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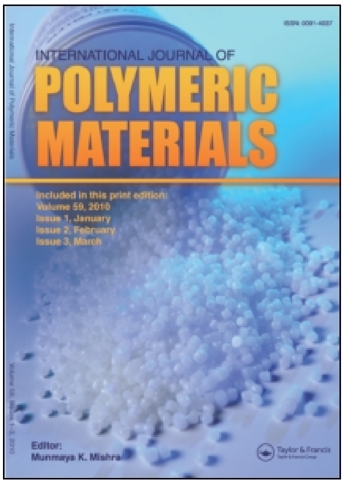

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Synthesis of Epoxycontaining Siliconorganic Compounds

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Epoxycompounds containing the methyl, phenyl, vinyl, chlormethyl, thienyl and chlorthienyl radicals with molecules containing one siloxane or cyclosiloxane, or two and more siloxane fragments are synthesised for the first time by the hydrosililization of alylglicidyl ester with organohydrosilanes or siloxanes in the presence of Speier catalizator H_2PtCl_6. The reaction of hydrosililization is studied using infrared spectroscopy and gas-liquid chromatography method. The anionic polymerization of epoxicompounds containing cyclosiloxane fragments using α,β-bis(tetramethilammonium)dimethilsilanolat is carried out.

KEY WORDS Silico organic, epoxides, siloxane, cyclosiloxane.

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EXPERIMENTAL SECTION

1,3-dichlortetramethyldisiloxane, boiling temperature 138°C, %Cl-34.60, n_D^{20} = 1.4050 (1), 1,5-dichlorhexamethyltrisiloxane, boiling temperature 80°C/20 mm mercury column %Cl-25.60, n_D^{20} = 1.4070, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane, boiling temperature 154–155°C/1 mm mercury column %Cl-21.64 n_D^{20} = 1.5719, 1,3-dichloro-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, boiling temperature 189°C/1 mm mercury column %Cl-15.40, n_D^{20} = 1.5370, 1,3-dichloro-1,3-dimethyldisiloxane, boiling temperature 103°C %Cl-40.48, %H(Si—H) 1.15, were obtained by the partial hydrolisis of corresponding organoclorsilanes using the accepted methodics.

The synthesis of heptamethylcyclotetrasiloxane, 120 ml of absolute ester and 31.6 g (0.4 mole) of pyridine was poured into a four-neck flask equipped with two dropping funnels, reverse refrigerator and mechanical stirrer. 48 g (0.2 mole) of dihydroxihexamethyltrisiloxane was added from one dropping funnel, while 23 g (0.2 mole) of methildichlorsylane from other dropping funnel, dissolved in 120 ml of absolute ester.

The whole reaction mixture was stirred and when temperature achieved 30°C, was heated during the 5 hours. After that the solution was cooled and sediments were filtered. The ester solution was washed off by the distilled water till the neutral reaction and was dried on waterless sodium sulphur. Volatile products were distilled under vacuum. The rest of reaction products were distilled. The boiling temperature is 165°C %H(Si—H) −0.36, n_D^{20} = 1.3965. This corresponds to Reference 2.

2,4,6-trimethyl-2,4-diphenylcyclotrisiloxane was obtained analogically. The boiling temperature is 160–162°C/1 mm mercury column, %H(Si—H) −0.28. This corresponds to Reference 2.

2,4,6,8-tetramethyl-2,4,6-triphenylcyclotetrasiloxane was obtained similarly. The boiling temperature is 190–191°C/1 mm mercury column, %H(Si—H) −0.20. n_D^{20} = 1.5330. This corresponds to Reference 2.

2,2,4,4,6,8-hexamethylcyclotetrasiloxane was similarly obtained. The boiling temperature is 154°C/1 mm mercury column, %H(Si—H) −0.72. n_D^{20} = 1.5330. This corresponds to Reference 2.

2,4,6-tetramethyl-2,4-diphenylcyclotetrasiloxane was similarly obtained. The boiling temperature is 139–153°C/1 mm mercury column, %H(Si—H) −0.51. n_D^{20}= 1.4905.

