Synthesis and chemical properties of silapiperazines and derivatives of 1,6-dioxa-3,8-diaza-5,10-disilacyclodecane-2,7-dione

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The results of studies dealing with the synthesis of six- and ten-membered silicon-nitrogen-containing heterocyclic compounds are presented. The structures and reactivities of these compounds have been studied. High reactivities of 2,5-disilapiperazines and 1,6-dioxa-3,8-diaza-5,10-disilacyclodecane-2,7-dione derivatives have been noted. Possible schemes of the formation of these compounds are discussed.

Key words: silapiperazines, synthesis and structure; chloromethylsilanes, reactions of silylation, transsilylation, *N*-siloxycarbonylation, carboxylation, and silamethylation.

In recent years, the chemistry of organosilicon derivatives of piperazine has been vigorously developed.[1] The introduction of an organosilyl substituent into a piperazine molecule changes dramatically its physical and chemical properties. The interest in the silicon-containing derivatives of piperazine is due to their specific structural features, specific reactivity, biological activity, and also to the fact that they can be used for the preparation of polyurethanes, polyureas, and polyamides, suitable for application in membrane engineering and for the development of strengthening coatings.[2]

In the present review, we survey the studies dealing with silicon-nitrogen-containing heterocyclic compounds, silapiperazines and 1,6-dioxa-3,8-diaza-5,10-disilacyclodecane-2,7-dione derivatives, formed upon silylation, desilylation, transsilylation, silamethylation, and *N*-siloxycarbonylation reactions.

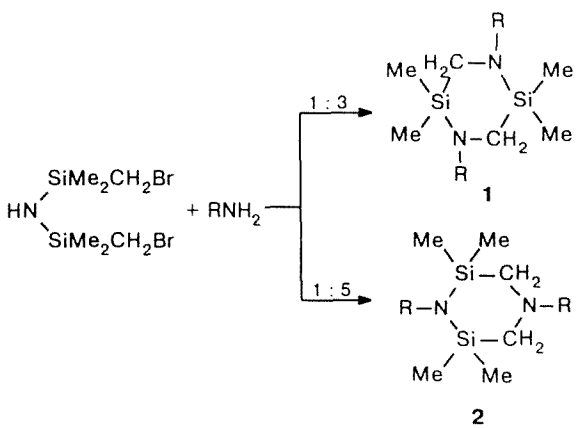
Methods for the preparation of silicon-containing piperazines

2,5- and 2,6-disilapiperazines (**1**) and (**2**) were synthesized for the first time by mere mixing of 1,3-bis(bromomethyl)-1,1,3,3-tetramethyldisilazane with excess primary amine (R = H, Me)[3] (Scheme 1).

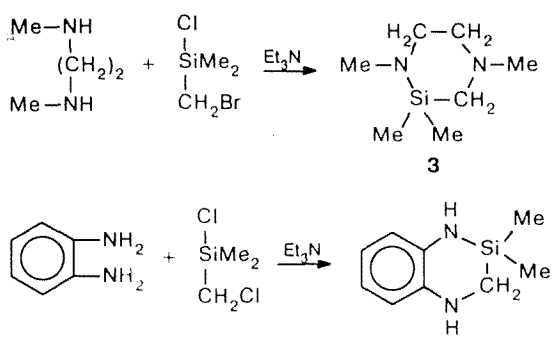
The first representatives of 2-silapiperazines, 1,2,2,4-tetramethyl-1,4-diaza-2-silacyclohexane[4] (**3**) and 1,2-benzo-4,4-dimethyl-3,6-diaza-4-silacyclohexane,[5] were obtained using bromomethyl(chloro)dimethylsilane and choromethyl(chloro)dimethylsilane, respectively (Scheme 2).

