Translated from *Uspekhi Khimii*, **44**, 897-934 (1975) U.D.C. 547.441

Silicon-containing Ureas

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In the review an attempt is made for the first time to survey studies on the synthesis, properties, and likely practical applications of silylureas. In view of the significant differences in the methods of their synthesis and properties, *N*-silylureas are examined separately from the carbofunctional compounds in which the urea moiety and the silicon atom are separated by a group of atoms.
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I. INTRODUCTION

Urea (carbamide) and its derivatives are some of the most widely used organic compounds. In recent years there has been a vigorous development of the chemistry of organic derivatives of the elements based on urea and in particular of its organosilicon derivatives. The introduction of an organosilyl substituent into the urea molecule alters sharply its physical and chemical properties. This applies especially to N-silyl derivatives. In particular, the hydrogen bonds are greatly weakened, which has found practical applications in the chromatography and separation of many urea derivatives. The high silylating capacity of *N*-silylureas has made them some of the most important auxiliary reagents in organic syntheses. There are good prospects also for practical applications of polymeric materials based on silicon-containing ureas.

N-Silylureas are of independent interest for the development of theoretical ideas on the tautomerism of amides, since, in contrast to organic derivatives of urea and amides, many physical properties of these compounds suggest that they exist in both the amide and isoamide forms.

II. *N*-SILYLUREAS

1. METHODS OF SYNTHESIS

a. Interaction of Silanes and Halogenosilanes with Ureas

The NH group in amines is known to react with halogenosilanes to form the corresponding *N*-silyl derivatives. However, this reaction is greatly hindered in the presence of the C=O group next to the amino-group[1-3], as happens in ureas, amides, urethanes, semicarbazides, and other similar compounds. When urea is acted upon by triorganohalogenosilanes under moderately mild conditions, silicon-substituted ureas are not formed[2,3] and the latter can be obtained only when metallated urea derivatives are used[4]:

$$Me_3SiCl + K[NHCONH_2] \rightarrow Me_3SiNHCONH_2 + KCl ,$$

or when the reaction is carried out in the presence of hydrogen halide acceptors[5-7].

Under severe conditions, the interaction of triorganohalogenosilanes with urea apparently leads to the formation of isocyanatosilanes in consequence of the decomposition of the intermediate quaternary salts[8]:

$$R_3SiCl + H_2N\overset{\overset{O}{\|}}{C}NH_2 \rightarrow [R_3SiNH_2\overset{\overset{O}{\|}}{C}NH_2]^+Cl^- \rightarrow R_3SiN{=}C{=}O + NH_4Cl$$

(when R = Ph, the reaction was carried out in the melt and for R = Me in an autoclave at 280–300°C).

When organotrihalogenosilanes, $SiCl_4$, and $SiBr_4$, react with urea or its alkyl and aryl derivatives, only hydrolytically unstable complexes are formed, for example[9,10]:

$$SiCl_4 \cdot 6H_2NCONH_2;\ SiBr_4 \cdot 6H_2NCONH_2;\ Si_2Cl_6 \cdot 10H_2NCONH_2$$
$$SiCl_4 \cdot 6H_2NCONHMe;\ SiCl_4 \cdot 6H_2NCONHPh;\ SiCl_4 \cdot 6H_2NCONMe_2.$$

The complexes do not have a distinct melting point and decompose into the initial components on dissolution in organic solvents, subliming with decomposition on heating to 150–200°C. The replacement of a halogen atom in silicon tetrahalide by an alkyl or alkoxy-group (but not by a hydrogen atom) reduces the coordination number with respect to urea by unity[10]:

$$MeSiCl_3 \cdot 5H_2NCONH_2;\ PhSiCl_3 \cdot 5H_2NCONH_2;\ SiHCl_3 \cdot 6H_2NCONH_2 .$$

The type of bond in the complexes formed has been studied inadequately because of the difficulties in the determination of their molecular weight and conductivity and in carrying out an exact X-ray diffraction analysis due to the decomposition of the complexes in solution and on fusion and also because of the difficulty of growing their crystals. X-Ray diffraction analysis of $SiCl_4.6H_2NCONH_2$ powder indicates a cubic crystal lattice with 7.79 Å faces[10]. The adducts of other halogenosilanes with urea have a similar lattice, which in the case of $SiBr_4$ has somewhat greater dimensions (8.11 Å). Bearing in mind the branching and considerable bulk of halogenosilane molecules and also the polarity of the silicon–halogen bond, the formation of clathrate compounds of the lattice type channel variety (the channel diameter is usually 5.1 Å), in which the halogenosilane molecule would be located within the crystal lattice of urea, is unlikely. The large number of urea molecules per halogenosilane molecule also rules out the possibility that they are incorporated as additional electron-donating ligands in the inner

sphere of the complex, partly with retention of Si–Cl bonds, as happens, for example, in the complex $SiCl_4 \cdot C_5H_5N$.[9]

