Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV, V. I. SIDOROV,

L. M. KHANANASHVILI, G. D. BAGRATISHVILI,

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV, V. I. SIDOROV,
L. M. KHANANASHVILI, G. D. BAGRATISHVILI,
Academician of the Academy of Sciences of the Georgian SSR G. V. TSITSISHVILI, M. L. KANTARIA

ON THE ADDITION REACTION OF CERTAIN HYDROGEN-CONTAINING ORGANOSILICON COMPOUNDS TO VINYL DERIVATIVES OF ORGANOCYCLOSILOXANES AND TO ISOPRENE

Despite the extensive literature on the addition of hydrosilanes to various unsaturated compounds, there are no data on the addition of hydrochlorosilanes to organoalkenylcyclosiloxanes and on the addition reaction of unsaturated organic compounds to organohydrocyclosiloxanes.

In the present work, the addition of methyl- and ethyldichlorosilanes to heptamethylvinylcyclotetrasiloxane and hexamethyldivinylcyclotetrasiloxane was studied. The experiments showed that the hydride-transfer reaction in the presence of chloroplatinic acid proceeds comparatively readily and with good yields of the desired products.

The addition of methyldichlorosilane to heptamethylvinylcyclotetrasiloxane proceeds according to the following scheme:

heptamethylvinylcyclotetrasiloxane + $H_3C-SiCl_2H$ ⟶ corresponding $CH_2CH_2Si(CH_3)Cl_2$-substituted cyclote (1)

Analogously, from heptamethylvinylcyclotetrasiloxane and hexamethyldivinylcyclotetrasiloxane with ethyldichlorosilane, the following derivatives were obtained:

ethyl-dichlorosilyethyl derivative of heptamethylcyclotetrasiloxane (II)

vinyl-containing ethyl-dichlorosilyethyl derivative of hexamethylcyclotetrasiloxane (III)

Fig. 1

Figure 1: Fig. 1

bis(ethyl-dichlorosilyethyl) derivative of hexamethylcyclotetrasiloxane (IV)

The addition reaction of unsaturated organic compounds to hydrogen-containing organocyclosiloxanes was studied using as an example the reaction of addition of isoprene to heptamethylcyclotetrasiloxane. The indicated reaction proceeded according to the following scheme:

$$\text{cyclic siloxane hydride} + CH_2 = C(CH_3) - CH = CH_2 \longrightarrow \text{adduct} \qquad \text{(V)}$$

The compounds obtained were identified; their structure and composition were proved by analysis and by determination of molecular weight and molecular refraction. To establish the structure of the synthesized compounds, IR absorption spectra were recorded, and for compound II an NMR spectrum was also recorded.

Fig. 1. 1 —β-(ethyldichlorosilyl)ethylheptamethylcyclotetrasiloxane; 2 —β-(ethyldichlorosilyl)ethylhexamethylcyclotetrasiloxane; 3 —bis-[β-(ethyldichlorosilyl)ethyl]-hexamethylcyclotetrasiloxane; 4 —β-(methyldichlorosilyl)ethylheptamethylcyclotetrasi 5 —(2-methylbuten-3-yl)-heptamethylcyclotetrasiloxane.

In the IR spectra (Fig. 1) there appears a very intense and broad band near 1080 cm^{-1}, characteristic of Si—O—Si in cyclic tetramers. The vinyl group in compound III is observed at 1595 cm^{-1}. As was shown earlier ([1]), such a lowering of the frequency of the stretching vibration of the C = C bond is characteristic of a double bond in the α-position to a silicon atom. At the same time, a C = C double bond in the γ-position to a silicon atom (compound V) is characterized by an absorption band near 1658 cm^{-1}, which indicates the practically complete absence of mutual influence between the π-electrons of the double bond and the free $3d$-orbitals of silicon.

In the IR spectra of compounds III and V, in the region of stretching vibrations of C—H bonds, two bands each appear near 3012 and 3068 cm^{-1}. These should be assigned to vibrations of the = CH and = CH_2 bonds in the C = C bond ([1,2]). The appearance of the indicated two bands in compound V makes it possible to assign precisely this structure to compound V.

In the IR spectra of compounds I–IV, in the region of stretching vibrations of C—H bonds, besides the bands of the methyl group (2887 and 2956 cm^{-1}), the same band of the methylene group is observed at 2914 cm^{-1}, which indicates

addition of the —Si(R)Cl_2 groups to the β-carbon atom of the vinyl group of the ring.

In the NMR spectrum of compound II, at a frequency of 40 MHz, peaks were found only for protons of the CH_2 and CH_3 groups, with the following chemical-shift values (relative to $(CH_3)_4Si$): $\delta_{CH_3} = 9.96$ m.d. and $\delta_{CH_2} = 8.86$ m.d.; peaks characteristic of a proton in the β-CH group are absent, which also indicates addition of the $Si(C_2H_5)Cl_2$ group to the β-carbon atom of the vinyl group in heptamethylvinylcyclotetrasiloxane.

The physical properties of the compounds obtained are given in Table 1.