Later, it has been found that 2-silapiperazines **3** are formed in high yields when choromethyl(chloro)dimethylsilane is used in this reaction.[6,7] When the starting diamine contains bulky substituents at the nitrogen atom ($R \geq C_3$) and also when the methylene chain is too long ($n \geq 3$), compounds **3** are not formed.

Scheme 1

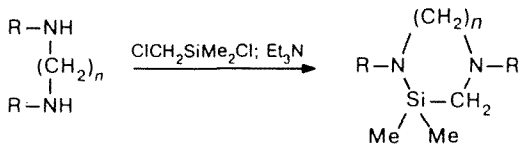


Scheme 2



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2407—2414, October, 1996.

Scheme 3



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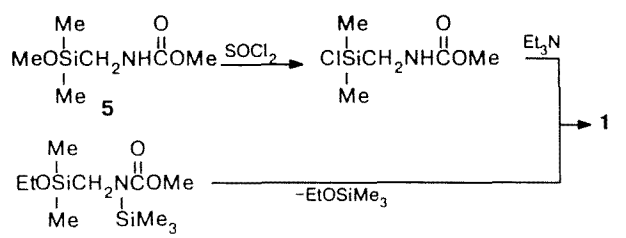
When monoamine is used instead of diamine and its content is increased (the ratio $ClCH_2SiMe_2Cl : RNH_2 = 1 : 5$), the reaction yields a mixture of disilapiperazines[2] **1** and **2** in an overall yield of 95%. The ratio between the 2,5- and 2,6-isomers is normally determined by the nature of substituent at the nitrogen atom.[2] When the amount of the amine taken is decreased to a twofold excess, the proportion of the 2,6-isomers in the mixture increases to 90%, but the overall yield decreases to 60%.

Later it has been found[8] that the 2,5-disilapiperazine derivative **1** (R = COOMe) can also be obtained by other reactions, in particular, by dehydrochlorination of chlorosilane, formed upon treatment of methyl *N*-(dimethylmethoxysilylmethyl)carbamate (**5**) with thionyl chloride, or by pyrolysis of methyl *N*-trimethylsilyl-*N*-(ethoxydimethylsilylmethyl)carbamate (**6**) (Scheme 4).

Scheme 4



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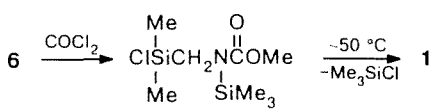
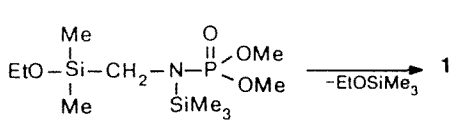
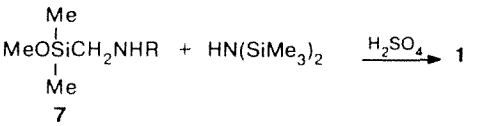
The replacement of the ethoxy group in urethane **6** by a Cl atom substantially decreases the temperature of the thermolysis and increases the yield of the corresponding 2,5-disilapiperazine **1** (R = COOMe):



Thermolysis of a phosphorus analog of ester **6**, *N*-trimethylsilyl-*N*-(ethoxydimethylsilylmethyl)amide of dimethylphosphoric acid, made it possible to obtain the first phosphorus-containing 2,5-disilapiperazine **1** ($R = P(O)(OMe)_2$):[9]



During systematic studies of α-silylalkylamines (**7**), 2,5-disilapiperazine derivatives **1** were synthesized by an alternative method, *i.e.*, by heating compounds **7** with hexamethyldisilazane in the presence of sulfuric acid.[10,11]



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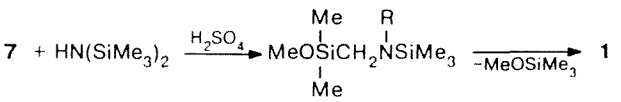
Initially, it has been suggested that heterocyclic derivatives **1** result from two consecutive reactions, *viz.*, silylation followed by the cyclization of the intermediate silylaminomethylsilane (**8**).[11,12]



