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Chemistry

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Abstract

Full Text

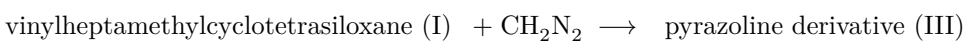
Chemistry

Academician K. A. ANDRIANOV, V. I. SIDOROV, L. M. KHANANASHVILI

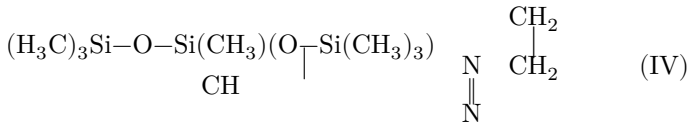
ON THE REACTIVITY OF ALKENYL-METHYLSILOXANES IN REACTIONS WITH DIAZOMETHANE AND PHENYLAZIDE

The reactivity of the vinyl group in different positions relative to the silicon atom in organosilicon compounds has been insufficiently studied. In a number of reactions it behaves analogously to organic unsaturated groups; however, in some cases (polymerization reactions, etc.) the silicon atom has a considerable influence on its behavior.

In the present work we studied addition reactions of diazomethane and phenyl azide, and the Diels–Alder diene-condensation reaction, using vinyl- and allyl-containing organosiloxanes of linear and cyclic structure as examples. Experiments showed that vinylheptamethylcyclotetrasiloxane (I) and 3-vinylheptamethyltrisiloxane (II) readily react with diazomethane:



This reaction proceeds readily under irradiation with ultraviolet light or without it at a temperature of −15 to +20°, with a yield of III up to 77.1%. Under the indicated conditions, 3-vinylheptamethyltrisiloxane forms compound IV with diazomethane in a yield up to 72.6%:



(IV)

It is interesting to note that siloxanes containing an alkenyl group in the β-position relative to the silicon atom (allylheptamethylcyclotetrasiloxane) react with difficulty with diazomethane, and the corresponding pyrazoline derivative cannot be isolated from the reaction products.

Compounds III and IV, when heated at 180–200°, decompose with liberation of nitrogen and formation of allyl derivatives of organosiloxanes. The thermal decomposition of the indicated compounds probably proceeds by a radical mechanism:

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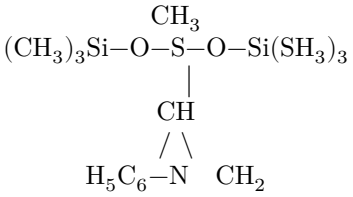
$$\text{pyrazoline derivative (III)} \xrightarrow[-N_2]{t^\circ} \text{allylheptamethylcyclotetrasiloxane (V)}$$

On thermal decomposition of compound IV, 3-allylheptamethyltrisiloxane (VI) was obtained.

The addition reaction of phenyl azide to I and to II leads to the formation of the corresponding *N*-phenylaziridinyl derivatives of organosiloxanes. It is possible that the reaction proceeds through the formation of triazoline derivatives, which decompose during isolation to the corresponding *N*-phenylaziridinyl derivatives:

$$\text{[3-vinylheptamethylcyclotetrasiloxane]} + C_6H_5N_3 \longrightarrow \text{[triazoline derivative]} \longrightarrow N\text{-phenylaziridinyl derivative}$$

Similarly, from phenyl azide and II, compound VIII was obtained:



Analogously to reactions with diazomethane, phenyl azide reacts only with difficulty with allylheptamethylcyclotetrasiloxane, and it is not possible to isolate the corresponding *N*-phenylaziridinyl derivative from the reaction product. These facts confirm the known proposition that, with respect to nucleophilic reagents in addition reactions, the vinyl group in the α-position to the silicon atom is incomparably more reactive than the same group in the β-position.

3-Vinylheptamethyltrisiloxane reacts with butadiene-1,3 comparatively easily and with a satisfactory yield of the condensation product, according to the scheme:

$$(CH_3)_3Si{-}O{-}Si(CH_3)(CH{=}CH_2){-}O{-}Si(CH_3)_3 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow (CH_3)_3Si{-}O{-}Si(CH_3)\,(\ \text{cyclohex}$$

(II) (IX)

The new compounds obtained were identified by elemental analysis, determination of molecular weight, and molecular refraction. For all synthesized compounds, i.r. absorption spectra were recorded.* For compound IV, in addition, an n.m.r. spectrum was recorded.

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In the i.r. spectra of compounds III and IV, a fairly intense band is observed at 1545 cm^{-1}, which apparently should be assigned to vibrations of the −N=N− bonds; at 1352 cm^{-1}, in compounds VII and VIII, a band is observed that is characteristic of C−N bonds; the phenyl groups in the indicated compounds appear in the regions 1505, 1605, and 3030 cm^{-1}.

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* The authors express their deep gratitude to M. T. Zaitseva for recording the i.r. absorption spectra.

In the IR spectra of compounds V and VI, bands appear at 1640-1635 cm^{-1}; in the region of stretching vibrations of C−H bonds, two bands appear at about 3010 and 3085 cm^{-1}, which should be assigned to vibrations of the bonds =CH −and $=CH_2$ in the C=C bond. The appearance of these three bands makes it possible to assign precisely this structure to compounds V and VI. In the spectrum of compound IX, a band appears at 1655 cm^{-1}, characteristic of the double bond of cyclohexene derivatives, which indicates the practically complete absence of mutual influence between the π-electrons of the double bond and the free 3*d*-orbitals of silicon.

