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Organosilicon Derivatives of Aminoalcohols

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The literature data and the present authors' investigations in the field of organosilicon derivatives of aminoalcohols are reviewed. The methods for the preparation, the chemical and biological properties, and the practical applications of organosilicon derivatives of aminoalcohols, in which the silicon atom is linked directly to the aminoalcohol heteroatom or via a carbon chain, are discussed.
The bibliography includes 204 references.

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I. INTRODUCTION

The increase of interest in the study of the properties and reactions of aminoalcohols and their derivatives is due to at least two causes: the specific biological properties and high reactivity associated with the presence of more than one functional group and the presence of competing reactive centres in their molecules. It is sufficient to mention that many aminoalcohols and their derivatives are biogenic amines playing an extremely important role in the vital processes of organisms (choline and acetylcholine). On the other hand, numerous widely employed medicinal preparations have been prepared on the basis of aminoalcohols (ephedrine, Pentaphen, Dimedrol, Novocaine, Dicaine, Spasmolytin, adrenaline, Ustimon, and others). Moreover, aminoalcohols are effective complex-forming agents and are used to remove from solutions various metal ions. Aminoalcohol complexes can be employed as models of oxidases and in all probability (after a detailed study of their biological properties) will find application in medicine.

The studies on the physical, chemical, and biological properties of organosilicon derivatives of aminoalcohols have provided valuable information about the influence of the amino-group on the strength and reactivity of the Si–O bond in aminoalkoxysilanes, about the degree of intramolecular interaction between the nitrogen atom of the aminoalkoxy-group and the silicon atom leading to the formation of a strong donor-acceptor Si ← N bond in cyclic organosilicon derivatives of triethanolamine (silatranes), and about the relation between the structure and biological activity of organosilicon derivatives of aminoalcohols, among which extremely toxic compounds have been discovered (1-arylsilatranes). The application or organosilicon derivatives of aminoalcohols as water repelling agents, hardening agents for epoxy-resins, dispersing agents, and intermediates for the synthesis of special polymers are no less important.

The results of studies in this interesting and extremely promising field of the chemistry of organosilicon compounds published up to May 1969 are reviewed in the present article.

II. ORGANOSILICON DERIVATIVES OF AMINOALCOHOLS IN WHICH THE SILICON ATOM IS LINKED DIRECTLY TO THE HETEROATOM OF THE AMINOALCOHOL

A. METHODS OF PREPARATION OF AMINOALKOXYSILANES

1. Reactions of Chlorosilanes with Aminoalcohols

When chlorosilanes and silicon tetrachloride react with ethanolamine and its *N*-substituted derivatives in the presence of hydrogen chloride acceptors, the first step is the silylation of the hydroxy-group of the aminoalcohol with formation of aminoalkoxysilanes [1–14]:

$$\equiv SiCl + HOCH_2CH_2NR_2 \xrightarrow{+B} \equiv SiOCH_2CH_2NR_2 + B \cdot HCl .$$

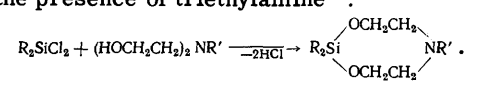
The reaction is carried out in chloroform [5,15], ethyl ether [5,8,9], petroleum ether [11], and benzene [13,14]. The hydrogen chloride acceptors employed are ammonia [8,15], triethylamine [5,9,10], pyridine [14], or an excess of the aminoalcohol itself [5,11,13]. Organosilicon derivatives of ethanolamine [5,8,13] and its *N*-substituted derivatives [1,9–11], 3-(α-pyridyl)propanol [10], and aminobutanols [14] have been obtained in this way.

When the reactant ratio is equimolar, the hydrogen chloride formed is bound by the aminoalkoxysilane itself, which is converted into the hydrochloride [5,7,16–20]:

$$\equiv SiCl + HOCH_2CH_2NR_2 \rightarrow \equiv SiOCH_2CH_2NR_2 \cdot HCl .$$

The reaction of trialkylchlorosilanes with diethanolamine takes place similarly to the reaction with monoethanolamine: in the first step both hydroxy-groups are silylated and only then also the amino-group, in the presence of an excess of the trialkylchlorosilane [5,7]. It has been noted in patents [16,19,20] that the hydrochlorides of 2-[(2′-hydroxyethyl)amino]ethoxysilanes are formed in the reactions of alkyltrichlorosilanes with diethanolamine, while the products of the reaction of silicon tetrachloride

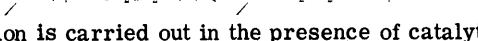
with di- and tri-ethanolamines in the presence of ammonia are polymers[15]. A cyclic compound was obtained by the reaction of dichlorodimethylsilane with *N*-ethyldiethanolamine in the presence of triethylamine[21]:



It has been pointed out[22] that a deposit is formed in the exothermic reaction of silicon tetrachloride with diethanolamine. This was attributed to complex formation via the free electron pair of the nitrogen atom and the vacant 3*d* orbitals of the silicon atom. It is surprising that the author completely fails to take into account the possibility of a substitution reaction with participation of hydroxy-groups.

2. Alcoholysis of Alkoxysilanes and Acyloxysilanes by Aminoalcohols

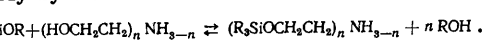
When alkoxysilanes are heated with ethanolamine and its *N*-derivatives with simultaneous distillation of the alcohol evolved, the corresponding aminoalkoxysilanes are formed:



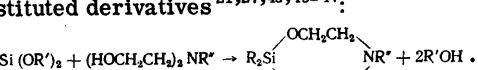
The reaction is carried out in the presence of catalytic amounts of potassium hydroxide[9], sodium methoxide[13,29], sodium aminoalkoxide[1,3,6,24], tetra-alkoxytitanium[25,26], or in the absence of catalysts[1,6,13,27-37].

