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Abstract

Full Text

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On the Possibility of Synthesizing Organosilicon Compounds Containing the Three-Membered Heterocycle Ethylenimine in the Hydrocarbon Radical

The addition reaction of ethylenimine at multiple carbon–carbon bonds is of interest as one of the methods for synthesizing ethylenimine derivatives. A special feature of the reaction is that addition of ethylenimine is possible only for compounds with conjugated multiple bonds. The presence of electron-acceptor functional groups at the multiple bond promotes the course of the addition reaction under milder conditions. Thus, for example, addition of ethylenimine to divinyl requires the presence of a catalyst, whereas acrylonitrile adds ethylenimine in the absence of a catalyst with strong heating of the reaction mixture ([1,2]).

Polarization of the multiple bond in alkenylsilanes and the particular behavior of these compounds in the addition reaction of thio acids, mercaptans, alcohols, as well as indications ([3–6]) of the possibility of adding a secondary amine to vinylsilanes, served as the basis for setting up a study aimed at investigating the reactivity of alkenylsilanes and amines of various structures in the addition reaction. In this connection, the following were taken for investigation: trimethylvinylsilane, triethylvinylsilane, dimethylphenylvinylsilane, methyldiphenylvinylsilane, triethoxyvinylsilane, trimethylallylsilane, trimethyl-γ-butenylsilane, neohexane, π-trimethylsilylstyrene, π-chlorostyrene, and the addition reaction to them of diethylamine and ethylenimine was studied.

Table 1

Effect of catalysts and temperature on the yield of triethyl-β-(N-ethylenimino)ethylsilane

Catalyst, name	Catalyst, wt. %	Temp., °C	Duration, h	Yield, %
Na	1	50	5	28
Na	1	100	1	70
Na	1	100	7	90
$NaNH_2$	1	50	5	55

Catalyst, name	Catalyst, wt. %	Temp., °C	Duration, h	Yield, %
Na_2NH_2	2.2	50	2	90
C_2H_5ONa	4.2	100	6	0

At temperatures up to 100° we did not succeed in adding diethylamine to alkenylsilanes in the presence of metallic sodium and sodium amide. For ethylenimine, this reaction proceeds comparatively readily already at temperatures of 50°, both in the presence of sodium amide and metallic sodium. The increased reactivity of ethylenimine can be explained by the strain of the three-membered heterocycle, which usually also affects a number of other properties of ethylenimine.

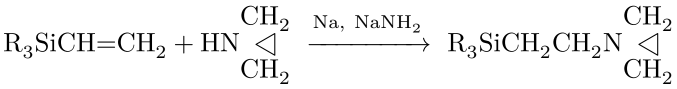
Using triethylvinylsilane as an example, it was shown that catalysts, their nature and amount, the reaction temperature, and the time substantially influence the yield of the addition product; this is clearly seen from the results presented in Table 1.

It was also established that substituents attached to the silicon atom have a very strong effect on the reactivity of vinylsilanes in the addition reaction. Thus, for example, triethylvinylsilane at a temperature of 100° for 7 h gives a 90% yield of triethyl-β-(N-ethylenimino)ethylsilane, whereas under the same conditions triethoxy-β-(N-ethylenimino)ethylsilane is obtained in 10 h with a yield of 69%. Methyldiphenylvinylsilane gives an addition product in the presence of metallic sodium at room temperature.

On the basis of IR spectra recorded for the compounds obtained, in which the absorption band corresponding to the C–CH_3 group (1380 cm^{-1}) is absent,

We believe that the addition of ethylenimine proceeds contrary to Markovnikov' s rule, and that the compounds obtained contain the ring (absorption bands at 3054, 1258, and 1135 cm^{-1})* in the β-position to the silicon atom. As an example, the spectrum (see Fig. 1) of dimethylphenyl-β-(N-ethylenimino)ethylsilane is presented.

The spectra were recorded on a UR-10 spectrophotometer in a layer of 0.005 mm.



$$R_3SiCH{=}CH_2 + HN\overset{CH_2}{\underset{CH_2}{\triangleleft}} \xrightarrow{Na,\ NaNH_2} R_3SiCH_2CH_2N\overset{CH_2}{\underset{CH_2}{\triangleleft}}$$

The products obtained are colorless, readily mobile liquids with a characteristic odor; their physical constants and analytical results are given in Table 2.

Fig. 1

Fig. 1

Figure 1: Fig. 1

For comparison of the reactivity of alkenylsilanes in the addition reaction, experiments were carried out with compounds of the general formula $R_3Si(CH_2)_nCH=CH_2$, where $n = 0, 1, 2$, as well as with π-trimethylsilylstyrene and the hydrocarbon analog of trimethylvinylsilane—neohexene. For vinylsilanes, as already described above, the reaction proceeds comparatively readily, and the substituents at the silicon atom influence the reactivity to a considerable degree. In the case of allylsilanes it was not possible to carry out the reaction, since under the accepted conditions decomposition of the starting allylsilane occurs. Trimethyl-γ-butenylsilane, in the presence of $NaNH_2$, does not enter into the addition reaction even at a temperature of 100°. Neohexene behaves analogously to γ-butenylsilane. π-Trimethylsilylstyrene adds ethylenimine in good yield at 50°.

