SYNTHESIS OF ORGANOCYCLOSILOXANES CONTAINING ALKENYL GROUPS ATTACHED TO SILICON

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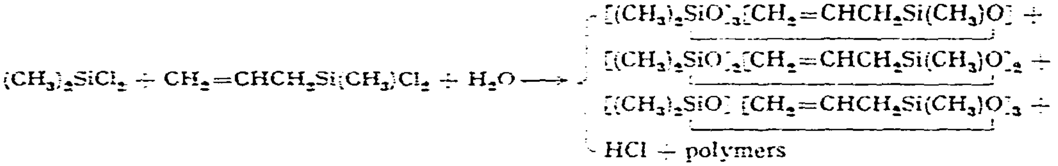
The syntheses of methylvinylcyclosiloxanes[1,2], ethylvinylcyclosiloxanes[3], tetraphenyltetravinylcyclotetrasiloxane[4] and allyl derivatives of cyclosiloxanes[5,6] by hydrolysis of the corresponding organochlorosilanes, and methylvinyldimethylcyclotetrasiloxanes by co-hydrolysis of methylvinyldichlorosilane with dimethyldichlorosilane[7], have been described in the literature.

In the present work, various allylmethyl- and allylethylcyclosiloxanes containing vinyl groups in the β-position to silicon were synthesized by co-hydrolysis of methylallyldichlorosilane with dimethyldichlorosilane and diethyldichlorosilane. A compound containing the vinyl group in the γ-position to silicon was prepared by the addition reaction of isoprene with heptamethylcyclotetrasiloxane.

The co-hydrolysis of methylallyldichlorosilane with dimethyldichlorosilane in ether solution proceeds according to the following scheme:

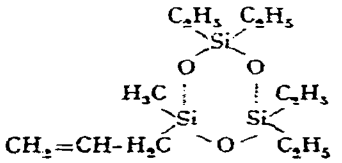


$$(CH_3)_2SiCl_2 + CH_2{=}CHCH_2Si(CH_3)Cl_2 + H_2O \longrightarrow \left\{\begin{array}{l} [(CH_3)_2SiO]_3\underline{[CH_2{=}CHCH_2Si(CH_3)O]} + \\ [(CH_3)_2SiO]_2\underline{[CH_2{=}CHCH_2Si(CH_3)O]_2} + \\ [(CH_3)_2SiO]\underline{[CH_2{=}CHCH_2Si(CH_3)O]_3} + \\ HCl + \text{polymers} \end{array}\right.$$

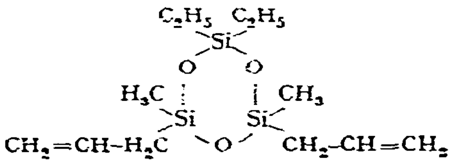
Under these conditions a mixture of cyclic compounds containing various numbers of allyl groups is always obtained.

1,3,5,7-Tetramethyl-3,5,7-trivinylcyclotetrasiloxane was obtained by co-hydrolysis of methylvinyldichlorosilane with methyldichlorosilane.

The co-hydrolysis of methylallyldichlorosilane with diethyldichlorosilane leads substantially to the formation of six-membered rings of the following structures:

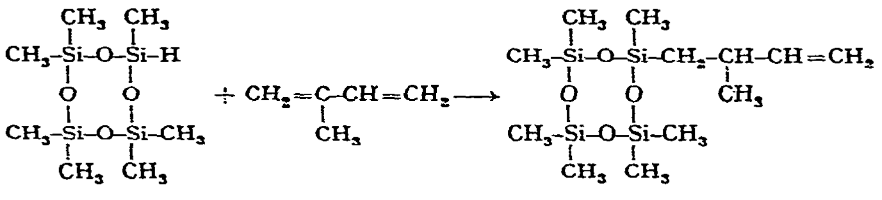


(VIII)



(IX)

The addition reaction of isoprene with heptamethylcyclotetrasiloxane proceeds according to the following scheme:



(X)

In the infrared spectrum of the resulting compound, two bands at 3012 and 3068 cm^{-1} appear in the region of valence vibrations of C–H bonds, which should be referred to vibrations of =CH– and =CH$_2$ groups in the C=C bond region[8]. The appearance of these two bands and the valence vibration band of C=C at 1658 cm^{-1} in the spectrum, allows this particular structure to be assigned to the compound.