For the synthesis of aminoalkoxysilanes, ethoxysilanes are most frequently employed[1-3,6,13,23-25,27-42] but methoxy-[1,9,28], n-propoxy-[33,40], isopropoxy-[33], and butoxy-silanes[34,43] can also be used. Among alkoxysilanes, alkoxysilanes with three further organic substituents[3], dialkoxysilanes with two further organic substituents[1,9,23-27,31,32,37], trialkoxysilanes with one additional organic substituent[1,27,28,31,32], tetra-alkoxysilanes[13,29-31,33-36], and polyalkoxysilanes[34,38-42,44] have also been used in the reaction with ethanolamine and its *N*-substituted derivatives. In all cases all the alkoxy-groups at the silicon atom are replaced by aminoalkoxy-groups with formation of the corresponding di-, tri-, and tetra-(aminoalkoxy)-silanes. The attempts to isolate the mixed ethers from the products of the transetherification of tetraethoxysilane or tetraisopropoxysilane with ethanolamine, with the molar ratio of the reactants ranging from 1 : 1 to 1 : 3, were unsuccessful[33]. Nevertheless the reaction of tetraethoxy-silane with 2-(diethylamino)ethanol (molar ratio 5 : 2) gave diethoxydi-[2-(diethylamino)ethoxy]silane[13]. Mixed aminoethoxyfurfuryloxysilanes containing between one and three furfuryloxy-groups have been obtained by the trans-etherification of tetraethoxysilane with a mixture of ethanol-amine and furfuryl alcohol[29].

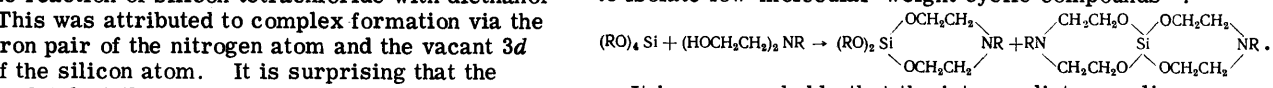
Two and three triethylsilyl groups can be introduced into the diethanolamine and triethanolamine molecules respectively by transetherification[3,6,7]:



Readily polymerised cyclic products have been obtained by the reaction of dialkoxysilanes containing two additional organic substituents with diethanolamine and its *N*-substituted derivatives[21,27,43,45-47]:

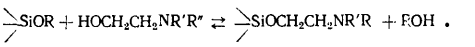


Usually ethoxysilanes are introduced into the reaction and the latter is carried out in the absence of a catalyst. However, best yields (80–86%) are achieved when dialkyl-dibutoxysilanes are employed in the presence of a catalytic amount of the corresponding sodium amino-alkoxide[43]. Polymers are obtained by the reaction of tri-alkoxysilanes containing an additional organic substituent with diethanolamine[48]. The reaction of tetra-alkoxy silanes with diethanolamine also leads to the formation of polymers[34,49]. However, in some cases it proved possible to isolate low-molecular-weight cyclic compounds[47]:

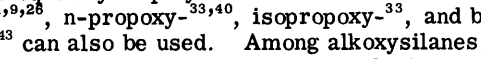


It is very probable that the intermediate acyclic compounds cyclise on distillation[13,47]:

The reaction of trialkoxysilanes containing a further organic substituent[47,50-53] and tetra-alkoxysilanes[47,50,51,53-56] with triethanolamine (1 : 1 molar ratio) does not lead to the formation of polymers but to monomeric chelate cyclic compounds—silatranes†, stabilised as a result of the presence in the molecule of the transannular coordinate bond Si ← N:



When the reaction of tetraethoxysilane with triethanol-amine is carried out in the presence of phenols[50,61] or carboxylic acids[50,62], the products are the corresponding 1-aryloxy- and 1-acyloxy-silatranes:



In some cases the formation of acyclic[37], spirocyclic[51], and also polymeric transetherification products[51] was observed in the reaction of tetra-alkoxysilanes with tri-ethanolamine (for other reactant ratios).

The reaction of acyloxysilanes with aminoalcohols has not been investigated at all. In only one patent[63] is there a mention of the possibility of preparing 2-aminoethoxy-siloxanes from acetoxysiloxanes and ethanolamine in the presence of tetraisopropoxytitanium. Another patent[64] describes the synthesis of a polymer from diheptadecyloxy-dimethylsilane (partially acylated by stearic acid) and tri-ethanolamine.

3. Reactions of Siloxanes and Siloxanols with Aminoalcohols

When a solution or a hydrogel of silicic acid is heated with ethanolamine[65-68] or 2-(diethylamino)ethanol[67], the hydroxy-groups are partially substituted by aminoalkoxy-groups, which leads to the formation of modified silica gels. The same type of exchange of hydroxy-groups for aminoalkoxy-groups can occur in the reaction of amino-alcohols with polysiloxanols having a number of other organic substituents[69]. The siloxane bond is probably not involved in these reactions. The reaction of poly-sesquisiloxanes $(RSiO_{1.5})_x$ and polysiloxanols $[RSiO_{1.5-y}(OH)_{2y}]_x$, both containing a number of other organic substituents, with aminoalcohols in the presence of potassium hydroxide on heating in an inert solvent with azeotropic distillation of water is of quite a different type. It involves the cleavage of the Si–O–Si bonds with forma-tion of tri-[2-(dialkylamino)ethoxy]silanes having one

†For details of the synthesis and properties of sila-tranes, see the appropriate reviews[50,57-60].

further organic substituent in the case of 2-dialkylaminoethanols [1] and silatranes with one organic substituent in the 1-position in the case of triethanolamine [50,57-60,70-72]:

$$2/x\,(RSiO_{1.5})_x + 6\,HOCH_2CH_2NR'_2 \rightarrow 2\,RSi(OCH_2CH_2NR'_2)_3 + 3\,H_2O\ ,$$

$$1/x\,[RSiO_{1.5-y}(OH)_{2y}]_x + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + (1.5+y)\,H_2O\ .$$

The rate of reaction increases with the degree of condensation of the initial siloxanes and also on passing from alkyl- to aryl- and vinylpolysiloxanols. Polyhydrosiloxanes substituted by a number of organic groups $(RSiHO)_X$ can also be employed in this reaction. Then dehydrocondensation with evolution of hydrogen takes place in the absence of the catalyst, but the addition of alkali is necessary for the cleavage of the siloxane bond [1,71].

