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SYNTHESIS AND PROPERTIES OF UNSATURATED AROMATIC OXIRANOSILANES

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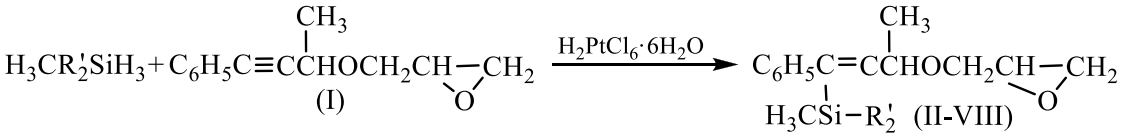
Abstract: *The method of the synthesis of unsaturated aromatic oxiranosilanes by interaction of trialkyl-(aryl)-hydridesilanes with aromatic oxiranes of the acetylene series in the presence of catalyst (platinum-hydrochloric acid) in a medium of absolute benzene (yield up to 82-85%) was developed and their properties studied. It was showed that the addition reaction proceeded on a triple bond according to Farmer's rule with the formation of trans-adducts and the maintenance of the oxirane ring. The composition and structure of the obtained unsaturated aromatic oxiranosilanes were confirmed by IR and PMR spectra. It revealed that the obtained unsaturated aromatic oxiranosilanes were highly reactive compounds and can undergo the reaction with nucleophilic and electrophilic reagents.*

Keywords: *acetylene bond, oxirane rings, unsaturated aromatic oxiranes, hydridesilanes, addition reaction.*

Introduction

The development of new fields of technique and technology and the use of thermostable materials in technological processes put forward a task of creation of new thermostable materials with valuable exploitation properties for science and industry. Among them, the element-organic (Si, Ge, Sn) compounds are of great interest, allowing to obtain oligomers and polymers with high thermal stability and petrol-resistance on their basis [1-3].

For continuation of the research and with the aim of synthesizing unsaturated aromatic oxiranosilanes and oxiranosiloxanes [4-5] and revealing a comparative estimation of the chemical activity of two reactive centers – the acetylene bond and the oxirane ring – and for clarification of the structural directionality, the addition reaction of trialkyl(aryl) hydridesilanes to 3-phenyl-1-methyl-1-glycidyloxyprop-2-ane in the presence of platinum-hydrochloric acid according to the scheme has been examined as follows:

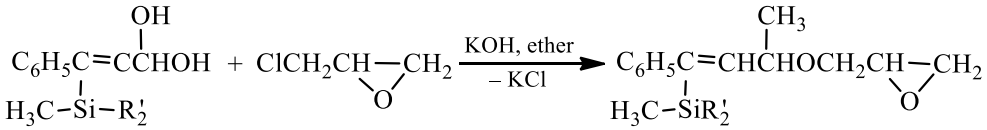


R'_2 = C_2H_5 (II); C_3H_7 (III); C_4H_9 (IV); C_5H_{11} (V); C_6H_5 (VI); $(CH_2)_4$ (VII); $-OC_2H_5$ (VIII)

Results and discussion

From the analysis of literature materials [5,6] one can expect the above-mentioned reaction behavior proceed along the oxirane ring. The presence of this ring in the epoxysilane spectrum is confirmed by the availability of frequency in the field of 3060 cm^{-1} belonging to the valence vibrations of the CH_2 group of the oxirane ring in the spectrum of adducts (II-VIII). Consequently, the triorganosilanes are joined to the investigated oxirano-olefins exclusively on C≡C bond, and the oxirane cycle remains unaffected in this case.

However, according to spectral data, it is impossible to establish the order of addition of hydridsilanes to the studied oxiranoolefins. In this connection, we carried out a counter synthesis with use of substances of the known structure:



R' = C_2H_5

Organosilanes obtained by both direct hydrosilylation and counter synthesis had identical properties and IR spectra. Thus, under the conditions accepted by us, the addition reaction of triorganosilanes to oxirano-olefins, catalyzed by platinum-hydrochloric acid, proceeds by a multiple C≡C bond with the formation of carbofunctional oxirano-silanes.