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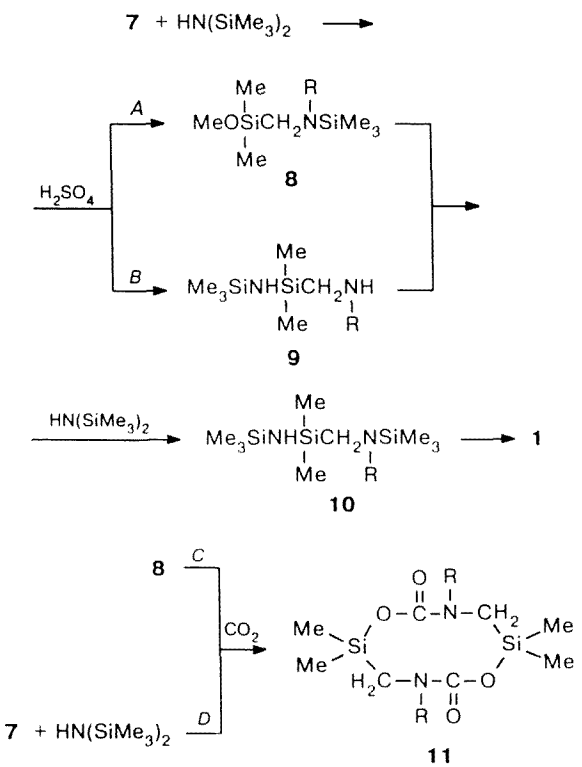
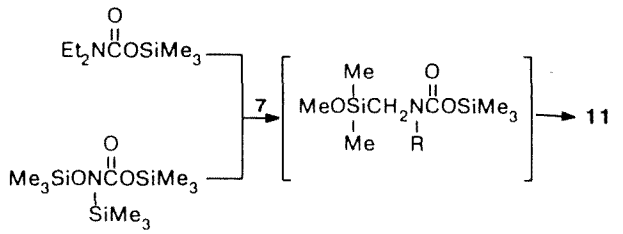
However, later it was found[10] that this process necessarily involves the intermediate formation of disilazane (**10**), since 2,5-disilapiperazine derivatives cannot be obtained by cyclization of specially prepared α-aminosilanes **8** and **9** in the absence of hexamethyldisilazane (Scheme 5).

Scheme 5



11

Scheme 6



The order in which reactions *A* and *B* occur is determined by the type of the substituent at the nitrogen atom in compound **7**. For example, at R = H, the product of reaction *A*, α-aminosilane **8**, is isolated in addition to derivative **1**, and at R = Bu^i and Ph, products of reaction *B* (compounds of type **9**) are obtained. The additional formation of compounds **8** and **9** can be apparently explained in the following way. The molecule of compound **7** incorporates two sites, capable of reacting with hexamethyldisilazane (the Si and N atoms), and the N—H bond is the most reactive of them, which is really manifested at R = H (pathway *A*). The introduction of a bulky substituent (R = Bu^i or Ph) hampers the attack by hexamethyldisilazane at the nitrogen atom, and, consequently, the process involves the second reaction site (pathway *B*).

The use of choromethyl(chloro)dimethylsilane for the synthesis of 2,5-disilapiperazines **1** seems more promising, because this markedly simplifies the process and extends the range of the compounds used. Although not all types of intermediate products have been detected in these reactions, the general scheme of the process has been established quite reliably.

Ten-membered silicon- and nitrogen-containing heterocyclic compounds, derivatives of 1,6-dioxa-3,8-diaza-5,10-disilacyclodecane-2,7-dione (**11**), were synthesized by carboxylation (pathway *C*) and *N*-siloxycarbonylation (pathway *D*) (R= H, Me, All, Bu)[13,14] (see Scheme 5).