The synthesis of glisidoxipropylheptamethylcyclotetrasiloxane. 27 g (0.1 mole) of heptamethylcyclotetrasiloxane and 0.05 ml 0.1 N solution of platinumclorhydrogen acid in propanol was poured into a three-neck flask equipped with dropping funnel, thermometer and mechanical stirrer. 12.5 g (0.11 mole) of alilglicidil ester was added from dropping funnel. After the growth dropping funnel was replaced by reverse refrigerator and the reaction mixture was heated to 70–80°C during 3 hours. Then the volatile products were distilled. Finally by the distillation glisidoxipropilheptamethylcyclotetrasiloxane was obtained. The boiling temperature is 268–270°C/2 mm mercury column n_D^{20} = 1.4432, the content of epoxi-groups is 10.56% (calculated −10.85).

6-(glicidoxipropil)-2,4,6-trimethyl-2,4-diphenylcyclotrisiloxane was obtained analogically. The boiling temperature is 240–245°C/1 mm mercury column n_D^{20} = 1.4453, the content of epoxi-groups is 9.95% (calculated −9.64).

8-(glicidoxipropyl)-2,4,6,8-tetramethyl-2,4,6-triphenylcyclotetrasiloxane was similarly obtained. The boiling temperature is 100–104°C/10 mm mercury column n_D^{20} = 1.4558, the content of epoxi-groups is 7.82% (calculated −7.39).

6,8-bis(glicydoxipropyl)-2,2,4,4,6,8-hexamethilcyclotetrasiloxane was similarly obtained. The boiling temperature is 127–129°C/10 mm mercury column n_D^{20} = 1.4530, the content of epoxi-groups is 17.91% (calculated 17.34).

6,8-bis(glicydoxipropyl)-2,4,6,8-tetramethyl-2,4-diphenylcyclotetrasiloxane was similarly obtained. The boiling temperature is 167–169°C/10 mm mercury column n_D^{20} = 1.4472, the content of epoxi groups is 14.46% (calculated 13.87).

RESULTS AND DISCUSSION

The literature describes the siliconorganic epoxy-monomeres with methyl and phenyl radicals bounded in silicon atom, containing one or two silicon atoms in chain. The oligomeric epoxysiloxanes containing a small quantity of epoxigroups have also been synthesized.

Our group was the first who synthesized the epoxy-compounds containing siloxane fragments with methyl, vinyl, chlorethyl, thienyl and chlorthienyl radicals. These compounds are synthesized by the hydrosililization of alylglicidyl ester with

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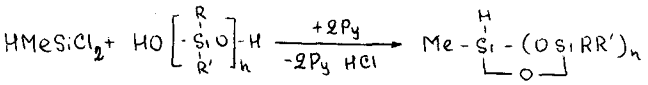
obtained using the reaction of heterofunctional condensation.[3] To obtain the six-component cyclosiloxanes with one Si—H functional group, the reaction of partial hydrolisis of diorganodichlorsilanes was held. By partial hydrolisis the 1,3-dichlorotetraorganosiloxanes were separated, and by their complete hydrolisis 1,3-dihydroxidiorganosiloxanes were obtained. By the heterofunctional condensation of 1,3-dihydroxidiorganosiloxanes with methyldichlorsilanes in the presence of pyridine, the six-component organocyclosiloxanes with one Si—H group was obtained.

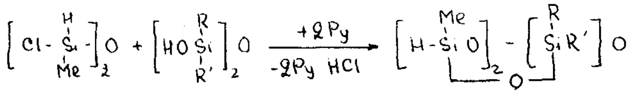
Using the same scheme, we have obtained eight-component compounds with one Si—H group. 1,5-dihidroxidiorganosiloxanes were obtained by the partial hydrolisis, then by their complete hydrolisis the 1,5-dihidroxidiorganosiloxanes were separated. By the heterofunctional condensation of the obtained compounds with methidichlorsilanes in the presence of pyridine, the eight-component organocyclosiloxanes with one Si—H group were obtained. The reaction can be described by the following formula:



$$HMeSiCl_2 + HO\left[-\overset{R}{\underset{R'}{Si}}O-\right]_n H \xrightarrow[-2Py\,HCl]{+2Py} Me-\overset{H}{Si}-(OSiRR')_n$$

where n = 2, R = R′ = Me; n = 3, R = R′ = Me; n = 2, R = Me, R′ = Ph; n = 3, R = Me, R′ = Ph.