4. Reactions of Aminosilanes with Aminoalcohols

When diaminodi-t-butoxysilane is heated with ethanolamine at 150–200°C, ammonia is evolved and di-(2-aminoethoxy)di-t-butoxysilane is formed [73]:

$$(RO)_2Si(NH_2)_2 + 2\,HOCH_2CH_2NH_2 \xrightarrow{-2NH_3} (RO)_2Si(OCH_2CH_2NH_2)_2\ .$$

The reaction of diaminodi-t-butoxysilane with *N*-alkyl- and *NN*-dialkylethanolamines and propanolamine derivatives takes place similarly. In the case of 2-diethylaminoethanol the product formed by the substitution of the 1-amino-group by a 2-diethylaminoethoxy-group was also isolated. t-Butoxytri(2-ethylaminoethoxy)silane was detected in addition to di-t-butoxydi-(2-ethylaminoethoxy)-silane in the products of the reaction of 2-ethylaminoethanol [73].

The possibility of employing triethylaminosilane for the silylation of ephedrine is mentioned (without indicating the experimental conditions) in a brief communication [74].

Diethylaminotrimethylsilane readily silylates the hydroxy-groups in mono-, di-, and tri-ethanolamines [4,6,7,75]:

$$n\,R_3SiNR'_2 + (HOCH_2CH_2)_nNH_{3-n} \xrightarrow{-n\,R'_2NH} (R_3SiOCH_2CH_2)_nNH_{3-n}\ ,$$

where $n = 1-3$.

With di- and tri-ethanolamines, it is possible to achieve the successive substitution of all the hydroxy-groups by trimethylsiloxy-groups. When diethylaminosilanes $R_{4-n}Si(NR'_2)_n$ containing between one and three diethylamino-groups are employed in this reaction, it is possible to obtain aminoethoxysilanes containing between one and three 2-aminoethoxy- or 2-dialkylaminoethoxy-groups [5,75,76]. When $n = 2$, the reaction with diethanolamine leads to monomeric cyclic compounds (as in the reaction with dialkoxysilanes), while the reaction with triethanolamine leads to polymers. On the other hand, when $n = 3$, diethanolamine gives a polymer, and a cyclic compound (a silatrane with an organic substituent in the 1-position) is formed in the reaction with triethanolamine [75]:

$$RSi(NR'_2)_3 + (HOCH_2CH_2)_3N \xrightarrow{-3R'_2NH} RSi(OCH_2CH_2)_3N\ .$$

5. Reactions of Silazanes with Aminoalcohols

Hexamethyldisilazane silylates the hydroxy-groups of ethanolamine [6,8,77,78] and its *N*-substituted derivatives [74,79,80], diethanolamine [77,81], triethanolamine [77], and heterocyclic aminoalcohols [79,82]. The silylation involves both trimethylsilyl groups:

$$n\,(R_3Si)_2NH + 2\,(HOCH_2CH_2)_nNR'_{3-n} \xrightarrow{-n\,NH_3} 2\,(R_3SiOCH_2CH_2)_nNR'_{3-n}\ .$$

When 1,3-dialkoxy-1,1,3,3-tetramethyldisilazanes are heated with ethanolamine, the silazane group is cleaved and ammonia is evolved. The subsequent heating of the reaction mixture with simultaneous distillation of the corresponding alkanol leads to the formation of di-(2-aminoethoxy)dimethylsilane [77]:

$$(R_2R'OSi)_2NH + 4\,HOCH_2CH_2NH_2 \xrightarrow{-NH_3} 2\,R_2Si(OCH_2CH_2NH_2)_2 + 2R'OH\ .$$

The reaction of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane with ethanolamine, 2-dialkylaminoethanols, derivatives of isomeric propanolamines, and 4-amino-1-butanol leads to the formation of the corresponding di(aminoalkoxy)dimethylsilanes [6,77,79,83]:

$$(R_2SiNH)_n + 2n\,HOCHR'(CH_2)_mNR''_2 \xrightarrow{-nNH_3} n\,R_2Si[OCHR'(CH_2)_mNR''_2]_2,$$

where R = CH_3, R′ = H or CH_3, R″ = H, CH_3, C_2H_5, C_4H_9, or $(CH_2)_5$, $n = 3-4$, and $m = 1-3$.

6. Dehydrocondensation of Hydrosilanes and Hydrosiloxanes with Aminoalcohols

Trialkylsilanes undergo dehydrocondensation with ethanolamine, its *N*-substituted derivatives, and 2-piperidinoethanol in the presence of sodium aminoalkoxides with formation of the corresponding aminoalkoxysilanes [1,3,6,74,84]:

$$\equiv SiH + HOCH_2CH_2NR_2 \rightarrow \equiv SiOCH_2CH_2NR_2 + H_2\ .$$

Polyalkylhydrosiloxanes $(RSiHO)_n$ react vigorously with ethanolamine in the absence of catalysts [1,85-89]. When cyclotetrasiloxanes ($n = 4$) and cyclopentasiloxanes ($n = 5$) are employed, the reaction products are gels to which the structure $[CH_3Si(OCH_2CH_2NH_2)O]_n$ is attributed and which are insoluble in benzene, toluene, xylene, and dioxan [88]. With higher oligomers ($n \simeq 13-16$) in which R = CH_3, the products of the reaction with ethanolamine are also gels, which rapidly become insoluble on storage. When R = C_2H_5 (GKZh-94), the exothermic reaction with ethanolamine involves a stage in which a rubberlike gel is formed (at 60–65°C), but on attainment of 140°C the reaction mass becomes liquid again and completely transparent. The liquid product is soluble in aromatic hydrocarbons, ether, and dioxan [87].