Table 1

	Name of synthesized compounds	B.p., °C/mm	n_D^{20}	d_4^{20}	MR found	MR calculated
I	β-(Methyldichlorosilyl)ethylheptamethylcyclotetrasiloxane	96–98/5	1.4289	1.0729	101.97	101.63
II	β-(Ethyldichlorosilyl)ethylheptamethylcyclotetrasiloxane	108–110/5	1.4335	1.0674	106.52	106.48
III	β-(Ethyldichlorosilyl)ethylvinylhexamethylcyclotetrasiloxane	128–130/5	1.4395	1.0708	110.03	110.64
IV	bis-[β-(Ethyldichlorosilyl)-ethyl]-hexamethylcyclotetrasiloxane	183–186/5	1.4498	1.1240	138.17	138.40
V	(2-Methylbuten-3-yl)heptamethylcyclotetrasiloxane	86–88/5	1.4208	0.9618	92.12	92.61

Experimental Part

Synthesis of β-(methyldichlorosilyl)-ethylheptamethylcyclotetrasiloxane (I). Into a flask fitted with a reflux condenser, stirrer, dropping funnel, and thermometer were charged 14.5 g of heptamethylvinylcyclotetrasiloxane and 0.02 ml of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, and from the dropping funnel ~1.0 g of methyldichlorosilane, out of a weighed 5.75 g, was added. After heating to 45–50°, a vigorous reaction began and the temperature rose to 90–100°. After cooling the mixture to 75°, the remaining amount of methyldichlorosilane was added in small portions; then the contents of the flask

were heated for 1.5 h at 160–180°. After distillation of the reaction product, 2.63 g (17.2%) of unreacted heptamethylvinylcyclotetrasiloxane and 13.83 g (65.5%) of I, b.p. 96–98°/5 mm, were isolated.

$$C_{10}H_{28}Cl_2Si_5O_4.$$

Found, %: Si 32.93; C 28.94; H 6.57; Cl 16.56
Calculated, %: Si 33.10; C 28.37; H 6.62; Cl 16.78

Molecular weight found 395; calculated 423; MR found 101.97, calculated 101.63.

Synthesis of β-(ethyldichlorosilyl)-ethylheptamethylcyclotetrasiloxane (II). Under conditions analogous to those given above, the addition of 8.37 g of ethyldichlorosilane to 20 g of heptamethylvinylcyclotetrasiloxane was carried out. By distillation, 3.07 g (15.4%) of unreacted heptamethylvinylcyclotetrasiloxane and 19.21 g (67.7%) of II, b.p. 108–110°/5 mm, were isolated.

$$C_{11}H_{30}Cl_2Si_5O_4.$$

Found, %: Si 32.08; Cl 15.90
Calculated, %: Si 32.04; Cl 16.25

Molecular weight found 409, calculated 437; MR found 106.52; calculated 106.48.

Synthesis of β-(ethyldichlorosilyl)-ethylvinylhexamethylcyclotetrasiloxane (III). By an analogous procedure, the addition of 8.07 g of ethyldichlorosilane to 20 g of hexamethyl-divinylcyclotetrasiloxane was carried out. By distillation, 2.96 g (14.8%) of un-

of unreacted hexamethyldivinylcyclotetrasiloxane and 17.76 g (63.2%) of III, b.p. 128–130°/5 mm.

$C_{12}H_{30}Cl_2Si_5O_4$. Found, %: Si 30.93; Cl 15.52
Calculated, %: Si 31.18; Cl 15.81

Molecular weight found 481, calculated 449; MR found 110.03, calculated 110.64.

Synthesis of bis-[β-(ethyldichlorosilyl)-ethyl]-hexamethylcyclotetrasiloxane (IV). By a procedure analogous to that described, 16.14 g of ethyldichlorosilane was added to 20 g of hexamethyldivinylcyclotetrasiloxane. Distillation gave 1.72 g (8.6%) of unreacted hexamethyldivinylcyclotetrasiloxane, 5.14 g (14.2%) of III, b.p. 128–130°/5 mm, and 14.32 g (39.6%) of IV, b.p. 183–186°/5 mm. For IV

$C_{14}H_{38}Cl_4Si_6O_4$.	Found, %:	Si 28.72; Cl 23.85
	Calculated, %:	Si 29.06; Cl 24.57

Molecular weight found 543, calculated 578; MR found 138.17, calculated 138.40.

Synthesis of (2-methylbuten-3-yl)-heptamethylcyclotetrasiloxane (V). Into an ampoule were sealed 1.16 g of isoprene and 4.81 g of heptamethylcyclotetrasiloxane with the addition of 2 drops of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol. Over 10 h the reaction temperature was raised to 160°, after which the reaction was continued for 2 h at 160–180°. Distillation gave 1.4 g (29.1%) of unreacted heptamethylcyclotetrasiloxane and 3.1 g (51.9%) of V, b.p. 86–88°/5 mm.

$C_{12}H_{30}Si_4O_4$.	Found, %:	Si 32.13; C 41.19; H 8.61
	Calculated, %:	Si 32.00; C 41.12; H 8.57

Molecular weight found 362, calculated 350; MR, found 92.12, calculated 92.61.

IR spectra in the region 600–1800 cm^{-1} were obtained on an IKS-14 spectrometer with a NaCl prism, and in the region 2500–3600 cm^{-1} on an IKS-12 spectrometer with a LiF prism. The substances were examined as dilute solutions in CCl_4 (solution concentration 0.5 mol/l, cuvette thickness 13 μ).

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

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