Compounds **11** can be considered to be either heterocyclic derivatives containing two carbamate groups (bis-*O*-silylurethanes) or the products of interaction of 2,5-disilapiperazines with carbon dioxide (see below).

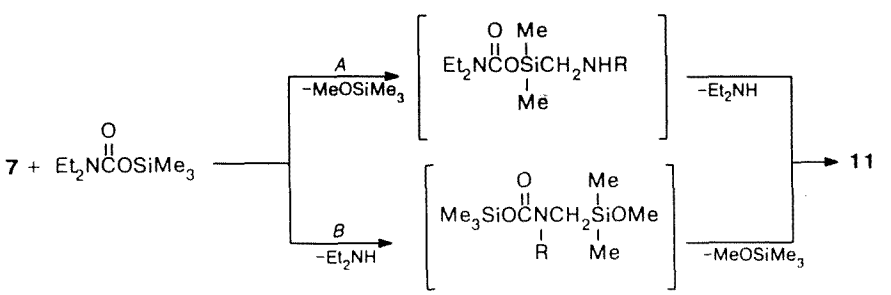
In more recent studies, it has been shown that heterocyclic compound **11** can be prepared by transamination of trimethylsilyl diethylcarbamate or *N*,*O*,*O*′-tris(trimethylsilyl)hydroxycarbamate with α-aminosilane, and a scheme has been suggested for this process (Scheme 6).[15,16]

Scheme 7 shows two possible pathways to the formation of heterocyclic compound **11** in the reaction involving trimethylsilyl diethylcarbamate. The first step in one of them is transsilylation (pathway *A*), while the first step of the other is transamination (pathway *B*). In order to find out which of these reactions proceeds in reality, experiments excluding the possibility of their simultaneous occurrence were carried out.

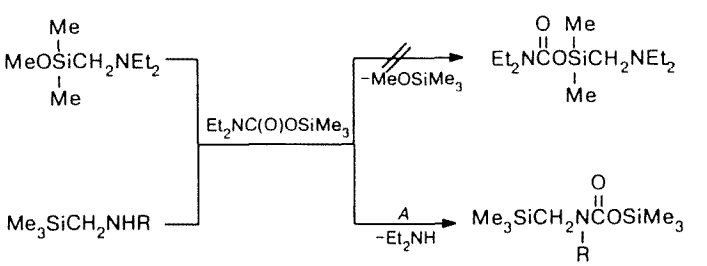
We found that trimethylsilyl diethylcarbamate is readily transaminated with trimethyl(alkylaminomethyl)-silane (reaction *A*) but does not undergo transsilylation with diethylaminomethyl(methoxy)dimethylsilane (Scheme 8).

Based on the results obtained, it may be concluded that the scheme of the formation of heterocyclic com-

Scheme 7



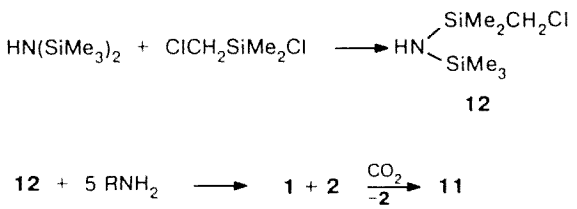
Scheme 8



pound **11** includes transamination as the first step (see Scheme 7, pathway *B*).

Yet another method for the preparation of compound **11** (Scheme 9) has been developed[17] in a study of the reactivity of chloro(chloromethyl)dimethylsilane.

Scheme 9



Treatment of asymmetrical disilazane **12**, obtained by transsilylation of hexamethyldisilazane with chloro(chloromethyl)dimethylsilane, with an excess of primary amine gave a mixture of 2,5- and 2,6-disilapiperazines **1** and **2**. This mixture was separated using carboxylation, which led not only to the expansion of the six-membered heterocyclic ring to a ten-membered ring but also to the transformation of liquid product **1** to solid compound **11**.

