REACTION OF TRIETHYL-N-ETHYLENIMINOSILANE WITH ALDEHYDES

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The action of alphatic, aromatic and heterocyclic aldehydes on triethyl-N-ethyleniminosilane in the presence of water gives α-alkyl (aryl)-α-N-ethyleniminomethoxysilanes of the type $R_3SiOCHR'N\langle CH_2-CH_2\rangle$ (R = Et; R' = alkyl, aryl, furyl). Similarly dimethyldi-N-ethylenimisoline and acetaldehyde give $(CH_3)_2Si\left[OCHCH_3N\langle CH_2-CH_2\rangle\right]_2$. A reaction mechanism is suggested.

Because N-ethyleniminosilanes [1,2] have strained rings and contain a quite reactive Si-N bond, they offer many possibilities of synthesizing compounds whose preparation was previously attended with considerable difficulty. Examples of this are the synthesis of ethers of hydroxyethyleniminomethanes, and a whole series of cases of anomalous reaction with aromatic and heterocyclic aldehydes [3,4].

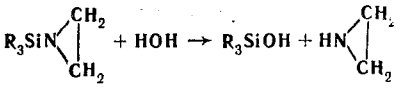
We have investigated the reaction of N-ethyleniminosilanes (I) with aliphatic, aromatic, and heterocyclic aldehydes, in the presence of catalytic quantities of water. The reaction always leads to the formation of α-N-ethyleniminoalkoxysilanes $R_{4-n}Si\left(O-CHR'-N\langle CH_2-CH_2\rangle\right)_n$ where n = 1, 2; R = alkyl; R' = = alkyl, aryl, furyl.

At present it is established [3–5] that the products of reaction of ethylenimine with aliphatic aldehydes are not oxazolidines, as was previously thought [6], but addition products containing the aziridine ring, α-N-ethyleniminoalkanols.

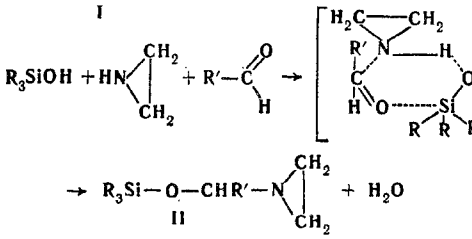
However it has been found [7] (in contradiction to [4]) that benzaldehyde and furfural give reaction products derived from 2 molecules of ethylenimine and 1 molecule of aldehyde, i.e., (N-benzylidene-β-aminoethyl)ethylenimine and (N-furfuylidene-α-aminoethyl)ethylenimine. Under no conditions was it possible to obtain the reaction product formed from equimolecular quantities of aldehyde and ethylenimine. The authors of those paper proposed a reaction mechanism.

The reaction which we investigated, of triethyl-N-ethyleneiminosilane with benzaldehyde, gave, for any ratio of the reactants, triethyl-α-N-ethyleniminobenzyloxysilane (IIa). Furfural reacts similarly with ethylenimine, to give IIb.

Formation of type II compounds can be ascribed to nucleophilic addition not being always accompanied by intramolecular proton migration. Another addition mechanism is possible, involving formation of a cyclic transition state, with change in structure due to cyclic transfer of electrons. In the presence of silanol formation of such a transition complex is quite probable. It would change to II according to equation 2, and not into products similar in structure to that reported isolated [7]:

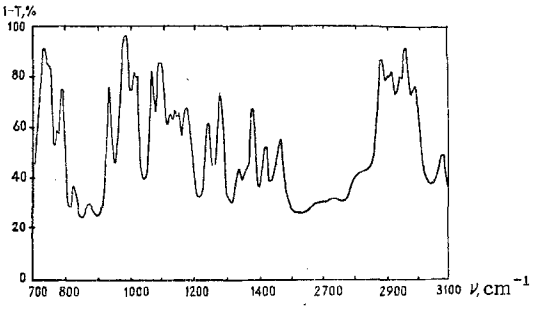


(1)



(2)

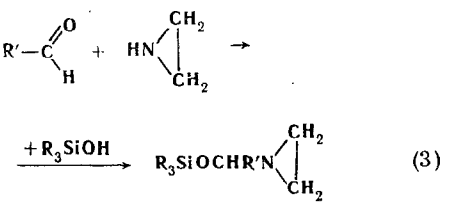
R = C_2H_5; R' = a C_6H_5, b furfuryl c Me, d n-C_3H_7



IR spectrum of IIc.