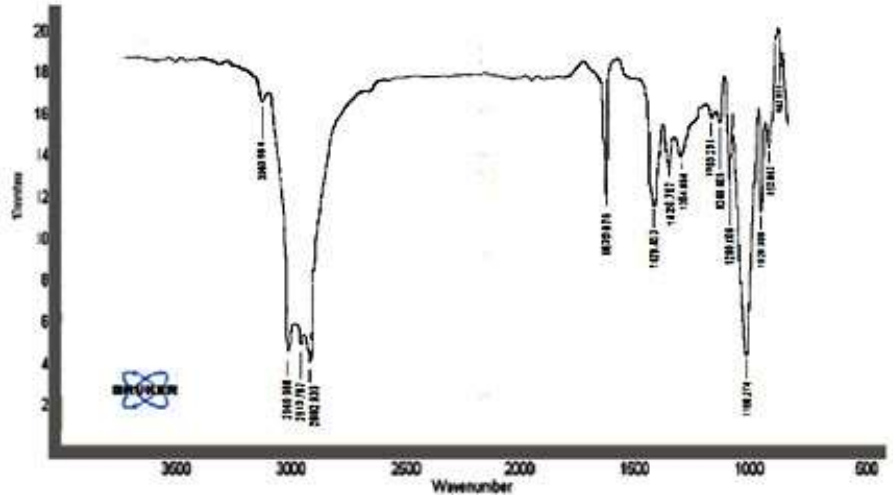
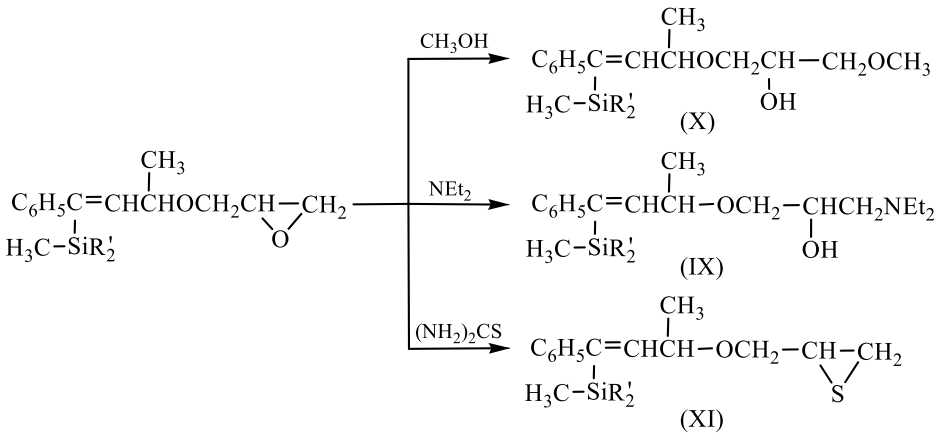


Fig.1. IR spectrum of 1-methyl-1-phenyl-1-glycidyloxy-3-methyldiethylsilylpropn-2-ene (III)

In the IR spectra there are absorption bands in the fields of 1615 cm^{-1} (Si–$C_{alk.}$), 1019 cm^{-1} (C–O–C), 1180, 950, 3060 cm^{-1} (oxirane bond), respectively [7]. The individuality of compounds (II-VIII) was proved by TLC data, and trans-configuration confirmed by the availability of the absorption band with a frequency 1310 and 965 cm^{-1} in the spectra and PMR spectra. The spin-spin interaction J (H_A, H_B) value is 13.5-14.5 Hz which indicates a trans-structure, and the triorganosilyl group is fixed at the peripheral carbon atom of C≡C bond. The investigations revealed that the oxirane groups in the synthesized oxiranosilanes had a high reactivity and easily underwent the interaction with electrophilic and nucleophilic reagents, forming the corresponding silicon derivatives [8-10]. In particular, it found that in the course of interaction of compound (III) with diethylamine, the oxirane cycle opening with the formation of the corresponding amino-alcohols with vibration of 2875 cm^{-1} occured; the interaction of compound (IV) with methanol led to the disappearance of the absorption band at 3060 cm^{-1} and the appearance of wide band with center 3450 cm^{-1} belonging to CH-group, associated with intermolecular hydrogen bond in the spectrum of ether alcohol (X), and the interaction of compound (V) with thiourea proceeds by substitution of the oxirane oxygen for sulfur with the formation of thiiranes (XI).



