes. 1—trimethyltrivinylcyclotrisilazane; 2—pentamethylvinylcyclotrisilazane; 3—hexamethylcyclotrisilazane

As follows from the values of ε given in Table 3, the absorption bands found are *R*-bands, i.e., the double bonds are isolated, nonconjugated ([5]). From this it may be concluded that in vinyl derivatives of cyclotrisilazane no conjugation of the double bonds of the vinyl groups through the inorganic heterocycle Si_3N_3 is observed, and it is limited only outside the ring, between the silicon atom and the group $-HC{=}CH_2$.

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Note: Figure translations are in progress. See original paper for figures.