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SYNTHESIS AND PROPERTIES OF ORGANOSILICON EPISULFIDES

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A study was made of the interaction of thiourea with saturated and unsaturated organosilicon oxiranes in absolute methyl alcohol in a medium of potassium hydroxide, and methods were developed for the synthesis of unsaturated and unsaturated organosilicon silicides with a yield of 65–75%. The studies carried out revealed that the synthesized organosilicon episulfides are very reactive compounds and can react with nucleophilic and electrophilic reagents, while forming the corresponding silicon derivatives. The IR- spectra of the products were studied. It should be noted that, when comparing the IR- spectra of oxiranes and episulfides, it was revealed that the stretching vibrations of the CH₂ group of the episulfide ring are underestimated by 50–70 cm⁻¹ in comparison with the oxirane ring.

Keywords: organosilicon episulfides, thiourea, potassium hydroxide, methyl alcohol, organosilicon oxirans.

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Introduction

The method of the synthesis of saturated and unsaturated organosilicon episulfides by interaction of saturated and unsaturated organosilicon oxiranes with thiourea in a medium of the absolute methyl alcohol in the presence of potassium hydroxide has been developed.

The interest in organosilicon epoxy and episulfide functionally substituted compounds containing functional groups in its composition has been caused not only by their theoretical significance, but also by their practical importance as monomers for obtaining the polymeric materials with valuable operational properties, in particular, frost and petrol resistance on their basis [1–7].

For creation of the thermostable materials

suitable for work at higher and lower temperatures, the organosilicon polymeric materials differed by high stability to work at higher temperatures, long aging, stability under conditions of lower humidity are the most perspective [3–6].

Considering the above-mentioned one and in continuation of our investigations [5–7], this work has been devoted to the method of synthesis of Cl-, Br- and methoxy-containing organosilicon saturated and unsaturated episulfides by interaction of saturated and unsaturated functionally substituted organosilicon oxiranes with thiourea in a medium of the absolute methyl alcohol in the presence of KOH, leading to the production of functionally substituted organosilicon episulfides, the yield of which is 65–75%, according to the scheme:

X = OCH₃, R = CH₂ – CH₂ – CH₂ – (I), R' = R'' = C₂H₅ (V),
R' = CH₃, R'' = C₂H₅ (VI), C₃H₇ (VII), C₄H₉ (VIII), C₆H₅ (IX)
X = Cl, R = CH₂ – CH₂ – CH₂ – (II), R' = CH₃, R'' = C₂H₅ (X),
C₃H₇ (XI), C₄H₉ (XII), C₆H₅ (XIII).

The composition and structure of the synthesized Cl-, Br- and methoxy-containing organosilicon episulfides (V–XXI) have been determined on the basis of their IR and PMR spectra, by chromatographic methods of analysis, as well as by counter synthesis by the interaction

of saturated and unsaturated organosilicon alcohols with thioepichlorohydrin in a medium of the absolute methyl alcohol in the presence of KOH, leading to the corresponding episulfides (V–XXI):

X=OCH₃, R=CH₂–CH₂–CH₂– (I), R'=R''=C₂H₅ (V),
 R'=CH₃, R''=C₂H₅ (VI), C₃H₇ (VII), C₄H₉ (VIII), C₆H₅ (IX)
 X=Cl, R=CH₂–CH₂–CH₂– (II), R'=CH₃, R''=C₂H₅ (X)
 C₃H₇ (XI), C₄H₉ (XII), C₆H₅ (XIII)

X=Br, R=CH₂=CHCH₂– (III), R'=CH₃, R''=C₂H₅ (XIV),
 C₃H₇ (XV), C₄H₉ (XVI), C₆H₅ (XVII).
 X=OCH₃, R=CH₂=CHCH₂– (IV), R'=CH₃, R''=C₂H₅ (XVIII),
 C₃H₇ (XIX), C₄H₉ (XX), C₆H₅ (XXI).

The structure and physical constants of functionally substituted organosilicon episulfides (V–XXI), obtained by both direct and counter synthesis, and were identical.

In the IR spectra of organosilicon episulfides (V–XXI) there are the absorption bands at 550 (C–Br), 715 (C–Cl), 1050 (C–O–C), 1615 (C=CH) and 3000 cm^{–1} referring to the indicated groups [8, 9]. It has been revealed by study of the comparative spectra of oxirane and episulfide that the lowering of the absorption band

of episulfide is a consequence of a lower electro-negativity of the sulfur atom in comparison with the oxygen atom.