On the basis of infrared spectra, which indicate a weakening of the N–H bond in the adducts, and also the identical compositions of the complexes of halogenosilanes with urea and *NN*-dimethylurea (1 : 6 in both cases for $SiCl_4$), it has been suggested[10] that ureas are linked to halogenosilanes only by one of the two amino-groups, while the other is probably involved in the formation of a hydrogen bond with another urea molecule.

In contrast to halogenosilanes, monoalkylsilanes $RSiH_3$, starting from n-hexylsilane, and di-n-alkylsilanes R_2SiH_2, starting from diethylsilane, form with urea true crystalline clathrate compounds[11–13]. In the first case the $RSiH_3$ molecules are located in the channels of the hexagonal crystal lattice of urea, like carboxylic acids, in the form of oriented double molecules[13]. The occluded di-n-alkylsilane molecules are distributed in a sequence, like their hydrocarbon analogues (paraffins)[11]. The lowest members of the above series do not form adducts with urea even at low temperatures (–15°C). Both types of clathrate compounds (with $RSiH_3$ and R_2SiH_2) are less stable than the analogous paraffin compounds, which is manifested by their dissociation into the initial components at a lower temperature. Unbranched di-n-alkoxysilanes form with urea analogous but more stable clathrate compounds[14]. Thioureas do not form adducts with the above organosilicon compounds[13,14].

Unbranched silanes such as trisilane, tetrasilane, and others (in contrast to the branched isomers) form clathrate compounds with both urea and thiourea[15], which are stable in air below their dissociation temperatures (–15°C for Si_3H_8 and 5°C for Si_4H_{10} in the adducts with urea). The stability of the adducts increases with increases in the silane chain length and falls on passing to urea and thiourea.

The clathrate compounds of higher silanes (starting from Si_5H_{12}) are stable even at room temperatures and the silanes in such compounds lose their capacity for self-ignition in air. In terms of their relative stabilities, compared with other organic and organosilicon clathrate compounds, they occupy the last place[15]: aliphatic acids > paraffins > di-n-alkoxysilanes > di-n-alkylsilanes > mono-n-alkylsilanes > silanes. The molecular diameters of certain types of silanes and their ability to form clathrate compounds with urea are indicated in the Table[11].

The formation of clathrate compounds by halogenosilanes with urea.

Silane	Molecular diameter		Formation of clathrate compounds	Silane	Molecular diameter		Formation of clathrate compounds
	max.	min.			max.	min.	
$RSiH_3$	5.1	4.3	+	$RSiCl_2R$	6.7	5.4	—
$RSiH_2R$	5.1	4.3	+	$RSiH_2OMe$	5.1	4.3	+
$RSiHCl_2$	6.6	5.4	—	$RSiH(OMe)_2$	8.5	4.3	—
$RSiCl_3$	6.6	5.7	—	$RSiH(OMe)R$	8.5	4.3	—
$RSiHClR$	6.6	5.4	—	$RSiH_2Cl$	5.3	4.3	*

Note: the + and – signs denote that the clathrate compounds are or are not formed; the asterisk (*) shows that the clathrate compounds can be formed in a non-solvating medium.

The selectivity of the action of urea with respect to normal (unbranched) silanes can be used for the preparative separation or purification of a mixture of normal silanes and isosilanes[15] as well as their alkyl and alkoxy-derivatives[11].

b. Transamination Reactions

The transamination reaction by Larsson's method[16], applied for the first time to the silylurea series in 1959 by Benneville and coworkers[5,17], proved to be a convenient procedure for the introduction of an organosilyl residue into urea with formation of the Si–N bond:

$$H_2NCONH_2 + Me_3SiNHCMe_3 \xrightarrow[12\,h]{110^\circ} Me_3SiNHCONH_2\,(89\%) + Me_3CNH_2 ,$$

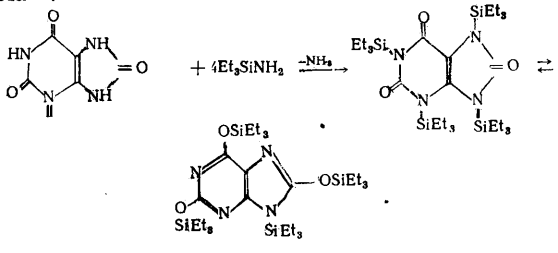
$$MeNHCONHMe + Me_3SiNHCMe_3 \rightarrow Me_3SiNCONHMe + Me_3CNH_2 .$$
$$\quad\quad\quad

resulting monotrimethylsilylacetamide can be readily removed at the end of the reaction by vacuum distillation[27].