INFRARED SPECTRA

The infrared absorption spectra of all the compounds synthesized were recorded.

The valence vibrations of the Si–O–Si group

All the eight-membered ring organocyclosiloxanes studied show an intense and wide band in the region 1072–1090 cm^{-1} corresponding to the valence vibrations of the Si–O–Si group (Table 1, Fig. 1)[9–13]. The intensity of the band is too strong to allow accurate measurements of its maxima even with absorption layers of minimum thickness. We were not able to relate the position of the Si–O–Si bands in the spectra with either the nature or quantity of the substituents, this being also true of the substituents containing π-electrons (alkenyl groups).

In the infrared spectra of the six-membered ring organocyclosyloxanes (VIII) and (IX) a band of the Si–O–Si valence vibration appears in the region 1011–1014 cm^{-1}. It should be noted that the Si–O–Si band in six-membered rings is much less intense than that in eight-membered rings.

TABLE 1

INFRARED SPECTRA

No.	*Compounds*	*Valence vibrations (cm^{-1})*		
		Si–O–Si group		*CH=CH$_2$ group*
		trimer	*tetramer*	
(I)	Vinylheptamethylcyclotetrasiloxane		1085	1596
(II)	1,5-Divinylhexamethylcyclotetrasiloxane		1085	1594
(III)	3,5,7-Trivinylpentamethylcyclotetrasiloxane		1086	1594
(IV)	1,3,5,7-Tetramethyl-3,5,7-trivinylcyclotetrasiloxane		1080	1594
(V)	Allylheptamethylcyclotetrasiloxane		1072	1617
(VI)	1,5-Diallylhexamethylcyclotetrasiloxane		1090	1621
(VII)	3,5,7-Triallylpentamethylcyclotetrasiloxane		1072	1622
(VIII)	1-Allyl-1-methyltetraethylcyclotrisiloxane	1011		1621
(IX)	3,5-Diallyl-3,5-dimethyldiethylcyclotrisoloxane	1014		1622
(X)	(2-Methyl-3-butenyl)heptamethylcyclotetrasiloxane		1081	1658

The $CH{=}CH_2$ *group bands*

The infrared spectra of the investigated vinylmethylcyclosiloxanes, allylmethylcyclosiloxanes and (2-methyl-3-butenyl)heptamethylcyclotetrasiloxane show bands characteristic of the $CH{=}CH_2$ group (Table 1, Fig. 1), the intensity of which increase with an increase in the number of alkenyl groups in the molecule.

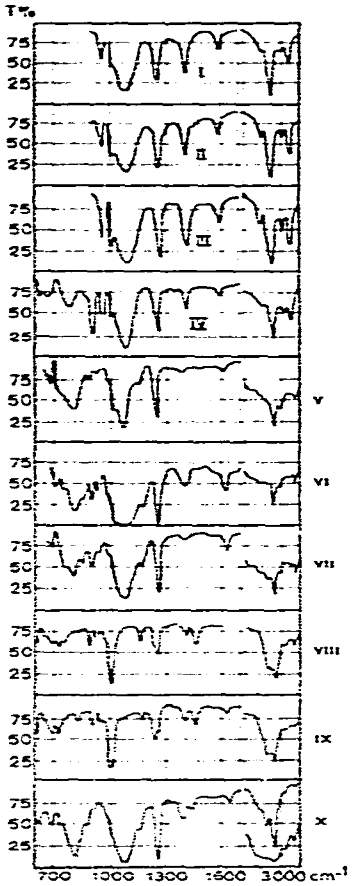


Fig. 1.

(I), vinylheptamethylcyclotetrasiloxane;

(II), 1,5-divinylhexamethylcyclotetrasiloxane;

(III), 3,5,7-trivinylpentamethylcyclotetrasiloxane,

(IV), 1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane;

(V), allylheptamethylcyclotetrasiloxane;

(VI), 1,5-diallylhexamethylcyclotetrasiloxane;

(VII), 3,5-triallylpentamethylcyclotetrasiloxane;

(VIII), 1-allyl-1-methyltetraethylcyclotrisiloxane;

(IX), 3,5-diallyl-3,5-dimethyldiethylcyclotrisiloxane;

(X), (2-methyl-3-butenyl)-heptamethylcyclotetrasiloxane.