In the region of stretching vibrations of C−H bonds, this compound shows a band at about 3010 cm^{-1}, characteristic of vibrations of =CH−bonds in a C=C bond.

In the region 2920-2910 cm^{-1}, bands of methylene groups are observed in the IR spectra of all the compounds.

In the NMR spectrum of compound IV at a frequency of 40 MHz, a peak for the protons of −CH groups and two doublet peaks for the protons of CH_2 groups were found, with the following chemical-shift values (relative to $(CH_3)_4Si$): δ_{CH} = 5.74 ppm, δ'_{CH_2} = 6.96 ppm, δ'_{CH_2} = 7.12 ppm, δ''_{CH_2} = 7.36 ppm, and δ''_{CH_2} = 7.58 ppm. The appearance of two doublet peaks for the protons of the CH_2 groups of the pyrazoline ring makes it possible to assign to compound IV the structure of a substituted Δ^1-pyrazoline.

Experimental Part

Synthesis of 3-(Δ^1-pyrazolinyl)-heptamethyltrisiloxane (IV) and Δ^1-pyrazolinylheptamethylcyclotetrasiloxane (III). An ethereal solution of diazomethane, prepared from 7.5 g of nitrosomethylurea and 8.1 g of KOH, was added to 8.7 g (0.035 mole) of II, after which the mixture was kept for 10 h at 0° and left at room temperature until the excess diazomethane had completely evaporated. Distillation afforded 7.4 g of IV (72.6%), b.p. 84-86°/4 mm, n_D^{20} 1.4285, d_4^{20} 0.9115.

Found, %: Si 29.37; C 41.68; H 9.08; N 10.01

$C_{10}H_{26}N_2Si_3O_2$. Calculated, %: Si 28.97; C 41.38; H 9.08; N 9.65

Molecular weight found 315, calculated 290. MR found 81.81, calculated 82.39.

By an analogous procedure, from 9.24 g (0.03 mole) of I, 8.1 g of III were obtained (77.1%), b.p. 82–83°/2 mm; n_D^{20} 1.4305, d_4^{20} 1.0177.

Found, %: Si 31.94; C 34.50; H 7.41; N 8.76

$C_{10}H_{26}N_2Si_4O_4$. Calculated, %: Si 32.00; C 34.29; H 7.43; N 8.00

Molecular weight found 341, calculated 350. MR found 88.76; calculated 89.39.

Upon decomposition of 42 g (0.0145 mole) of IV for 30 min in a flask with a reflux condenser at 170–200°, 2.63 g (69.4%) of 3-allylheptamethyltrisiloxane (VI) were obtained, b.p. 57.5–59°/10 mm, n_D^{20} 1.4049; literature data ([1]): b.p. 103–103.5°/59 mm; n_D^{25} 1.4013.

Upon decomposition of 5.1 g (0.0146 mole) of III for 3.5 h at 170–200°, 1.23 g (26.1%) of allylheptamethylcyclotetrasiloxane (V) were obtained, b.p. 42–43°/3 mm; n_D^{20} 1.4318; literature data ([2]): b.p. 41°/3 mm; n_D^{20} 1.4319.

Synthesis of 3-(N-phenylaziridinyl)-heptamethyltrisiloxane (VIII) and N-phenylaziridinylheptamethylcyclotetrasiloxane (VII). Into a flask with a ground-glass stopper were added 4.96 g (0.02 mole) of II and 2.38 g (0.02 mole) of phenyl azide. The mixture was left to stand for 40 days. Attempts to isolate a crystalline product gave no results; therefore the reaction product was isolated by distillation. In all, 0.78 g (10.6%) of VIII was isolated, b.p. 105–107°/2 mm, n_D^{20} 1.4673; d_4^{20} 0.9571.

Found, %: Si 25.29; C 52.01; H 8.05; N 3.85

$C_{15}H_{29}NSi_3O_2$. Calculated, %: Si 24.78; C 53.09; H 8.55; N 4.13

Molecular weight found 357, calculated 339; MR found 98.15, calculated 98.79.

Similarly, from 5.16 g (0.0167 mole) of I and 1.99 g (0.0167 mole) of phenyl azide, 0.71 g (9.9%) of VII was isolated, b.p. 109–111°/1 mm, n_D^{20} 1.4678; d_4^{20} 1.0500.

$C_{15}H_{29}NSi_4O_4$.	Found, %:	Si 27.45; C 45.10; H 7.30; N 3.41
	Calculated, %:	Si 28.07; C 45.11; H 7.27; N 3.51

Molecular weight found 387, calculated 399; MR found 105.37, calculated 105.79.

Compounds III, IV, VII, and VIII are unstable liquids that decompose on standing, with a characteristic odor of amines.

Synthesis of 3-(cyclohexenyl-3)-heptamethyltrisiloxane (IX). Into an ampoule were sealed 7.44 g (0.03 mole) of II and 1.62 g (0.03 mole) of butadiene-1,3.

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The mixture was heated for 10 h from 20 to 160°, then for 20 h at 160–180°. Distillation gave 4.7 g (52%) of IX, b.p. 62–64°/1 mm, n_D^{20} 1.4309, d_4^{20} 0.8834.

$C_{13}H_{30}Si_3O_2$.	Found, %:	Si 27.56; C 51.11; H 9.75
	Calculated, %:	Si 27.81; C 51.65; H 9.93

Molecular weight found 326, calculated 302; MR found 88.32, calculated 87.96.

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