7. Other Methods

A number of other methods which have as yet not acquired general importance have been employed for the synthesis of individual examples of aminoalkoxysilanes with different structures. The reaction of substituted oxirans with trimethyl(diorganyl)silanes at 80°C takes place with the opening of the oxygen-containing ring by the mechanism [90]

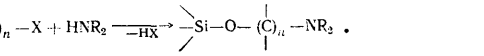
$$(CH_3)_3SiNR_2 + R'CHCH_2O \rightarrow (CH_3)_3SiOCHR'CH_2NR_2\ .$$

This apparently very simple and promising reaction cannot be used as a general method for the synthesis of aminoalkoxysilanes, since it can only be achieved when powerful electron-accepting substituents are present in the group R′ of the substituted oxiran. For example, whereas in the reaction of trimethylpiperidinosilane with trichloromethyloxiran the yield of (1-trichloromethyl-2-piperidinoethoxy)-trimethylsilane is 89% after only 1.3 h, in the reaction with chloromethyloxiran the yield does not exceed 45% even

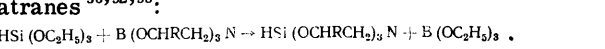
after heating for 22 h. Methyloxiran does not react at all with trimethylpiperidinosilane in a sealed tube at 80°C.[90] The rate of this reaction decreases also on passing from piperidinosilanes to diethyl- and dimethyl-aminosilanes, which is consistent with the sequence of decreasing basicity of the above amines[90].

The reaction of oxiranylmethoxysilanes with amines can also lead to the formation of aminoalkoxysilanes. In the only known example of such a reaction described in a patent[91], diethylenetriamine was employed as the amine, which led to the formation of infusible, insoluble resins.

Aminoalkoxysilanes can also be synthesised by substituting halogen atoms in halogenoalkoxysilanes by amino-groups[18]:



1-Hydrosilatranes, which are very difficult to obtain by the reaction of triethoxysilane with trialkanolamines (because of the substitution at the Si—H bond), have been synthesised by the transetherification of triethoxysilane with boratranes[50,92,93]:



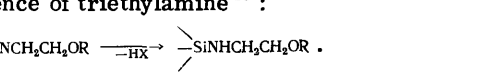
1-(triorganylsiloxy)titanatranes are obtained by the general method for the formation of the group Si—O—Ti.[94]

B. METHODS FOR THE PREPARATION OF ORGANOSILICON DERIVATIVES OF AMINOALCOHOLS CONTAINING THE Si—N BOND

The dehydrocondensation of substituted silanes $RSiH_3$ with ethanolamine and diethanolamine takes place vigorously with evolution of heat[95]. The structure of 2-hydroxyethylaminosilanes containing the Si—N bond, for example $RSi(NHCH_2CH_2OH)_3$, is attributed to the reaction products[95-99]. However, bearing in mind the comparative ease of the cleavage of the Si—N bond by alcohols[100,101] (including ethanolamine[7,75]) with formation of the Si—O bond, the structure proposed for the products of the reaction of substituted silanes with ethanolamine is very doubtful.

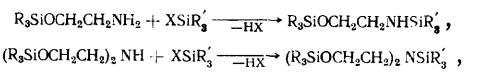
Also doubtful is the structure $RCH[(CH_2OH)NHSi(CH_3)_3]$ allegedly formed when di(trimethylsilyl) derivatives of the corresponding aminoacids $RCH[NHSi(CH_3)_3]COOSi(CH_3)_3$ are reduced with lithium aluminium hydride[102]. On hydrolysis of the reaction mixture with moist ether, the Si—N bond in these compounds is hardly likely to be retained. The final hydrolysis product might be formed with equal success from the *O*-derivative $RCHNH_2CH_2OSi(CH_3)_3$.

Organosilicon derivatives of aminoalcohols in which the presence of the Si—N bond has been unquestionably demonstrated have so far been synthesised from amino-ethers not containing a free hydroxy-group. They have been synthesised by the reaction of aminoethers with trialkyldiethylaminosilanes[103], trialkyl-t-butylaminosilanes[103], hexamethyldisilazane[80], and substituted chlorosilanes in the presence of triethylamine[103]:



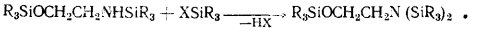
C. METHODS FOR THE PREPARATION OF ORGANOSILICON DERIVATIVES OF AMINOALCOHOLS CONTAINING BOTH Si—O AND Si—N BONDS

Organosilicon derivatives of aminoalcohols containing both Si—O and Si—N bonds are synthesised by a number of reactions used for the preparation of aminoalkoxysilanes: by the reaction of aminoalcohols with chlorosilanes[1,5,6], dialkylaminosilanes[6,75,104], and hexamethyldisilazane[77]. The application of an excess of these organosilicon reagents leads to the formation of di- and tri-organylsilyl derivatives containing both the Si—O and the Si—N bonds. However, in many cases best results in the synthesis of these compounds are obtained on further silylation of the amino-group in individual aminoalkoxysilanes[4-7,75,77]:

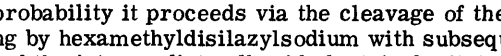


where X = Cl, $(C_2H_5)_2N$, $(CH_3)_3SiNH$, or H.

It proved possible to introduce three trimethylsilyl groups into the ethanolamine molecule by allowing diethylaminotrimethylsilane[6,75] and hexamethyldisilazane[77] to react with its di(trimethylsilyl) derivative in the presence of ammonium sulphate:

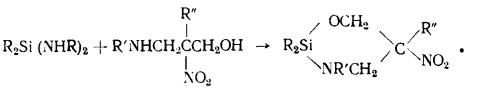


Another reaction involving the formation of *N*-[2-(trisubstituted-siloxy)ethyl]hexamethyldisilazanes (yield 65%) takes place by the mechanism[105,106]



In all probability it proceeds via the cleavage of the oxiran ring by hexamethyldisilazylsodium with subsequent silylation of the intermediate alkoxide by trisubstituted chlorosilane. It is very surprising that, in contrast to trialkylchlorosilanes, chlorodimethylsilane forms in this reaction dimethylsilyldi(trimethylsilyl)amine instead of the aminoalcohol derivative[105,106].

When dimethyldi(diorganylamino)silanes react with 2-alkyl-3-alkylamino-2-nitro-1-propanol (in molar proportions of 1 : 1) in the presence of ammonium chloride, the reaction involves both the hydroxy- and the amino-group with evolution of two equivalents of the primary amine and the formation of a cyclic product[107]:



It is asserted[86,88] that the products of the reaction of polyalkyl hydrosiloxanes with ethanolamine are siloxanes containing alternating $SiOCH_2CH_2NH_2$ and $SiNHCH_2CH_2OH$ groups. This has been confirmed by the reaction with hydrogen chloride in which only half the amino-groups were bound into salts. However, bearing in mind the possibility of the reaction of compounds containing Si—N bonds with alcohols to form Si—O bonds and also the possibility of the cleavage on the Si—N bond by hydrogen chloride, more reliable evidence is required to confirm the proposed structure of the reaction products.