The band of the valence vibration of the vinyl group of compound (X) in which the vinyl group is in the γ-position with regard to silicon, appears in the region 1658 cm^{-1} corresponding to the band of the unconjugated $C{=}C$ bond in hydrocarbons[8]; this probably points to the absence of mutual influence between silicon and the vinyl group in the γ-position.

As the vinyl group approaches silicon there is a decrease in the frequency of the vinyl group bond which in the β-position appears in the region 1617–1623 cm^{-1} and in the α-position in the region 1594–1596 cm^{-1}.

The values of the frequencies of the valence vibrations of the $C{=}C$ bonds obtained for compounds (I)–(IX) practically coincides with those obtained earlier for the alkenylsilanediols[14] and alkenylalkylsilanes[15,16]. The results obtained from the infrared spectra show that the conjugation of the double-bond p-electrons with the $3d$-orbitals of silicon in cyclosiloxanes is not weakened, as is to be expected taking into consideration the weakened ability of silicon as an electron acceptor (due to the partial p_π–d_π interaction of silicon and oxygen, characteristic of the organocyclosiloxane Si–O–Si bond).

Other bands of the vinyl group (non-planar deformation vibrations of the $=CH_2$ and $=CH$-groups) appear in the region 960 and 1005 cm^{-1}, the latter being often overlapped by a broad and intense band of the Si–O–Si group valence vibration. The band of the planar deformation vibration of the $=CH_2$ group at 1400 cm^{-1} partly overlaps the deformation vibration band of the methylene group.

The bands of the $=CH$ and $=CH_2$ group valence vibrations are situated in the normal part of the spectra (about 3020 and 3070 cm^{-1}); this points to the absence or negligibly weak influence of silicon on the valence vibrations of the corresponding bonds.

EXPERIMENTAL

The physical properties of the compounds synthesized are given in Table 2

TABLE 2

PHYSICAL PROPERTIES

No.	*Synthesized compound*	*B.p. (°C/mm)*	n_D^{20}	d_D^{20}	MR_D	
					Found	*Calcd.*
(V)	Allylheptamethylcyclotetrasiloxane	41/3	1.4119	0.9616	83.31	83.61
(VI)	1,5-Diallylhexamethylcyclotetrasiloxane[a]	57–58/3	1.4243	0.9684	91.78	92.10
(VII)	3.5.7-Triallylpentamethylcyclotetrasiloxane	82/3	1.4347	0.9718	100.38	100.85
(VIII)	1-Allyl-1-methyltetraethylcyclotrisiloxane	70–72/1	1.4340	0.9615	82.19	82.93
(IX)	3.5-Dimethyl-3.5-diallyldiethylcyclotrisiloxane	67–69/1	1.4375	0.9629	82.12	82.88
(IV)	1,3,5,7-Tetramethyl-3.5.7-trivinylcyclotetrasiloxane	49/5	1.4247	0.9919	81.94	82.67
(X)	(2-Methyl-3-butenyl)heptamethylcyclotetrasiloxane	86–88/5	1.4208	0.9618	92.12	92.61

[a] For this compound an isomeric structure is possible.

(1) *Co-hydrolysis, general technique*

A mixture of organochlorsilanes (in ether solution or neat) was added to a mixture of water and ether. When the reaction was complete the ether layer was separated, washed with water until the washings were neutral and dried with calcium chloride. The ether was then removed by distillation. The reaction products obtained were distilled several times to recover the individual compounds. Detailed data on the co-hydrolysis and the results of the elementary analysis of the compounds recovered are given in Table 3.