The interaction of trimethylsilyl *N*-trimethylsilyl-*N*-alkylcarbamates (**13**) with chloro(chloromethyl)dimethylsilane studied by us made it possible to discover a rearrangement[18] of the Cl—C—Si—N system of bonds into a new system of bonds, Cl—Si—C—N, which opened up the way for easy transition from linear *O*-silylurethanes to cyclic compounds **11** *via* intramolecular (pathway *A*) or intermolecular (pathway *B*) desilylation (Scheme 10).

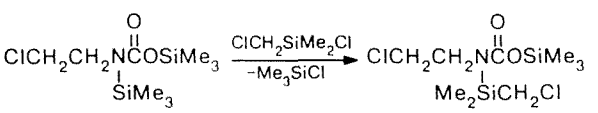
Using silylated formamides and *O*-silylurethanes as examples,[19,20] it has been shown that the first step of this reaction involves transsilylation of carbamate **13** at the nitrogen atom, which occurs very rapidly and gives trimethylsilyl *N*-chloromethyldimethylsilyl-*N*-alkylcarbamate (**14**). The subsequent 1,2-(SiN→SiC)-rearrangement of intermediate **14** affords silamethylation product (**15**), which is subsequently converted into[21] heterocyclic derivative **11**.

This interpretation of the scheme of the process was proposed based on the properties of *O*-silylurethanes and formamides, studied by us, with allowance for the structure and composition of the heterocyclic derivative **11** formed and resorting to the available published data. For example, in a previous paper,[22] it has been shown that *N*-silyl-substituted azoles react with chloromethylsilanes of type $Me_n(MeO)_{3-n}SiCH_2Cl$ ($n = 0$, 1, 2) to give compounds of two types: products of transsilylation and of *N*-silamethylation. From the data of NMR spectra and X-ray diffraction analysis,[23,24] it has been found that the reaction of *N*,*O*-bis(trimethylsilyl)acetamide with chloro(chloromethyl)dimethylsilane yields a product of silamethylation in which the silicon atom has a coordination number of 5. The above tentative scheme for this process[15] has been later confirmed experimentally.[25]

It was shown in special experiments that chloromethyltrimethylsilane, chloromethyl(methoxy)dimethylsilane, and disilazane **12** do not react with *O*-silylurethane **13** (R = Me) even with heating.

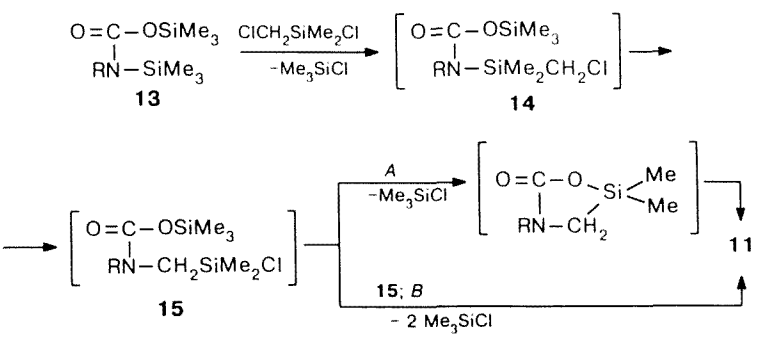
It was found that the type of the final product formed, and, hence, whether or not a particular step of the process takes place, is determined by the character of the substituent at the nitrogen atom in *O*-silylurethanes **13**.[26]

For example, the reaction of trimethylsilyl *N*-trimethylsilyl-*N*-(β-chloroethyl)carbamate **13** (R = $ClCH_2CH_2$) with chloro(chloromethyl)dimethylsilane stops after the first stage, *viz.*, transsilylation:

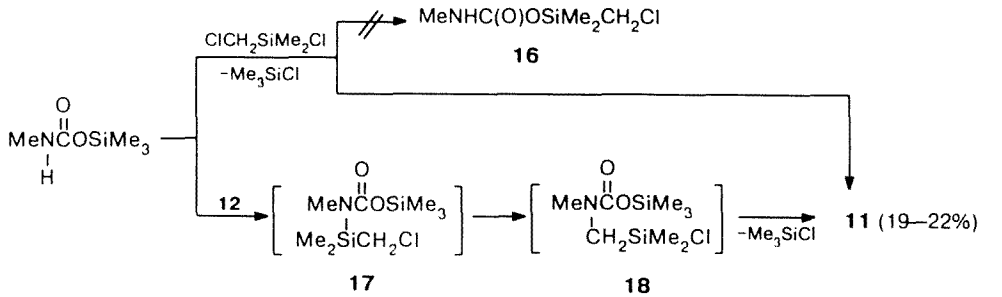


The reaction of trimethylsilyl methylcarbamate with chloro(chloromethyl)dimethylsilane afforded the above-mentioned heterocyclic derivative **11** (R = Me) in a low yield, instead of the expected product of *O*-transsilylation

Scheme 10



Scheme 11



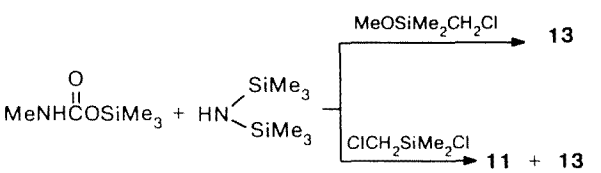
(**16**). A similar result was obtained with disilazane **12** (Scheme 11).

These reactions are unusual, since heterocyclic compound **11** arises from *O*-silylurethane [RNHC(O)OSiMe$_3$], which contains no Si—N bond, and this makes transsilylation at the nitrogen atom impossible. Nevertheless, the result obtained indicates that chloro(chloromethyl)dimethylsilane and disilazane **12** are capable of *N*-chloromethyldimethylsilylating trimethylsilyl methylcarbamate.

The possibility of sylilating *O*-silylurethanes, containing N—H bonds, at the nitrogen atom by organodisilazanes is indicated by the formation of MeN(SiMe$_3$)C(O)OSiMe$_3$ (25%) upon mere heating of trimethylsilyl methylcarbamate with hexamethyldisilazane.

Finally, it was found that when chloro(chloromethyl)-dimethylsilane is present as an additional reagent in the reaction of trimethylsilyl methylcarbamate with hexamethyldisilazane, the yield of compound **13** (R = Me) increases to 60% and that of heterocyclic derivative **11** (R = Me) increases to 31% (Scheme 12).

Scheme 12



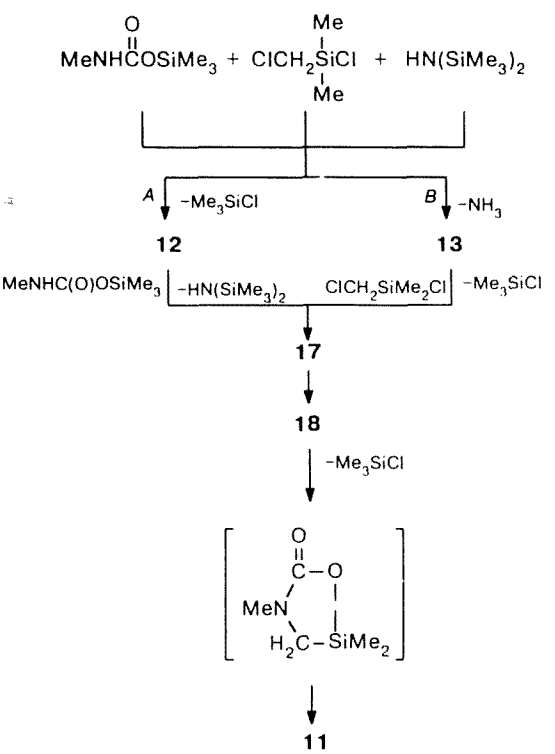
The replacement of chloro(chloromethyl)dimethylsilane by chloromethyl(methoxy)dimethylsilane changes sharply the reaction route. In this case, neither is heterocyclic derivative **11** formed nor does the yield of *O*-silylurethane **13** (R = Me) increase (25%).