D. PHYSICAL PROPERTIES

The infrared[52,108] and ^1H NMR[60,109] spectra and the dipole moments[110] of silatranes have been investigated and their crystallographic parameters have been determined[111-113]. Silatranes have high dipole moments (5.3–7.1 D), greatly exceeding (by 4.6–5.8 D) the values calculated for the structure without taking into account the donor–acceptor interaction between the nitrogen and silicon atoms[110]. This demonstrates convincingly the presence in silatrane molecules $RSi(OCH_2CH_2)_3N$ of an N → Si coordinate bond the length of which in 1-phenylsilatrane is 2.193 Å.[113] The presence of the same coordi-

nate bond was attributed without any proof to the cyclic organosilicon derivatives of diethanolamine $R_2Si(OCH_2CH_2)_2NH$.[46,47] The study of their dipole moments did not confirm this hypothesis[45].

The ^1H NMR spectra of 2-aminoethoxysilanes indicate a lowering in these compounds (compared with ethoxysilanes) of the extent of p_π–d_π interaction between the oxygen and silicon atoms[114].

E. CHEMICAL PROPERTIES

1. Hydrolysis

The hydrolysis of aminoalkoxysilanes has been little investigated. Some of them are readily hydrolysed by water[6,7,33,52]. At the same time it has been stated that compounds of the type $Si(OCH_2CH_2NR_2)_4$, where $R = C_2H_5$ or C_4H_9, are relatively stable in aqueous solution[33]. Silatranes are even more resistant to moisture and are hydrolysed with greater difficulty than the corresponding substituted triethoxysilanes[50,115]. The hydrolysis of silatranes in an aqueous medium is kinetically of first order with respect to the silatrane. The logarithms of the rate constants are linearly correlated with the σ^* constants of the substituents at the silicon atom[59].

Compounds of the type $R_3SiOCH_2CH_2NHR'$ are hydrolysed quantitatively by a 30% solution of alkali[8,116]. In contrast, *N*-[2-(trialkylsiloxy)ethyl] hexamethyldisilazanes are not hydrolysed even on refluxing with a solution of alkali, but are readily cleaved by dilute hydrochloric acid[104].

2. Alcoholysis

The alcoholysis of aminoalkoxysilanes takes place when they are heated with alcohols and the lower-boiling component of the equilibrium system is distilled off[6,7,31,33,34]:

$$\equiv SiOCH_2CH_2NH_2 + HOCH_2R \rightleftarrows \equiv SiOCH_2R + HOCH_2CH_2NH_2 ,$$

$$(R_3SiOCH_2CH_2)_2NH + 2\,HOCH_2CH_2NH_2 \rightleftarrows R_3SiOCH_2CH_2NH_2 + (HOCH_2CH_2)_2NH .$$

The organosilicon derivatives of ethanolamine and diethanolamine containing both Si–O and Si–N bonds can be selectively desilylated by alkanols[5–7,117]:

$$(R_3SiOCH_2CH_2)_nNH_{2-n}SiR'_3 + HOR'' \rightarrow (R_3SiOCH_2CH_2)_nNH_{3-n} + R'_3SiOR'',$$

where $n = 1$ or 2.

The cleavage of the Si–N bond by alkanols in compounds of the silazane type takes place in the presence of a catalytic amount of ammonium phosphate[6,7,118] or traces of hydrochloric acid[105,106]. If one uses C_2H_5OD for desilylation under these conditions, an *N*-deuterated derivative is formed[6,7]:

$$R_3SiOCH_2CH_2N(SiR_3)_2 + 2R'OM \rightarrow R_3SiOCH_2CH_2NM_2 + 2R_3SiOR',$$

where M = H or D.

3. Reactions with Acids and Their Anhydrides

Aminoalkoxysilanes are fairly strong bases and can be titrated with hydrochloric acid in the presence of Methyl Red.[75] The formation of salts of aminoalkoxysilanes with inorganic[16,18–20,86,119–121] and carboxylic acids[13,16,121–123] has been noted in a number of patents. However, in only two cases[5,11] were the corresponding hydrochlorides isolated in a pure form and adequately characterised. The difficulty of obtaining the hydrochlorides of aminoalkoxysilanes can be accounted for by the ready cleavage of the Si–O bond in these compounds by hydrogen chloride[6,7,90,107]:

$$(R_3SiOCH_2CH_2)_nNH_{3-n} + (n+1)\,HCl \rightarrow n\,R_3SiCl + (HOCH_2CH_2)_nNH_{3-n}\cdot HCl,$$

where $n = 1$–3.

The cleavage of these compounds by acetic acid[6,7,90] and also acetic anhydride[107] and *p*-nitrobenzoyl chloride[105,106] takes place similarly. The reaction of disubstituted di-(2-aminoethoxy)silanes with the dianhydride of pyromellitic acid[26,63] and di-isocyanates[27] leads to the formation of polymers.