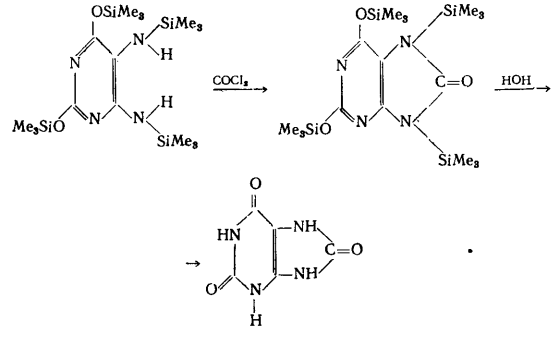
It is noteworthy that the possibility of the rapid and quantitative silylation of urea, amines, amides, and other compounds with extensive hydrogen bonding is important for organic and biological chemistry, since it makes it possible to convert high-melting non-distilling and sparingly soluble compounds into stable and volatile silyl derivatives, which are readily soluble in organic solvents and are susceptible to separation and chromatographic analysis[28,31]. The introduction of the trimethylsilyl residue as a temporary protecting group is extensively used in a wide variety of organic syntheses[32-35].

N-Silylureas, particularly those of the aromatic series, are themselves powerful silylating agents like carboxylic acid silylamides[22,25,26,36] (see also the chemical properties of *N*-silylureas). *NN'*-Diphenyl-*N*-trimethylsilylurea is particularly suitable as a donor of the trimethylsilyl group[22].

The resulting diphenylurea does not dissolve in the majority of organic solvents and therefore can be readily removed from the reaction mixture by filtration. The insolubility of diphenylurea is apparently also the reason why the equilibrium in silyl–proton exchange reactions is in this case almost wholly displaced to the right. Silylureas which could not be obtained with the aid of HMDS[18] are readily formed when a mixture of *NN'*-diphenyl-*N*-trimethylsilylurea is stirred with the corresponding urea derivative in acetonitrile at 30–35°C.[22] The reaction reaches completion in the course of several minutes or several hours for particularly sparingly soluble compounds. In particular, *NN'*-bis(trimethylsilyl)thiourea and *NN*-dimethyl-*N'*-trimethylsilylurea were obtained in this way in yields of 82 and 79% respectively. A series of cyclic analogues of urea were also synthesised by the silylation of the amide group. Thus, when uric acid is heated in triethylaminosilane, tetra(triethylsilyl)uric acid, which can exist in both lactam and lactim forms, is formed in 90% yield[37]:



When 5,6-diaminouracil reacts with HMDS, the product is 2,4-bis-(*O*-trimethylsilyl)-5,6-bis(trimethylsilylamino)-uracil, which cyclises on reaction with phosgene to form a uric acid derivative[38]; the latter cannot be obtained without using a silyl protecting group:



c. Reactions of Isocyanatosilanes with Amines

Organosilicon derivatives of urea of different structures, $R_3SiNHCON\langle$, $R_2Si(NHCON\langle)_2$, $RSi(NHCON\langle)_3$, and $Si(NHCON\langle)_4$ (where R = alkyl, aryl, or alkoxy-group), are as a rule formed in high yields by the reaction of the corresponding mono- or poly-isocyanatosilanes with aliphatic and aromatic primary and secondary amines†[18,39-50], for example:

$$Me_3SiN{=}C{=}O + Et_2NH \xrightarrow{55-60^\circ} Me_3SiNHC(=O)NEt_2 \quad (91\%)\ .$$

Exceptions are amines of low basicity (diphenylamine, HMDS) which do not react with Me_3SiNCO even under severe conditions[41], and the reaction of H_3SiNCO with NH_3 at −78°, which leads to the formation of monosilanes SiH_4 and an involatile solid residue[48].

Amines can be arranged in the following sequence in terms of their reactivities in the reaction with isocyanatosilanes[40]: $AlkNH_2 > Alk_2NH > ArNH_2 > ArNHR > Ar_2NH$. In the series of isocyanatosilanes $Si(NCO)_4$ is more reactive than in its alkyl and aryl derivatives[41,45,49].