Experimental part

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

The PMR spectra were recorded on the spectrometer Tesla BS-487C in $CDCl_3$ solution, working frequency – 80 MHz, internal standard – hexamethyldisiloxane.

The individuality of the obtained compounds was controlled by the method of TLC on Silufol UV-366 plates (eluent – benzene-diethyl ether (3:1)) and gas chromatography on the chromatograph LKhM-8MD, column – 200×0.4 cm. Stationary phase was SE-30 on Chromaton UW (3%).

The physical-chemical characteristics of the newly synthesized organo-silicon oxiranes are given in Table.

1-methyl-1-phenyl-1-glycidyloxy-3-methyl-diethylsilylprop-2-ene (II). 10.1 g (0.05 mol) of freshly distilled compound (I), 50 ml of anhydrous benzene and 1 ml of 0.1 N platinum-hydrochloric acid in isopropyl alcohol were placed in a three-necked flask equipped with a reflux condenser and a dropping funnel. Then the mixture was boiled at the boiling point of benzene, 5.1 g (0.05 mol) of methyldiethylsilane was added and the mixture boiled for 20 h. After distillation of the solvent, 11.85 g of oxiranosilane (II) was isolated from the residue by vacuum. Yield – 78%, B.p. 198-199°C (0.5 mm merc.c.), n_D^{20} = 1.5400, d_4^{20} = 1.0267. Calculated, %: C 70.40; H 9.25; Si 8.98. $C_{18}H_{29}SiO_2$. Found, %: C 70.25; H 9.00; Si 8.98.

Similarly, the compounds (III-VIII) were obtained, the properties of which are given in Table.

Table 1. Properties of aromatic oxirano-silanes

№ comp.	Yield, %	B.p., °C (mm merc.c.)	n_D^{20}	d_4^{20}	MR_D		Brutto formula
					found	calculated	
II	76	190-191 (0.5)	1.5400	1.0267	92.91	91.26	$C_{18}H_{28}O_2Si$
III	70	197-198 (0.5)	1.5405	1.0218	101.52	101.86	$C_{20}H_{32}O_2Si$
IV	81	210-211 (0.5)	1.5435	1.0207	110.60	110.86	$C_{22}H_{36}O_2Si$
V	68	209-210 (0.5)	1.5401	0.9989	120.31	120.58	$C_{24}H_{40}O_2Si$
VI	74	225 (0.5)	1.6255	1.1498	122.63	122.88	$C_{26}H_{28}O_2Si$
VII	83	192-193 (0.5)			92.00	92.06	$C_{20}H_{33}O_2Si$
VIII	73	180-181 (0.5)	1.5510	0.8609	119.60	119.94	$C_{18}H_{29}O_2Si$

Interaction of 1-methyl-3-phenyl-1-glycidyloxymethyldiprop-2-ene (III) with diethylamine. A mixture consisting of 30 ml of diethylamine and 20 g of oxiranosilane (III) was stirred at temperature 30°C for 40 h, and then was subjected to the vacuumization. 39 g of amino-alcohol (IX) was isolated by vacuum. Yield – 82%, B.p. 221°C (0.5 mm merc. c.), n_D^{20} = 1.5415, d_4^{20} = 1.0633, MR_D 120.38 (calculated), 120.00 (found). Found, %: C 71.04; H 10.60; Si 6.92; N 3.45. $C_{24}H_{49}SiO_2N$. Calculated, %: C 71.00; H 10.45; Si 7.00; N 3.40.