The results obtained may serve as an illustration confirming the special features of intramolecular interaction caused by the presence of silicon and a multiple bond.

Using trimethylvinylsilane $(CH_3)_3SiCH=CH_2$ and its hydrocarbon analog—neohexene $(CH_3)_3C-CH=CH_2$—as an example, one can see how strikingly they differ in their reactivity in the addition reaction. Polarization of the multiple bond in vinylsilanes due to electron-acceptor silyl groups facilitates the addition reaction of ethylenimine. The considerable weakening of the polarization of the multiple bond of γ-butenylsilane and the presence of a weak electron-donor substituent in neohexene exclude the possibility of this reaction proceeding under analogous conditions. These facts, as well as the opposite change in reactivity in the case of addition of electrophilic reagents

* The IR spectra were recorded by L. D. Oppenheim in the laboratory of physical methods of investigation of the Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, of Prof. M. M. Kusakov.

Table 2

Physical constants and analytical data of the compounds obtained

Compound, formula	B.p., °C/mm	n_D^{20}	d_4^{20}	Mol. wt., found	Mol. wt., calculated	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Found, % Si	Found, % N	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % N
$(CH_3)_3$-$SiCH_2CH_2N<\begin{array}{l}CH_2\\CH_2\end{array}$	40–41/18	1.4300	0.8123	143.4	143	45.41	45.85	58.72	11.93	19.53	10.03	58.74	11.88	19.58	9.8

Compound, formula	B.p., °C/mm	n_D^{20}	d_4^{20}	Mol. wt., found	Mol. wt., calculated	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Found, % Si	Found, % N	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % N
$(C_2H_5)_3SiCH_2CH_2N<$ CH_2 CH_2	59–60/2	1.4540	0.8453	185.5	185	59.05	59.38	64.94	12.43	15.23	7.40	64.86	12.43	15.13	7.58
$(CH_3)_2$ C_6H_5 $SiCH_2CH_2N<$ CH_2 CH_2	93/2	1.5127	0.9414	203	205	65.33	65.67	70.25	9.32	13.64	6.79	70.24	9.27	13.66	6.83
CH_3 $(C_6H_5)_2$ $SiCH_2CH_2N<$ CH_2 CH_2	170–172/4	1.5665	1.0022	264	267	85.25	85.49	76.55	7.91	10.36	5.18	76.40	7.86	10.44	5.3
$(C_2H_5O)_3SiCH_2CH_2N<$ CH_2 CH_2	80–81/3.5	1.4218	0.9513	237	233	61.90	62.02	51.55	9.87	12.08	5.82	51.50	9.87	12.03	6.00
$(CH_3)_3Si-C_6H_4-CH_2CH_2N<$ CH_2 CH_2	127–128/5.5	1.5085	0.9320	216	217	69.97	70.30	71.39	9.15	12.55	6.61	71.23	9.59	12.78	6.40
$Cl-C_6H_4-CH_2CH_2N<$ CH_2 CH_2	89–90/1.5	1.5335	0.9141	179	181	61.67	61.56	66.19	6.33	–	8.44	66.29	6.63	–	7.73

to alkenylsilanes give grounds for assuming that the addition of ethylenimine to alkenylsilanes may be classified as a nucleophilic-addition reaction, for which the above-mentioned features are characteristic. This conclusion requires a more detailed investigation of the reaction, and the authors are carrying out work in this direction.

Experimental Part

Experiments on the addition of ethylenimine were carried out in flasks at atmospheric pressure at 50° and in sealed ampoules at a temperature of 100°. In all cases the amount of catalyst varied within the range 1–4.2 wt. % based on the products taken into the reaction. Metallic sodium, sodium amide (Na 70% and $NaNH_2$ 30%), and sodium ethoxide were used as catalysts.

Triethyl-β-(N-ethylenimino)ethylsilane. Into a flask fitted with a reflux condenser, stirrer, and thermometer were placed 7 g of triethylvinylsilane, 4.3 g of ethylenimine, and 0.11 g of metallic sodium. The mixture was kept at 50° for 5 h, then separated from the catalyst and fractionated. A 2.5 g (28%) fraction with b.p. 59-60°/2 mm was obtained. $n_D^{20} = 1.4547$; $d_4^{20} = 0.8458$; MR_D found 59.05; calculated 59.38. Molecular weight found 185.5, calculated 185.0.

Triethoxy-β-(N-ethylenimino)ethylsilane. Into an ampoule were placed 9.5 g of vinyltriethoxysilane, 4.3 g of ethylenimine, and 0.13 g of metallic sodium. The ampoule was sealed and kept at 100° for 10 h. An 8 g (69%) fraction with b.p. 80-81°/3.5 mm was obtained. $n_D^{20} = 1.4218$; $d_4^{20} = 0.9531$; MR_D found 62.02, calculated 61.90. Molecular weight found 237, calculated 233.

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Note: Figure translations are in progress. See original paper for figures.