Probably, the results obtained can be explained by the fact that a good leaving group (in nucleophilic substitution reactions) at the silicon atom (Cl) is replaced by a poorly leaving group (MeO).

Thus, the successful synthesis of heterocyclic derivative **11** (R = Me) involving disilazane **12** or a mixture, consisting of hexamethyldisilazane and chloro(chloromethyl)dimethylsilane and the formation of *O*-silylurethane **13** (R = Me), together with the absence of the interaction between compounds **12** and **13** (R = Me), indicates that 3,5,5,8,10,10-hexamethyl-1,6-dioxa-3,8-diaza-5,10-disilacyclodecane-2,7-dione can arise *via* two pathways (Scheme 13).

According to the first of them (see Scheme 13, pathway *A*), intermediate **12** is formed initially. After that, depending on the type of the compounds used and on the reaction conditions, the initial *O*-silylurethane is silylated and the silylation product **17** isomerizes to give the product of silamethylation (**18**); the latter undergoes intramolecular desilylation giving a five-membered heterocyclic compound, which, in its turn, dimererizes to give compound **11** (R = Me).

Scheme 13



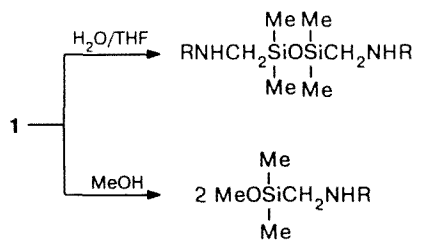
According to the second pathway (see Scheme 13, pathway *B*), the first step of the process involves the silylation of *O*-silylurethane to give compound **13** (R = Me), which is then converted into heterocyclic derivative **11** (R = Me), in conformity with the scheme proven previously.

The hypothesis that the reaction occurs predominantly by pathway *A* is supported by the fact that treatment of disilazane **12** with excess amine affords heterocyclic derivative **1** (see Scheme 9).

Chemical transformations of silicon-containing piperazines

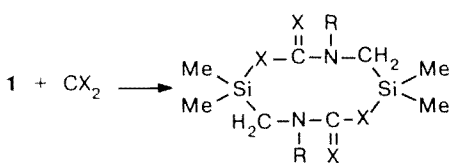
It was established that the endocyclic Si—N bond in silapiperazines is relatively stable with respect to air moisture, but in a homogeneous medium, it easily reacts with water or alcohols to give disiloxanes and carbaminosilanes (Scheme 14).

Scheme 14



Heterocumulenes CX_2 and RNCO are inserted into the Si—N bond of silapiperazines.[2,27–29] When CO_2 or CS_2 is used, the six-membered rings in **1** (X = O, S) are expanded to ten-membered rings (Scheme 15).

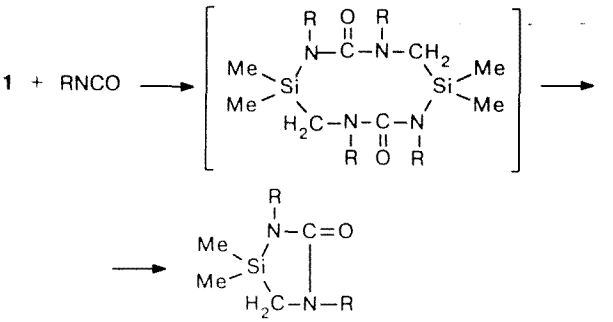
Scheme 15



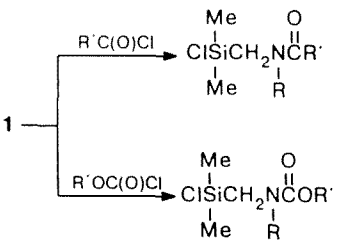
It was suggested that the reaction with isocyanates is also accompanied by ring expansion; however, the compounds thus formed are unstable and readily isomerize to five-membered cyclic ureas (Scheme 16).