4. Reactions with Organosilicon Compounds

The silylation of the amino-group in aminoalkoxysilanes by chlorosilanes, aminosilanes, and silazanes was discussed in Section B, 3. Aminoalkoxysilanes are silylated by chloroalkylsilanes[5,8,116]:

$$\equiv SiOCH_2CH_2NH_2 + ClCH_2Si\equiv \xrightarrow{-HCl} \equiv SiOCH_2CH_2NHCH_2Si\equiv .$$

In a study of the rate of reaction of various amines with (chloromethyl)dimethylethoxysilane in ethanol solution, the following series of decreasing reactivities was obtained[124]:

$$HOCH_2CH_2NH_2 > (CH_3)_3SiOCH_2CH_2NH_2 > C_2H_5NH_2 > (C_2H_5)_2NH .$$

The study of the products of this reaction showed that in the presence of triethylamine intramolecular cyclisation with elimination of ethoxytrimethylsilane takes place in addition to the silylation of the amino-group[9,125]:

$$R_3SiOCH_2CH_2NH_2 + ClCH_2Si(OC_2H_5)R_2 \xrightarrow[-R'_3N\cdot HCl]{+R'_3N} R_2Si\begin{matrix}CH_2NH\\ O-CH_2\end{matrix}>CH_2 + R_3SiOC_2H_5.$$

5. Other Reactions

Aminoalkoxysilanes with an unsubstituted amino-group are readily hydroxyalkylated by oxiran and substituted oxirans[5,27,33,34,42,126]. The reaction of aminoalkoxysilanes with alkyl iodides yielded the corresponding ammonium salts[24,75,76]. The basic properties of the nitrogen atom in silatranes are reduced so much owing to the formation of the N → Si donor–acceptor bond that they do not react with methyl iodide[50,71].

1-Hydrosilatranes undergo dehydrocondensation with alcohols and phenols in the presence of alkali metal alkoxides (phenoxides) or zinc chloride[127] and with carboxylic acids in the presence of zinc chloride[50]:

$$N(CH_2CH_2O)_3SiH + HOR \rightarrow N(CH_2CH_2O)_3SiOR + H_2 .$$

It proved impossible to carry out the dehydrocondensation of 1-hydrosilatranes with alcohols[127] and also to use them for the hydrosilylation of olefins (cyclohexene and styrene)[93] in the presence of $H_2PtCl_6.6H_2O$.

The reaction of 1-substituted silatranes with SbF_3 involves an exchange reaction by the mechanism[128]

$$N(CH_2CH_2O)_3SiR + SbF_3 \rightarrow RSiF_3 + N(CH_2CH_2O)_3Sb .$$

1-Vinylsilatrane reacts with silver nitrate in aqueous solution in the presence of fluoride ions, giving a characteristic blue colour, which rapidly becomes black. It is suggested that the reaction takes place with elimination of the vinyl group from the silicon atom by silver fluoride with subsequent decomposition of the vinylsilver formed initially[128,129].

F. BIOLOGICAL PROPERTIES

Like the corresponding aminoalcohols, the majority of aminoalkoxysilanes have a depressant effect on the central nervous system. After their administration, an inhibition of respiration and motor activity and convulsions are observed. However, triethyl-[2-(diethylamino)ethoxy]-silane and tri-[2-(diethylamino)ethoxy]phenylsilane have a stimulating effect.

2-(Diethylamino)ethoxytrimethylsilane and di(diethyl-aminoethoxy)dimethylsilane reduce the motor activity of mice and impair the coordination of motion in doses much lower than the median lethal dose (by a factor of 12.6 and 11.3 respectively).

Derivatives of ethanolamine in the series $R_{4-n}Si(OCH_2CH_2NH_2)_n$ with $n = 1-3$ are 2–9 times more toxic than ethanolamine itself. On the other hand, derivatives of 2-dialkylaminoethanols are less toxic than the corresponding aminoalcohol $HOCH_2CH_2NR_2$ (particularly for $R = CH_3$ or C_4H_9) or their toxicity is of the same order of magnitude (for $R = C_2H_5$). The toxicity of compounds in the series $(R_3SiOCH_2CH_2)_nNH_{3-n}$, where $R = CH_3$ or C_2H_5 and $n = 1-3$, decreases markedly with increase of n. On the whole, the toxicity of organosilicon esters of amino-alkanols is low and varies in the range from 120 mg kg^{-1} for di-(2-aminoethoxy)diethylsilane to 4000 mg kg^{-1} for tri-[2-(triethylsiloxy)ethyl]amine [7,130]. 1-Alkyl- and 1-alkoxysilatranes have a low toxicity [50,57-60,131-134].

In contrast, 1-arylsilatranes are highly toxic [135]. The median lethal dose of 1-phenylsilatrane in experiments on white mice administered intraabdominally is 0.43 mg kg^{-1} [132] (0.33 mg kg^{-1} according to Voronkov [59]). Even in doses of 0.2–0.25 mg kg^{-1} 1-phenylsilatrane causes marked motor excitation of the animal accompanied by a change in the position of the tail (the Straub symptom). 1-Tolylsilatrane is even more toxic (LD_{50} = 0.20 mg kg^{-1}). [59] In contrast to warm blooded animals, 1-phenylsilatrane has completely no effect on frogs in doses up to 30–40 mg kg^{-1} [50,132].

[2-(Dimethylamino)ethoxy]trimethylsilane methiodide exhibited a H-cholinolytic activity in experiments on the smooth muscle of the stomach ($EC_{50} = 4.5 \times 10^{-4}$). [76]

G. PRACTICAL APPLICATIONS

Aminoalkoxysilanes are used to make water repellent fabrics [15,32,53,64,136,137], leather [64], glass [16,120], paper [64], and building materials [31]. Coatings with improved adhesion to metals [27,121], coatings with satisfactory dielectric and thermal properties [26,63,64,126], and also coatings for casting moulds [38] have been obtained on their basis.

Polyaminoalkoxysiloxanes are used as surface-active substances [42] and binders for refractory materials [34,39,40,138,139].

Aminoalkoxysilanes, their carboxylic acid salts, and products of their interaction with oxirans have been proposed as hardening agents for epoxy-resins [35,46,51,126], dispersing agents [13,37,119,122,123,140], viscosity-reducing agents in non-aqueous systems [13], vulcanisers [13], plasticisers [25], binders for fibre glass [53,141], and intermediates in the synthesis of polymers [26,27,53,63,126].

2,3-Di(difluoroamino)propoxysilanes can be employed as rocket fuel and as binders for solid rocket fuel [25].

III. ORGANOSILICON DERIVATIVES OF AMINOALCOHOLS IN WHICH THE SILICON ATOM IS LINKED TO THE AMINOALCOHOL HETEROATOM VIA A CARBON CHAIN

A. METHODS OF SYNTHESIS

Trialkylchloroalkylsilanes silylate the amino-group of ethanolamine [2,142], 2-alkylaminoethanols [142-144], and diethanolamine [145], forming organosilicon aminoalcohols:

$$\equiv Si(CH_2)_nCl + RNHCH_2CH_2OH \xrightarrow{-HCl} \equiv Si(CH_2)_nNRCH_2CH_2OH .$$

The reactions of chloroalkylsiloxanes with β-(2-hydroxy-ethylamino)ethylamine take place similarly [146,147].