(2) *Synthesis of (2-methyl-3-butenyl)heptamethylcyclotetrasiloxane* (X)

Isoprene (1.16 g) and 4.81 g of heptamethylcyclotetrasiloxane containing two drops of an 0.1 N solution of H_2PtCl_6 in isopropyl alcohol were placed in an ampoule. The ampoule was sealed, the temperature gradually raised to 160° over 10 h and then the ampoule was heated at 160–180° for 2 h; 1.4 g (29.1 %) of unreacted heptamethyl-

TABLE 3

CO-HYDROLYSIS

No	Reaction components						Water (ml)	Reaction temp.	Time of reaction
	Organochlorosilanes		Quantity of organochlorosilanes (ml)		Ether (ml) introduced with A and B	introduced in a bulb			
	A	B	A	B					
1	Dimethyldichlorosilane	Methylallyldichlorosilane	120.5	132	—	200	500	< 30	2.0
2	Dimethyldichlorosilane	Methylallyldichlorosilane	48.0	117.6	—	200	500	< 30	2.0
3	Diethyldichlorosilane	Methylallyldichlorosilane	78.5 g	31 g	—	100	300	< 30	1.5
4	Diethyldichlorosilane	Methylallyldichlorosilane	31.4 g	77.5 g	—	100	300	< 30	1.5
5	Methyldichlorosilane	Methylvinyldichlorosilane	51.5	130	185	185	370	−10–15°	1.5

cyclotetrasiloxane and 3.1 g (51.9 %) of (X), b.p. 86–88°/5 mm, were isolated by distillation. (Found: C, 41.19; H, 8.61; Si, 32.12; mol. wt. 362; MR_D 92.12. $C_{12}H_{30}O_4Si_4$ calcd.: C, 41.12; H, 8.57; Si, 32.0 %; mol. wt. 350; MR_D, 92.61.)

Infrared absorption spectra in the region 5–15 μ were recorded on a IKS-14 double-beam spectrophotometer using a NaCl prism and in the region 2.5–5 μ on a IKS-12 spectrophotometer using a LiF prism. The compounds were investigated in the liquid state (samples obtained between two closely pressed KBr plates) and in dilute carbon tetrachloride solutions (concn. 0.5 M; thickness of the cuvettes 0.014 and 0.052 mm, respectively.)

SUMMARY

1. Co-hydrolysis reactions of methylallyldichlorosilane with dimethyldichlorosilane and diethyldichlorosilane have been studied. It is shown that in the co-hydrolysis reaction of methylallyldichlorosilane with dimethyldichlorosilane various eight-membered ring organocyclosiloxanes are mainly formed. In the co-hydrolysis reaction of methylallyldichlorosilane with diethyldichlorosilane six-membered ring organocyclosiloxanes are formed.

2. The reaction of isoprene with heptamethylcyclotetrasiloxane gives (2-methyl-3-butenyl)heptamethylcyclotetrasiloxane containing the vinyl group in the γ-position to silicon.

3. Infrared spectra of vinylmethylcyclosiloxanes, allylmethylcyclosiloxanes and (2-methyl-3-butenyl)heptamethylcyclotetrasiloxanes have been recorded. Shifting of

Reaction product	*Yield (g)*	*Yield (%)*	*Mol. wt.*		*Elementary analysis*						
			Found	*Calcd.*	*Found (%)*			*Empirical formula*	*Calcd. (%)*		
					C	*H*	*Si*		*C*	*H*	*Si*
(V)	21.14	19.7	298	322	38.15	8.38	33.93	$C_{10}H_{26}O_4Si_4$	37.26	7.45	34.78
(VI)	17.09	10.9	325	348	41.35	8.46	31.86	$C_{12}H_{28}O_4Si_4$	41.37	8.07	32.18
(VI)	13.62	19.6	355	374	44.91	7.99	29.97	$C_{14}H_{30}O_4Si_4$	44.92	8.03	29.95
(VII)	12.74	12.8									
(VIII)	32.3	53.2	312	304	47.26	9.42	27.24	$C_{12}H_{28}O_3Si_3$	47.37	9.21	27.63
(IX)	23.8	39.4	295	302	47.10	9.32	27.47	$C_{12}H_{26}O_3Si_3$	47.68	8.61	27.81
(IV)	35.54	33.6	329	318	37.42	6.99	35.27	$C_{10}H_{22}O_4Si_4$	37.74	6.92	35.22

absorption bands is observed for the vinyl groups in the α- and β-positions with regard to silicon. For these groups in the γ-position there is no shift in the absorption bands.

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