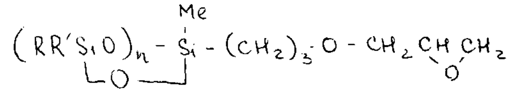
The synthesis of cyclotetrasiloxanes with two Si—H-groups. By the partial hydrolisis of methidiclorsilanes we have obtained 1,3-dichlordimethyldisiloxane. By its heterofunctional condensation with 1.3-dihidroxitetraorganosiloxanes we have obtained eight-component cycles with two Si—H groups:



$$\left[Cl-\overset{H}{\underset{Me}{Si}}-\right]_2 O + \left[HO\overset{R}{\underset{R'}{Si}}\right]_2 O \xrightarrow[-2Py\,HCl]{+2Py} \left[H-\overset{Me}{Si}O\right]_2 - \left[SiRR'\right] O$$

where R = R′ = Me; R = Me, R′ = Ph.

By the reaction of alilglicidil ester with organosiloxanes containing one Si—H group in the presence of $H_2\,PtCl_6$ at 80°C, were obtained the monoepoxides containing cyclosiloxane fragments described by general formula:



$$(RR'SiO)_n-\overset{Me}{Si}-(CH_2)_3-O-CH_2\underset{O}{CH-CH_2}$$

where n = 3, R = R′ = Me (XIV); n = 2, R = Me, R′ = Ph (XV); n = 3, R = Me, R′ = Ph (XVI).

By the reaction of organocyclosiloxanes with two Si—H group with alilglicidil ester we have obtained the following diepoxides:

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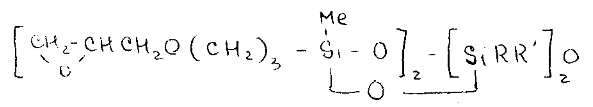

$$\left[\overset{\displaystyle\ \ }{\underset{O}{CH_2-CH}}CH_2O(CH_2)_3-\overset{Me}{Si}-O\right]_2-\left[SiRR'\right]O_2$$

where $R=R'=Me$ (XVII), $R=Me$, $R'=Ph$ (XVIII).

The physical and chemical properties of synthesized epoxides are given in Table II.

The hydrosililization of alylglicidyl ester with hexamethyltrisiloxane was studied by the method of infra-red spectroscopy. The decrease of intensity of lines of absorbtion 2125–2130 cm^{-1}, corresponding to Si—H group and 1600–1680 cm^{-1}, corresponding to C═C group, points to the fact, that the reaction of hydrosililization takes place with the participation of the double link. This is also proved by the fact, that there was no 3400–3600 cm^{-1} line of absorbtion, corresponding to associated and nonassociated secondary hydroxile groups. Lines of absorbtion 850, 917 cm^{-1} corresponds to epoxi-groups.

The reaction of hydrosililization was also studied with the method of gas chromatography. The analysis was held on LXM-8 with the following properties:

Active ionization detector: 3 m length and 4 mm diameter metallic chromatographic column. Following chromatographic phases were used: SE-30, REOPLEX-400, and OV-17. The best fractionization was achieved with OV-17. The different temperature regimes were selected for different monomeres. For example the best fractionization temperature for tetramethildisiloxane was 100°C, while for diphenilsilane this temperature was 130°C. The temperature of evaporator and detector was 250°C. In the taken samples the quantities of compounds not interacting in reaction was measured, and correspondingly the rate of transformation of reagents. The anionic polymerization of epoxiorganocyclosiloxanes with α,ω-bis(tetramethylammonium)dimethylsilanolat was performed, with amonium content 6.09% and silicon chain $n = 38$. The optimal quantity of initiator was $5*10^{-2}$ mole/litre. Reaction was held on 80°C.