Acyl halides easily cleave the Si—N bond in compounds **1**, which leads to silicon-containing amides[4] and urethanes[2,28] (Scheme 17).

Scheme 16

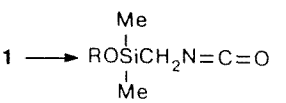


Scheme 17

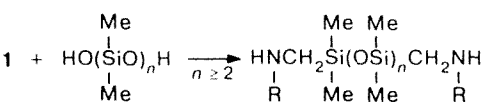


In the case of phosgene, this reaction follows a somewhat different pathway. The type of products formed is determined both by the order in which the starting reactants are mixed and by the nature of the substituent at the nitrogen atom (Scheme 18).

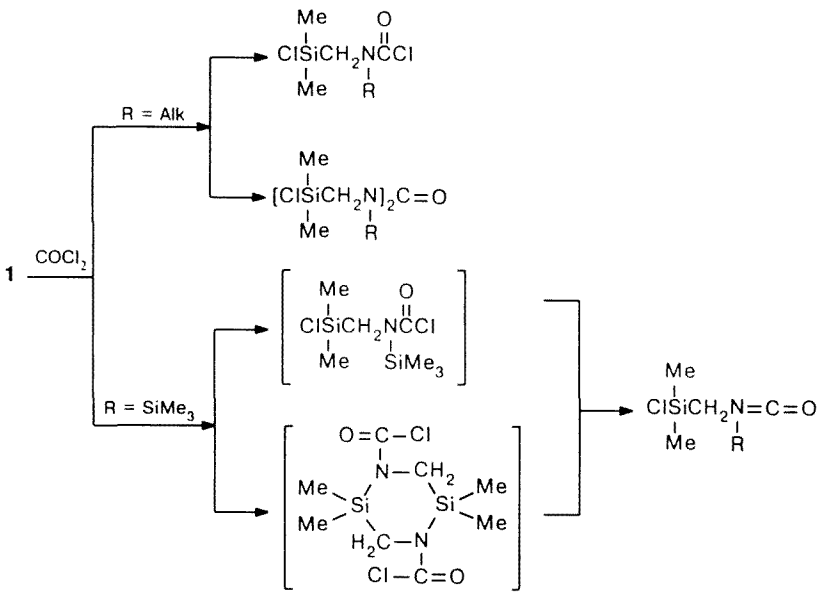
It should be noted that isocyanate is formed irrespective of which bond, endo- or exocyclic, is cleaved by phosgene.[30] Since urethanes tend to eliminate alkoxysilanes, carbofunctional isocyanates can also be obtained by isomerization of compounds **1** (R = C(O)OR′)[8,31]:



2,5-Disilapiperazine derivatives can be used as starting compounds for the preparation of oligosiloxanes containing α,ω-bis-carbofunctional groups,[31] and as curing agents for epoxy resins:[2]

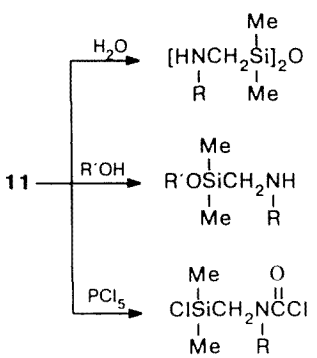


Scheme 18



The heterocyclic system in **11** exhibits higher reactivity than that in 2,5-disilapiperazines. All reactions involving this compound occur, as a rule, much more easily and are accompanied by elimination of CO_2 [32] (Scheme 19).

Scheme 19



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