It has been revealed that the synthesized organosilicon episulfides (V–XXI) are very reactive compounds and can react with electrophilic and nucleophilic reagents. It has been shown that in interaction of organosilicon episulfides with diethylamine it is opened an episulfide ring with the formation of aminomercaptans according to the scheme:

A yield of the compounds (XXII, XXIII) is 75–80%, the structure has been confirmed by IR and PMR spectroscopy.

An absence of the absorption band characteristic for episulfide group in the IR spectra, and an appearance of the bands at 2785 (N–Et) and in the field of 2600–2550 cm^{-1} characteristic for vibrations of SH-group indicate that the reaction proceeds on episulfide group. It should be noted that in comparison of IR spectra of oxiranes and episulfides (V, XIV), it has been revealed that the valence vibration of the CH_2 -group of the episulfide ring has been lowered in comparison with oxirane ring by 50–70 cm^{-1} .

In the PMR spectrum of aminomercaptan (XXII), the signals of the aminomethyl group have been detected as a quartet at $\delta=2.35$ ppm, and the dimethyl groups of the diethyl radical enter as a singlet at $\delta=1.30$ ppm.

Experimental part

The IR spectra of the synthesized compounds were taken on spectrophotometer UR-20 in the range of 400–3600 cm^{-1} in a thin layer.

The PMR spectra were taken on spectrophotometer Tesla BS-487-B (60, 80 MHz) in a solution of carbon tetrachloride with internal standard HMDS. The purity of the synthesized compounds was controlled by a method TLC on the plates "Silufol UV-254" in the various systems of solvent and gaseous chromatography on chromatograph LKhM-8MD-5.

Synthesis of organosilicon episulfides.

a) 9.7 g (0.024 mol) of organosilicon oxirane (I), 27.4 g (0.036 mol) of thiourea, 50 g of absolute methyl alcohol and KOH are placed in round-bottom flask equipped with mechanical mixer. The content of flask is mixed for 24 h. After usual treatment and distillation of the solvent by vacuum 4.7 g of episulfide was isolated (V): B.p.145 (0.5 mm merc.c.), n_D^{20} 1.4550, d_4^{20} 0.9444, MR 96.10 (found), 96.51 (calculated). Yield – 58.3%. Found, %: C 57.76, 57.60; H 10.32, 10.43; S 9.75, 9.66; Si 8.60, 8.44. $\text{C}_{16}\text{H}_{34}\text{O}_3\text{SSi}$. Calculated, %: C 57.44; H 10.24; S 9.56; Si 8.39. The IR spectrum of this compound is presented in Figure 1.

There have been obtained the compounds (VI–XXI), physical-chemical constants of which have been presented in Table 1.

b) The reaction mixture consisting of 17.0 g (0.12 mol) of episulfide (V), 10.9 g (0.15 mol) of diethylamine is stirred at 40°C to formation of thick mass. After distillation of the low-boiling components, 22.5 g of the compound (XXII) was isolated from residue by vacuum distillation. After the second distillation: B.p. 181°C (1mm merc.c.), n_D^{20} 1.4640, d_4^{20} 0.8555. The compound XXIII was obtained similarly with b.p. 192°C (1.5 mm merc.c.), n_D^{20} 1.4670, d_4^{20} 0.9480.

Fig.1. IR spectrum of the compound (V).

Table 1. Physical-chemical characteristics of episulfides

Compounds	Formula of compounds	Yield, %	B.p., (mm merc.c.)	n_D^{20}	d_4^{20}	MR _D	
						Found	Calculated
VI	$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	63	152 (0.3)	1.4530	0.9568	89.96	90.43
VII	$\text{CH}_3(\text{C}_3\text{H}_7)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	60	158 (0.5)	1.4540	0.9476	95.03	95.02
VIII	$\text{CH}_3(\text{C}_4\text{H}_9)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	62	165 (0.5)	1.4510	0.9370	103.64	104.52
IX	$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	65	221 (0.5)	1.5430	1.07017	122.66	122.70
X	$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{Cl} \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	66	156–157 (0.5)	1.4620	0.9217	91.00	90.44
XI	$\text{CH}_3(\text{C}_3\text{H}_7)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{Cl} \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	68.4	181 (0.5)	1.4630	0.9820	99.40	98.96
XII	$\text{CH}_3(\text{C}_4\text{H}_9)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{Cl} \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	72	178 (0.5)	1.4650	0.9645	109.20	109.40
XIII	$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_2)_3\text{OCH}_2-\text{CH} \begin{array}{l} \text{CH}_2\text{Cl} \\ \text{OCH}_2\text{CH}-\text{S}-\text{CH}_2 \end{array}$	79	221–222 (1)	1.5165	1.1006	121.20	121.04