Interaction of 1-methyl-3-phenyl-1-glycidyloxymethyldibutylprop-2-ene (IV) with methanol. 16 g of oxiranosilane (IV) was slowly added to 50 g of absolute methanol containing 0.1 ml of boron trifluoride etherate at 0°C. The reaction mixture was then stirred at room temperature for 40 h. After distillation of excess methanol, 11 g of ether alcohol (X) was isolated from the residue by vacuum. Yield – 78%, B.p. 228-229°C (0.5 mm merc.c.), n_D^{20} = 1.5473, d_4^{20} = 1.0975, MR_D 119.00 (calculated), MR_D 119,7 (found). Found, %: C 72.12; H 10.16; Si 7.34. $C_{23}H_{40}SO_3$. Calculated, %: C 72.00; H 10.11; Si 7.10

Interaction of 1-methyl-3-phenyl-1-glycidyloxymethyldiamylprop-2-ene with thiourea (V). 9.7 g (0.024 mol) of oxiranosilane (V), 27.4 g (0.036 mol) of thiourea and 50 ml of absolute methyl alcohol were placed in a round-bottomed flask with a reflux condenser and a mechanical stirrer. The contents of the flask were stirred at temperature 30°C for 25 h. After the usual treatment and distillation of unreacted components, 4.7 g of episulfide was isolated (XI) by vacuum. B.p. –. 209°C (0.5 mm merc.c.), n_D^{20} = 1.540**1**, d_4^{20} = 0.5889, MR_D 125.76 (calculated), 125.40 (found). Found, %: C 71.03; H 10.06; Si 6.96; S 7.85. $C_{24}H_{40}$ Si S. Calculated, %: C 70.93; H 9.96; Si 6.91; S 7.91.

Conclusions

The addition reactions of trialkyl(aryl)hydridesilanes to aromatic acetylene compounds with oxirane groups in the presence of platinum-hydrochloric acid were investigated. It established that the addition reaction proceeded exclusively on the acetylene bond with the maintenance of the oxirane ring with the formation of unsaturated organosilicon oxiranes.

It shown that the obtained unsaturated organosilicon oxiranes easily underwent the interaction with compounds containing a mobile hydrogen atom with the formation of the appropriate silicon derivatives.

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DOYMAMIŞ AROMATİK OKSİRANSİLANLARIN SİNTEZİ VƏ XASSƏLƏRİ

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Trialkil(aril)silanlarla asetilen sıralı aromatik oksiranların reaksiyası ilə doymamış aromatik oksiransilanların sintez üsulları işlənmiş (çıxımı 82-85%) və xassələri öyrənilmişdir. Reaksiya mütləq benzol mühitində və katalizatorun (xloroplatin turşusu) iştirakında aparılır. Göstərilmişdir ki, birləşmə reaksiyası Farmer qaydasına uyğun olaraq üçqat rabitədən gedir, trans adduktlar alınır və oksiran halqası toxunulmaz qalır. Alınmış doymamış aromatik oksiranların quruluşları İQ və NMR spektrləri ilə təsdiq edilmişdir. Müəyyən edilmişdir ki, doymamış aromatik oksiranlar yüksək reaksiyayagirmə qabiliyyətinə malik olub nukleofil və elektrofil reagentlərlə reaksiyaya girə bilirlər.
Açar sözlər: asetilen rabitəsi, oksiran halqası, doymamış aromatik oksiranlar, hidridsilanlar, birləşmə reaksiyası.

СИНТЕЗ И СВОЙСТВА НЕПРЕДЕЛЬНЫХ АРОМАТИЧЕСКИХ ОКСИРАНОСИЛАНОВ

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Разработан метод синтеза непредельных ароматических оксираносиланов путем взаимодействия триалкил-(арил)-гидридсиланов с ароматическими оксиранами ацетиленового ряда в присутствии катализатора (платинохлористоводородная кислота) в среде абсолютного бензола (выход до 82-85%) и изучены их свойства. Показано, что реакция присоединения протекает по тройной связи по правилу Фармера с образованием транс-аддуктов и сохранением оксиранового кольца. Состав и строение полученных непредельных ароматических оксираносиланов подтверждены данными ИК и ПМР- спектров. Показано, что полученные непредельные ароматические оксираносиланы являются весьма реакционноспособными соединениями и могут вступать в реакцию с нуклеофильными и электрофильными реагентами.
Ключевые слова: ацетиленовая связь, оксирановые кольца, непредельные ароматические оксираны, гидридсиланы, реакция присоединения.