Water acts as a catalyst, and starts the reaction, forming silanol and ethylenimine according to equation 1. Perfectly anhydrous I does not react with aldehyde. In all the experiments which we carried out, we established the presence of water and the intermediate formation of ethylenimine.

With aliphatic aldehydes there was another possible reaction mechanism, formation of ethyleniminocarbinol by addition of ethylenimine to aldehyde, followed by condensation of the product with silanol:



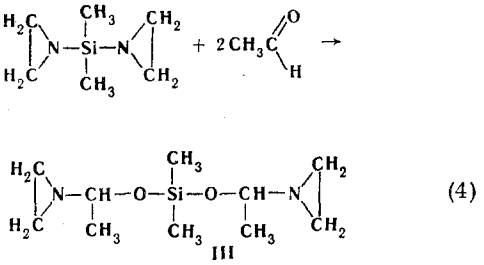
(3)

However an attempt to condense ethyleniminocarbinol with silanol was unsuccessful, indicating that with aliphatic aldehydes 1 and 2 are the equations for the reaction.

Reaction Products from N-Ethyliminosilanes and Aldehydes

Compound		Bp °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Found, %				Calculated, %				Yield, %
					Found	Calculated		C	H	Si	N	C	H	Si	N	
$(C_2H_5)_3Si-O-CH(CH_3)-N(CH_2-CH_2)$	(IIc)	65—67 (2.5)	1.4410	0.8833	60.00	60.14	$C_{10}H_{23}NOSi$	60.20	11.42	14.66	6.20	59.97	11.40	14.01	6.95	80
$(C_2H_5)_3Si-O-CH(C_3H_7)-N(CH_2-CH_2)$	(IId)	102 (6)	1.4450	0.8856	68.98	69.40	$C_{12}H_{27}NOSi$	62.83	11.98	12.13	6.11	63.00	11.80	12.21	6.13	43
$(C_2H_5)_3Si-O-CH(C_6H_5)-N(CH_2-CH_2)$	(IIa)	140—141 (5)	1.4985	0.9691	79.72	79.69	$C_{15}H_{25}NOSi$	68.57	9.67	10.62	4.93	68.50	9.50	10.62	5.32	40
$(C_2H_5)_3Si-O-CH(C_4H_3O)-N(CH_2-CH_2)$	(IIb)	120—122 (5)	1.4742	0.9865	72.20	72.36	$C_{13}H_{23}NO_2Si$	61.61	9.12	11.13	5.98	61.00	9.20	11.00	5.50	50
$CH_2(CH_2)N-CH(CH_3)-O-Si(CH_3)_2-O-CH(CH_3)-N(CH_2)CH_2$	(III)	96—98 (9)	1.4405	0.9660	62.97	62.94	$C_{10}H_{22}N_2O_2Si$	52.25	9.50	11.69	11.12	52.20	9.57	12.18	12.20	68

When dimethyldi-N-ethyleniminosilane reacted with acetaldehyde (mole ratio 1:2), the sole product was dimethylbis (α-N-ethylenimino)ethoxysilane (III):



(4)

III

The table gives the physical constants, analytical data, and yields of the II and III obtained.

The decreased reactivity of the carbonyl group when one passes from aliphatic to aromatic aldehydes is reflected in the yields of products obtained by reacting them with I. Thus in the case of acetaldehyde, the yield of IIc was 80%, while benzaldehyde gave about a 40% yield of IIa. The IR spectra of II have bands at 1270 and 3070 cm^{-1}, characteristic of the ethylenimine ring, and also a band in the 1170 cm^{-1} region, corresponding to the Si-O-C group. The IR spectrum of IIc is reproduced by way of example.

EXPERIMENTAL

The reaction products from I and aldehydes were obtained in the usual way. A 3-necked flask was fitted with a stirrer, condenser, and dropping funnel, and 0.05 mole triethyl-N-ethyleniminosilane plus a few drops of water made alkaline placed in it, then 0.05 mole of the appropriate aldehyde was dropped in with stirring and cooling. The mixture was refluxed gently (4-8 hr), then fractionally distilled. The reactions with benzaldehyde and furfural were run without cooling.

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