During the process of polymerization viscosity and the quantity of epoxi-groups

TABLE II

Physical and chemical properties and elementary content of synthesized epoxicyclosiloxanes

No	B.P. °C	d_D^{20}	d_4^{20}	Obtained MR	Obtained CHCH$_2$	Calculated MR	Calculated CHCH$_2$	Formula
XIV	268–270 2 MM	1.4432	1.0343	100.8	11.05	101.79	10.85	$Si_4C_{13}H_{32}O_6$
XV	240–245 1 MM	1.4553	1.0097	120.0	9.95	119.88	9.64	$Si_3C_{21}H_{30}O_5$
XVI	100–104 10^{-2} MM	1.4558	1.1208	158.2	7.82	158.99	7.39	$Si_4C_{28}H_{38}O_6$
XVII	127–129 10^{-2} MM	1.4530	1.0809	123.0	17.91	123.68	17.3	$Si_4C_{18}H_{40}O_8$
XVIII	167–169 10^{-2} MM	1.4472	1.0102	163.2	14.46	163.98	13.87	$Si_4C_{28}H_{44}O_8$

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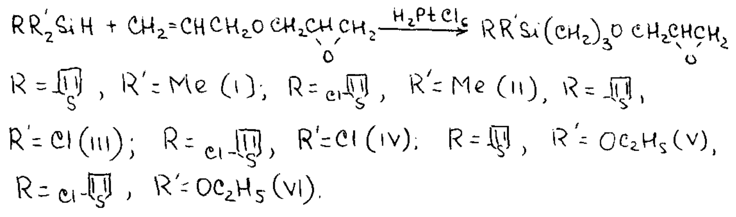
hydridsilanes or siloxanes in the presence of Speier catalizator (H_2PtCl_6) in inert medium at 80°C. By the hydrosililization of alylglicidyl ester with dimethylthienilsilane, dimethylchlorthienylsilane, thienyldichlorsilane and chlorthienyldichlorsilane the compounds containing one epoxy-group in molecule are obtained.

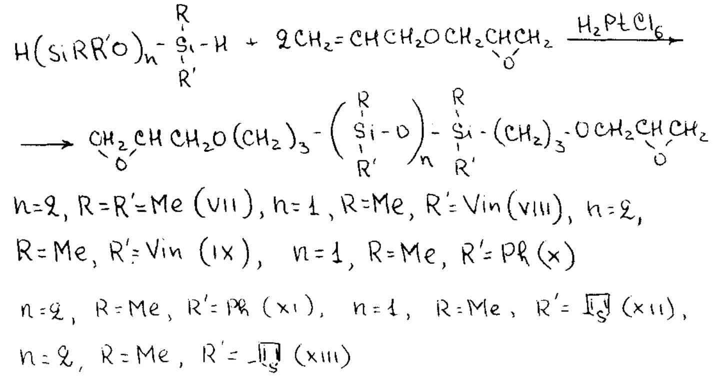
where



the characteristics of obtained compounds are given in Table I.

To obtain the diepoxides containing one or more silicon atom, the following scheme was used: first by the partial hydrolisis of organodichlorsilanes we have obtained the α,ω-dichlorodiorganosiloxanes and then by its fractionization we have collected the organosiloxanes containing two or three silicon atoms, and by its regeneration with $LiAlH_4$ we were separating corresponding dihidroorganic siloxanes. The reaction of hydrosililization of alylglicidyl ester and dihydrosiloxanes can be described by:

where



The synthesized silicon-containing epoxides are transparent liquids, which can be distilled at low pressures. Their physical and chemical properties are given in Table I. After the distillation of obtained liquids by the method of gas-liquid chromatography the individual properties of synthesized mono and diepoxides are determined. Analysis was held by the chromatographic column, with chromosorb-carrier W, with SE-30 mark siliconorganic caouchuk 50% solution, and helium as gas-carrier.