The highest yields of organosilicon aminoalcohols have been achieved in the hydroxyalkylation of organosilicon amines by oxirans [142,145,147]:

$$\equiv Si(CH_2)_nNH_2 + CH_2CH_2O \rightarrow \equiv Si(CH_2)_nNHCH_2CH_2OH \xrightarrow{CH_2CH_2O} \equiv Si(CH_2)_nN(CH_2CH_2OH)_2 .$$

The hydroxyethylation of organosilicon anilines [149] and aminoalkylsiloxanes [150,151] is carried out similarly. Diglycidyl ether is also employed instead of oxiran [151,152]. Aminoalkylsilanes have been hydroxyethylated by ethylene chlorohydrin [144,148] and 2-chloroethyl vinyl ether [148,153].

Silicon-containing aminoalcohols are readily obtained by the reaction of silylated oxirans with ammonia [154,155] or amines [154,156-169]. Not only (oxiranylalkyl)silanes but also (oxiranylalkoxyalkyl)silanes [156,157,159,161,165,168-173] and (oxiranylalkylaminoalkyl)silanes [156,160,162] have been introduced into the reaction

$$\equiv Si-(C)_n-X-CH_2CHCH_2 + RR'NH \rightarrow \equiv Si-(C)_n-X-CH_2CHCH_2NRR' ,$$

where X = CH_2, O, or NR″.

The opening of the oxiran ring of trialkyl-[β-(1-methyl-oxiran-1-yl]ethynyl] silanes by aliphatic amines takes place at the carbon atom directly attached to the triple bond, which leads to the formation, in contrast to (oxiranylalkyl)silanes, of primary silylated acetylenic aminoalcohols [174].

Silylated ethers of aminoalcohols have also been synthesised by the hydrosilylation of alkylene ethers of aminoalcohols by hydrosilanes and hydrosiloxanes in the presence of $H_2PtCl_6.6H_2O$: [175,176]

$$\equiv SiH + CH_2{=}CHCH_2OCH_2CH_2NR_2 \rightarrow \equiv Si(CH_2)_3OCH_2CH_2NR_2 ,$$

by the reaction of (chloroalkyl)silanes with sodium amino-alkoxides in toluene solution [177,178]:

$$\equiv Si(CH_2)_nCl + NaOCH_2CH_2NR_2 \xrightarrow{-NaCl} \equiv Si(CH_2)_nOCH_2CH_2NR_2 ,$$

and also by the catalytic reduction of the products of the cyanoethylation of silylated alcohols in the presence of Raney nickel [179]:

$$\equiv Si(CH_2)_nOCH_2CH_2CN + 2H_2 \rightarrow \equiv Si(CH_2)_nOCH_2CH_2CH_2NH_2 .$$

Among other reactions involving the formation of silylated aminoalcohols and their ethers, mention may be made of the reduction of silylated aminoacids [180] and esters of cyanoacids [181] by lithium aluminium hydride [180]

or sodium borohydride [181], the reaction of silylated diazoketones with ethanolamine [182,183], the acylation of aminoalcohols by the chlorides of trisubstituted silylbenzoic acids [184] and finally organolithium synthesis by the mechanism [185]

$$LiC_6H_4N(CH_2CH_2OLi)_2 + 3R_3SiCl \xrightarrow[-3LiCl]{+2H_2O} R_3SiC_6H_4N(CH_2CH_2OH)_2 + 2R_3SiOH.$$

B. CHEMICAL PROPERTIES

Silylated aminoalcohols and their ethers enter into a number of reactions common to aminoalcohols: the formation of hydrochlorides [116,142,173] and quaternary ammonium salts [143,173,175,176], esters [76,143,145], oxazolidines by reaction with aldehydes [144], oxides of aminoethers [175,176], substitution of the hydroxy-group by chlorine when acted upon by thionyl chloride [142,143], silylation by dialkylaminosilanes [5], and also coupling with diazonium salts in the case of *N*-(triorganylsilylaryl) derivatives [185].

C. BIOLOGICAL ACTIVITY AND PRACTICAL APPLICATIONS

Salts of trialkyl(aminoalkyl)silyl benzoates with organic acids and their quaternary ammonium salts have an analgesic and local anesthetic effect [184]. Many hydrochlorides of the type $[R_3SiC_6H_4COOCH_2NHR_2']Cl$ have an antibacterial activity against *S. haemolyticus* and *M. avium*. [184]

Dialkylaminoethyl esters of trimethylsilylphenylhydroxypropionic acid exhibit anticholinergic activity and some of them have a protective effect on poisoning with organophosphorus compounds [186].

The methiodides of trimethyl-[*N*-methyl-*N*-(2-acetoxyethyl)aminomethyl]silane and trimethyl-[*N*-methyl-*N*-(2-benzoyloxyethyl)aminomethyl]silane exhibit H-cholinolytic [*N*-cholinolytic ? (Ed. of Translation)], ganglion blocking, and hypotensive activity [76].

Polysiloxanes containing hydroxyethylaminoalkyl or dialkylaminoalkoxy-groups, their salts, and oxides can be used as emulsifying agents [147,175,176], surface-active substances [147], coatings for fibre glass [146,152], anticorrosion coatings for metals [150], and also for the preparation of foam plastics [187].

Polysiloxanes of the type $[CH_3Si(O)(CH_2)_4N(CH_2CH_2OH)_2]_n$ are used for the flocculation of aqueous suspensions of clays and for the binding of copper and iron ions [151].

