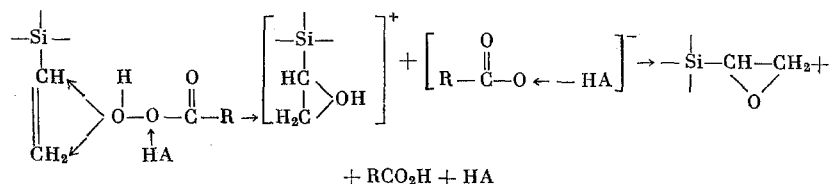


SOME LAWS GOVERNING EPOXIDATION OF VINYLORGANOSILOXANES

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Organic peracids are, of course, electrophilic agents and the velocity of the reaction of an olefin with an organic peracid increases markedly with heightening of the nucleophilic nature of the olefin by replacement of hydrogen atoms (at the double bond) by electron-donor substituents [1]. In the oxidation of a peracid, the attacking agent is the electrophilic hydroxyl group $[\ddot{O}:]^+$. However, it should be noted that the reaction with peracids displays stereospecificity. The postulated mechanism of this reaction is transfer of the $[\ddot{O}:H]^+$ group to the olefin by a complex of the acid (HA) with the peracid; it may be represented as follows



It is known [2-6] that the reaction of tetra-substituted silicoolefins with peracids gives the corresponding epoxy compounds. The presence of the electron-donor atom of Si, linked with the unsaturated aliphatic group, facilitates its oxidation by peracids. In the presence of a double bond in the organosilane molecule, the epoxidation velocity of perbenzoic acid decreases in the following order: trimethyl-, tripropyl-, triethyl-, tribenzyl-, and triphenylalkylenesilane [2].

We have studied the possibility of epoxidation by perbenzoic acid of organosilicon unsaturated compounds containing the siloxane group, and the effect of certain substituents on the Si atom on the vinyl group's reactivity (from the change in the amount of active oxygen in the reaction medium).

It was found that the reaction of compounds with the general formula $(\text{CH}_2=\text{CH})\text{RSi} \cdot [\text{OSi}(\text{CH}_3)_3]_2$, where $\text{R} = -\text{CH}_3$, $-\text{C}_6\text{H}_5$, $-\text{OSi}(\text{CH}_3)_3$ with perbenzoic acid gives the corresponding epoxyethylorgano-siloxanes.

From data on the kinetics of oxidation by perbenzoic acid of the vinyl group in the above-mentioned compounds (see Fig. 1), it follows this is a 2nd-order reaction, expressed by the kinetic equation

$$-\frac{dx}{dt} = k [\text{C}_6\text{H}_5\text{CO}_2\text{H}] \cdot [\text{silicoolefin}]$$

A comparison of the velocity constants of the reaction (see Fig. 1) confirms that in the case of organosiloxanes we observe the usual general characteristics of epoxidation, due to the reaction's stereospecificity and the polarity of the groups in the olefin. Introduction of either an electrophilic phenyl radical or a trimethylsilyl radical into the silane molecule, which causes steric hindrance, has virtually the same effect (a decrease in the reactivity of the vinyl group on the silicon atom), whereas the presence of the small electron-donor methyl radical increases the epoxidation velocity.

Figure 2 gives the infrared spectra of the compounds obtained.

EXPERIMENTAL

Vinylphenyldi(trimethylsiloxy)silane (I). To a solution of 18 g of vinylphenyldiethoxysilane and 178 g of trimethylchlorosilane in 196 ml of toluene was added slowly 16 g of water while the

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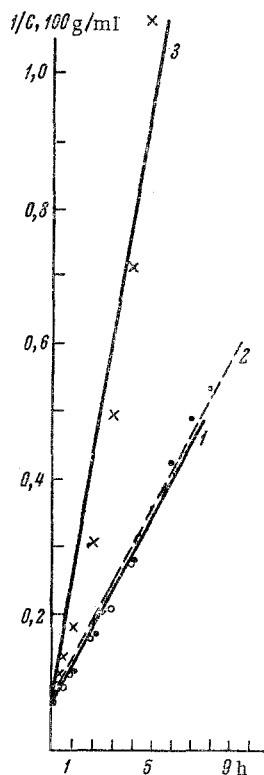