Compounds	Formula of compounds	Yield, %	B.p., (mm merc.c.)	n_D^{20}	d_4^{20}	MR _D	
						Found	Calculated
XIV	$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	74	131.5 (0.5)	1.4630	0.9756	85.40	84.75
XV	$\text{CH}_3(\text{C}_3\text{H}_7)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	72	141 (0.5)	1.4610	0.9578	94.70	94.75
XVI	$\text{CH}_3(\text{C}_4\text{H}_9)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	70	158 (0.5)	1.4620	0.9490	103.50	104.05
XVII	$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{OCH}_3 \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	80	201 (0.5)	1.5050	1.0460	95.98	95.25
XVIII	$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	79	186–187 (1)	1.5100	1.1779	92.4	92.81
XIX	$\text{CH}_3(\text{C}_3\text{H}_7)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	76	191–192 (1)	1.5160	1.1802	102.3	101.25
XX	$\text{CH}_3(\text{C}_4\text{H}_9)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	78	168–169 (1)	1.5240	1.1658	111.41	111.00
XXI	$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SiCH}=\text{CHCH}_2\text{OCH}_2\text{CH} \begin{array}{l} \text{CH}_2\text{Br} \\ \text{OCH}_2\text{CH}-\text{CH}_2 \\ \text{S} \end{array}$	80	203–204 (1)	1.5260	1.2250	114.5	114.00

Conclusions

1. The method of the synthesis of chloro-, bromo-, methoxy-containing saturated and unsaturated episulfides based on the interaction reaction of organosilicon saturated and unsaturated oxiranes with thiocarbamide in a medium of the absolute methyl alcohol in the presence of potassium hydroxide has been developed.

2. It has been shown that chloro-, bromo-, methoxy-containing saturated and unsaturated organosilicon episulphides are very reactive compounds and easily undergo the reaction with electrophilic and nucleophilic reagents, thus forming the corresponding silicon derivatives.

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SİLİSIUM ÜZVİ EPISULFİDLƏRİN SİNTEZİ VƏ XASSƏLƏRİ

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Tədqiqat nəticəsində tiokarbamidlə doymuş və doymamış silisium oksiranların mütləq metil spirti mühitində kalium hidroksidin iştirakı ilə qarşılıqlı təsiri nəticəsində 65–75% çıxımla doymuş və doymamış silisium üzvi episulfidlərin sintez üsulları işlənib hazırlanmışdır. Aparılan tədqiqatlar nəticəsində aşkar olunmuşdur ki, sintez olunmuş silisium üzvi episulfidlər yüksək reaksiyaya girmə qabiliyyətinə malik olub nukleofil və elektrofil reagentlərlə reaksiyaya girərək müvafiq silisiumlu törəmələrini əmələ gətirirlər. Alınan maddələrin İQ- spektrləri öyrənilmişdir. Bu zaman müəyyən edilmişdir ki, episulfid zəncirinin CH_2 qrupunun valent sürüşməsi, oksiran zəncirinin CH_2 qrupunun valent sürüşməsindən 50–70 cm^{-1} aşağıdır.

Açar sözlər: silisium üzvi episulfid, tiokarbamid, kalium hidroksid, metil spirti, silisium üzvi oksiranlar.

СИНТЕЗ И СВОЙСТВА КРЕМНИЙОРГАНИЧЕСКИХ ЭПИСУЛЬФИДОВ

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Разработан метод синтеза предельных и непредельных кремнийорганических эписульфидов путем взаимодействия тиомочевина с предельными и непредельными кремнийорганическими оксиранами в среде абсолютного метилового спирта в присутствии KOH (выход до 65–75%). Выявлено, что синтезированные кремнийорганические эписульфиды, являются весьма реакционноспособными соединениями и могут вступать в реакцию с нуклеофильными и электрофильными реагентами, образуя при этом соответствующие производные кремния. Изучены ИК-спектры продуктов. Выявлено что, при сопоставлении ИК-спектров оксиранов и эписульфидов, валентное колебание CH_2 -группы эписульфидного кольца смещено, по сравнению с оксирановым кольцом, на 50–70 cm^{-1} .

Ключевые слова: кремнийорганические эписульфиды, тиомочевина, гидрооксид калия, метиловый спирт, кремнийорганические оксираны.