IV. ORGANOSILICON DERIVATIVES OF AMINOALCOHOLS CONTAINING BOTH Si–O–C AND Si–C_n–N GROUPS

A. METHODS OF PREPARATION

Acyclic organosilicon derivatives of aminoalcohols of the type $\geqslant SiOCH_2CH_2NRCH_2Si\leqslant$, containing both Si–O–C and Si–C_n–N groups have been obtained by the silylation of organosilicon aminoalcohols with trisubstituted dialkylaminosilanes [5,7] and by the silylation of trialkyl(2-aminoethoxy)silanes with chloroalkylsilanes [5,8,116]:

$$R_3SiCH_2NHCH_2CH_2OH + R_3SiNR_2' \xrightarrow[-R_2'NH]{} R_3SiCH_2NHCH_2CH_2OSiR_3,$$

$$R_3SiOCH_2CH_2NH_2 + ClCH_2SiR_3' \xrightarrow[-HCl]{} R_3SiOCH_2CH_2NHCH_2SiR_3'.$$

If instead of trialkylchloromethylsilanes one employs alkyl(chloromethyl)alkoxysilanes of the type $(R'O)_{3-n}R_nSiCH_2Cl$, then after substitution in the amino-group intramolecular cyclisation also takes place on heating, with elimination of alkoxytrimethylsilane [9,125]‡. For example, when $n = 2$, the reaction takes place via the mechanism

$$R_2(C_2H_5O)SiCH_2Cl + H_2NCH_2CH_2OSi(CH_3)_3 \xrightarrow[-(C_2H_5)_3N\cdot HCl]{+(C_2H_5)_3N} \rightarrow (CH_3)_3SiOC_2H_5 + R_2Si\begin{matrix}CH_2NH\\ O-CH_2\end{matrix}CH_2.$$

With di-(2-aminoethoxy)dimethylsilane, cyclic compounds having a similar structure are formed. Moreover, the Si–CH_2Cl bond is cleaved in the initial (chloroalkyl)-silanes with further methylation of the N–H bond in the cyclic compounds formed.

When dialkyl(bromomethyl)ethoxysilanes react with 2-(*N*-organylamino)ethanols in the presence of triethylamine, substitution in the amino-group and intramolecular condensation with liberation of ethanol takes place, which also leads to the formation of 2-silamorpholine derivatives [189,192]:

$$R_2(C_2H_5O)SiCH_2Br + R'NHCH_2CH_2OH \xrightarrow[-(C_2H_5)_3N\cdot HBr]{+(C_2H_5)_3N} R_2Si\begin{matrix}CH_2N(R')\\ OCH_2\end{matrix}CH_2.$$

Instead of dialkyl(bromomethyl)ethoxysilanes, one may employ in this reaction also dialkyl(bromomethyl)chlorosilanes, but the yield of 2-silamorpholine derivatives is then reduced (from 62 to 37%). [192] When R′ = H, a cyclic derivative of ethanolamine could be obtained only when dimethyl(bromomethyl)chlorosilane was employed in the alkylation. On the other hand, when dimethyl(bromomethyl)ethoxysilane is used, the reaction product is the corresponding derivative of 2-(*N*-methylamino)ethanol, the formation of which has been explained by the cleavage of the Si–CH_2Br bond by ethanol and the methylation of ethanolamine by the methylbromide liberated in this process [193].

The reaction of 1,3-di(bromomethyl)-1,1,3,3-tetramethyldisiloxane with 2-(*N*-alkylamino)ethanols takes place with the cleavage of the siloxane bond [192–194]:

$$BrCH_2Si(CH_3)_2-O-Si(CH_3)_2CH_2Br + RNHCH_2CH_2OH \rightarrow BrCH_2Si(CH_3)_2OH + (CH_3)_2Si\begin{matrix}CH_2N(R)\\ OCH_2\end{matrix}CH_2.$$

With ethanolamine, the product of the substitution of the amino-group, formed without the cleavage of the siloxane bond, was obtained [192,193,195,196]:

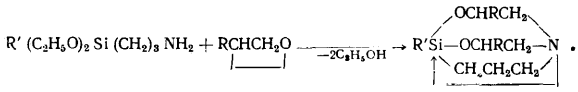
$$[(CH_3)_2SiCH_2Br]_2O + H_2NCH_2CH_2OH \rightarrow O\begin{matrix}Si(CH_3)_2-CH_2\\ Si(CH_3)_2-CH_2\end{matrix}NCH_2CH_2OH.$$

The reaction of substituted (3-chloropropyl)diethoxysilanes with diethanolamine in the presence of triethylamine leads to the silylation of the amino-group followed by intramolecular transetherification with liberation of ethanol and the formation of cyclic compounds (1-organyl-2-carbasilatranes): [4,197,198]

$$R(C_2H_5O)_2Si(CH_2)_3Cl + HN(CH_2CH_2OH)_2 \xrightarrow[-HCl]{} RSi\begin{matrix}OCH_2CH_2\\ OCH_2CH_2\\ CH_2CH_2CH_2\end{matrix}N.$$

‡According to patent data [188], an acyclic substitution product was also obtained in this reaction.

Similar compounds are formed also in the reaction of alkyl-(3-aminopropyl)diethoxysilanes and of (3-aminopropyl)triethoxysilane with oxirans [198,199]:



It has been stated that cyclisation takes place also in the case of 4-aminobutyl derivatives [199]. Other examples of this type of reaction for the synthesis of products employed in the treatment of fibre glass and for the preparation of adhesives have been described in a number of papers and patents. However, an acyclic structure is attributed to the reaction products and the possibility of cyclisation is not discussed [200-204].

B. PHYSICAL, CHEMICAL, AND BIOLOGICAL PROPERTIES

The comparatively high experimental dipole moments of 2-carbasilatranes (4.2–4.9 D), greatly exceeding the dipole moments calculated without taking into account the presence of the N → Si bond (0.2–0.8 D), indicate the presence in their molecules of a stable transannular coordinate bond N → Si. [4,7,45,198] Accordingly, they are not titrated by hydrochloric acid at room temperature and do not react with methyl iodide even on prolonged heating [198].

Intra-abdominal administration of 1-phenyl-2-carbasilatrane to white mice causes pronounced motor excitation accompanied by the Straub symptom, indicating the excitation of the spinal nervous system. When administered in doses close to the median lethal dose (LD_{50} = 8 mg kg^{-1}), this compound gives rise to clonicotonic convulsions [198].

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