Apart from the above mentioned siliconorganic epoxides, for the first time, by our group, the mono and diepoxides containing cyclosiloxanic fragments with methyl and phenyl radicals in the main chain are synthesized. In order to obtain the above mentioned compounds we have synthesized the organocyloxanes, which contained one or two hydrogen atom with silicon atom. These organocyclosiloxanes were

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TABLE I

Physical and chemical properties and elementary content of synthesized epoxicyclosiloxanses

				MR		Elementary					Elementary			
						Obtained					Calculated			
N	B.P. °C	n_D^{20}	d_{20}^4	Ob-tained	Calcu-lated	Si	S	Cl	—CH—CH$_2$ \ / 0	Formula	Si	S	Cl	—CH—CH$_2$ \ / 0
I	131–133 2 MM	1.4590	0.9337	73	73.51	10.20	12.17	—	16.20	$Si_1C_{12}H_{20}O_2S$	10.93	12.50	—	16.80
II	140–142 2 MM	1.4927	1.0671	78	78.35	10.14	11.43	11.36	15.08	$Si_1C_{12}H_{19}O_2ClS$	9.63	11.02	12.22	14.80
III	148–149 2 MM	1.4994	1.2036	72	72.77	9.61	11.08	24.56	14.33	$Si_1C_{10}H_{14}O_2Cl_2S$	9.42	10.77	24.14	14.48
IV	149–151 1.5 MM	1.4990	1.2428	78	77.61	8.64	10.24	31.86	12.32	$Si_1C_{10}H_{13}O_2Cl_3S$	8.44	9.65	32.13	12.97
V	155–156 2 MM	1.5040	1.1205	83	84.29	8.26	11.12	—	13.93	$Si_1C_{14}H_{24}O_4S$	8.86	10.13	—	13.61
VI	170–172 2 MM	1.4992	1.1642	88	88.20	8.24	10.02	9.25	12.86	$Si_1C_{14}H_{23}O_4ClS$	7.99	9.13	10.12	12.26
VII	182–183 1 MM	1.4410	0.9942	115	116.68	19.64	—	—	20.08	$Si_3C_{18}H_{40}O_6$	19.27	—	—	19.72
VIII	178–180 1 MM	1.4521	0.9844	106	106.36	14.97	—	—	23.25	$Si_2C_{18}H_{34}O_5$	14.50	—	—	22.28
IX	211–212 1 MM	1.4576	0.9945	129	129.16	17.21	—	—	18.80	$Si_3C_{21}H_{40}O_6$	17.80	—	—	18.22
X	210–212 1 MM	1.4510	0.9599	137	137.56	11.70	—	—	16.72	$Si_2C_{26}H_{38}O_5$	11.52	—	—	17.69
XI	240 1 MM	1.4572	0.9681	175	175.96	13.90	—	—	13.26	$Si_3C_{33}H_{46}O_6$	13.50	—	—	13.83
XII	194–196 1 MM	1.4564	0.0111	135	135.38	12.31	12.2	—	17.00	$Si_2C_{22}H_{34}O_5S_2$	11.24	12.85	—	17.27
XIII	240–242 1 MM	1.5010	1.0873	172	172.69	14.10	14.2	—	14.06	$Si_3C_{27}H_{40}O_6S_3$	13.12	15.00	—	13.44

was determined. During first 15–20 minutes the increase of viscosity was observed (η = 0.15), then the formation of space polymere takes place.

RESULTS

By the hydrosililization of alilglizidil ester with organohydridsiloxanes and hydridcyclosiloxanes in the presence of Speier catalizator H_2PtCl_6 and epoxicompounds containing siloxane and cyclosiloxane fragments are separated. The reactions of hydrosililization are studied using the methods of infra-red and gas chromatography.

REFERENCES

1. K. A. Andrianov, "Siliconorganic Compounds," Moscow, GHI, 1955, pp. 317–347 (in Russian).
2. V. Bazant, V. Chvalovsky and J. Rathousky, Organosilicon Compounds.
3. L. M. Khananashvili, Ts. N. Vardosanidze, E. G. Markarashvili and N. O. Kupatadze, "Synthesis and Properties of Thienylorganosilanes and Siloxanes," *J. Polym. Mater.*, **17**, 195–203 (1992).

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