Fig. 1

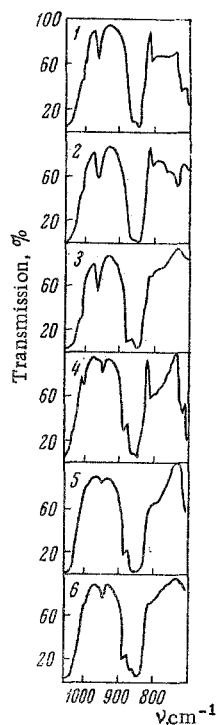


Fig. 2

Fig. 1. Inverse concentration $1/C$ of perbenzoic acid versus epoxidation time: 1) $(CH_2=CH) \cdot C_6H_5Si[OSi(CH_3)_3]_2$; $k = 2.1 \cdot 10^{-4}$ liter \cdot M $^{-1} \cdot$ sec $^{-1}$; 2) $CH_2=CH-Si[OSi(CH_3)_3]_2$; $k = 2.1 \cdot 10^{-4}$ liter \times M $^{-1} \cdot$ sec $^{-1}$; 3) $(CH_2=CH)CH_3Si[OSi(CH_3)_3]_2$; $k = 7.2 \cdot 10^{-3}$ liter \cdot M $^{-1} \cdot$ sec $^{-1}$.

Fig. 2. Infrared spectra of the compounds obtained: 1) $(CH_2=CH)C_6H_5Si[OSi(CH_3)_3]_2$; 2) $CH_2=CH-Si[OSi(CH_3)_3]_2$; 3) $(CH_2=CH)CH_3Si[OSi(CH_3)_3]_2$; 4) $(CH_2-CH)C_6H_5Si[OSi(CH_3)_3]_2$; 5) $CH_2-CH-Si[OSi(CH_3)_3]_2$; 6) $(CH_2-CH)CH_3Si[OSi(CH_3)_3]_2$.

mixture was stirred. The contents of the flask were heated and stirred for 1 h at 40°, another 140 ml of water added and heated for 2 h at 60° and 3 h at 80°. The reaction product was washed with water to remove HCl. Fractionation gave 15 g of (I) with bp 77-78° (1 mm). Under the same conditions we obtained vinyltri(trimethylsiloxane) silane (II) and methylvinyl-di(trimethylsiloxo) silane (III). The properties of these compounds are given in Table 1.

Epoxyethylphenyldi(trimethylsiloxo)silane (IV). To 13.35 g of (I) was added rapidly a solution of 5.94 g of perbenzoic acid in 13.35 g of toluene while the mixture was stirred. The reaction mixture was heated at 40° and stirred for 8 h until 88% of the perbenzoic acid had decomposed. The reaction product was washed free from acid, first with 5% aqueous NaOH and then with water. Fractionation gave 8 g of (IV) with bp 94° (1 mm). The reaction was monitored by iodimetric titration of the active oxygen. The results of the reaction velocity determination are given in Fig. 1.

Under similar conditions we obtained epoxyethyltri(trimethylsiloxo)silane (V) and methylepoxyethyl-di(trimethylsiloxo)silane (VI). The properties of these compounds are given in Table 1.

TABLE 1

No.	Formula	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
					found	calc.	C	H	Si	C	H	Si
I	$\text{CH}_2=\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ C_6H_5	77-78 (1)	1,4530	0,9224	93,84	91,91	54,16	8,48	27,08	54,19	8,38	27,14
II	$\text{CH}_2=\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$	58-61 (4)	1,3971	0,8657	89,68	89,65	—	—	—	—	—	—
III	$\text{CH}_2=\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ CH_3	164-166 (760)	1,3980	0,8430	71,0	71,72	43,44	9,81	33,89	43,50	9,60	33,94
IV	$\text{CH}_2-\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ C_6H_5	94 (1)	1,4610	0,9771	91,55	90,82	51,50	8,11	25,87	51,53	7,97	25,81
V	$\text{CH}_2-\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ O	87 (2)	1,4060	0,9190	90,26	90,47	39,03	8,90	33,13	39,00	8,86	33,14
VI	$\text{CH}_2-\text{CH}-\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ O	62-64 (4)	1,4080	0,9024	72,15	71,95	40,80	9,15	31,66	40,90	9,09	31,87

CONCLUSIONS

1. We have synthesized and characterized epoxyethylphenyldi(trimethylsiloxy)silane, epoxyethyltri-(trimethylsiloxy)silane, and methylepoxyethyltri(trimethylsiloxy)silane.

2. Epoxidation of vinylorganosiloxanes by perbenzoic acid is a second-order reaction; the reaction velocity depends on the polarities and volumes of the substituent radicals at the silicon atom.

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