Silylsemicarbazides were obtained by the reaction of isocyanatosilanes with hydrazines[21]:

$$Me_3SiN{=}C{=}O + H_2NNH_2 \rightarrow H_2NNHC(=O)NHSiMe_3 \quad (90\%)\ .$$

d. The Interaction of Aminosilanes and Silazanes with Organic Isocyanates

Reactions with monoisocyanates. The reactions of organoaminosilanes and silazanes with organic isocyanates, discovered in 1964 independently by several groups of workers (Zhinkin[52], Klebe[53], Oertel[54,55], and Fink and coworkers[56-58]), constitute a convenient method for the preparation of *N*-silylureas. According to the reports of Wannagat and coworkers[18,21,59,60] concerning the interaction of organic isocyanates with compounds containing simultaneously Si–N and N–H bonds (silylamines, silylhydrazines, and silylhydroxylamines) published before 1964, it was believed that the reaction involves only the N–H bond with migration of the hydrogen atom to the nitrogen atoms of the isocyanate group, for example:

$$(Me_3Si)_2NH + PhNCO \rightarrow (Me_3Si)_2NCONHPh\ .$$

However, the evidence quoted in this connection for the structure of the resulting compound, i.e. data obtained from their hydrolysis to the corresponding organic urea derivatives, cannot be regarded as convincing, since even when the reaction involves the Si–N bond, hydrolysis should yield the same results owing to the silyl–proton exchange in the *N*-silylureas[53].

A detailed study of this reaction by the above workers[26-36,52-58,61-65] and primarily by Zhinkin and coworkers[52,61-63,66,67] showed that organoaminosilanes and silazanes containing not only primary but also secondary and tertiary hydrogen atoms, i.e. compounds without N–H bonds, react with isocyanates. When Si–N and N–H bonds are present

† In early studies on reactions of isocyanatosilanes with amines it was concluded erroneously that the reaction proceeds via the elimination of the silyl group with formation of organic urea derivatives[49,51].

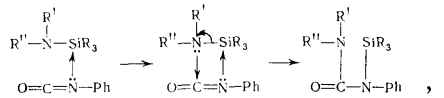
simultaneously, the latter does not take a direct part in the reaction with isocyanate, which involves preferentially the Si–N bond. The only exception‡ is the reaction of isocyanates with aminosilanes containing a primary nitrogen atom, which was shown by a study of the structure of the final product to proceed via the classical isocyanate condensation mechanism, i.e. with migration of the hydrogen atom from the nitrogen atom of the aminosilane to the nitrogen atom of the isocyanate group[62,66,70]:

$$R_3SiNH_2 + PhNCO \rightarrow R_3SiNHC(O)NHPh \quad (R=Et, Bu, Ph)\ .$$

When other organoaminosilanes and organosilazanes react with isocyanates in 1 : 1 proportion, the Si–N bond dissociates and the triorganosilyl group migrates to the nitrogen atom of the isocyanate with formation of organosilicon urea derivatives[26,36,52–56,58,61–63,66,71,72]:

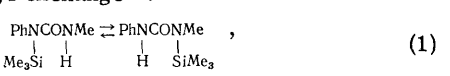
$$R_2NSiMe_3 + R'NCO \rightarrow R_2NC(O)N(R')SiMe_3\ ,$$
$$(Me_3Si)_2NH + R'NCO \rightarrow Me_3SiNHC(O)N(R')SiMe_3\ ,$$
$$RNHSiMe_3 + R'NCO \rightarrow RNHC(O)N(R')SiMe_3\ ,$$
$$(Me_3Si)_2NR + R'NCO \rightarrow Me_3SiN(R)C(O)N(R')SiMe_3\ .$$

The reaction mechanism apparently involves the formation of an unstable complex comprising four units, in which the shift of electron density to the nitrogen atom of the aminosilane or silazane weakens the Si–N bond and leads to its dissociation as well as the dissociation of the C=N π bond in the isocyanate group[63,66,73,74]:



where R′ = H or alkyl and R″ = H, alkyl, aryl, or SiR_3.

It follows from ^{1}H NMR data that silylureas with a proton and a triorganosilyl group at the N and N′ atoms respectively can be involved in the presence of a solvent in intramolecular (Scheme 1) or intermolecular (Scheme 2) proton–trimethylsilyl exchange[53]:



(1)

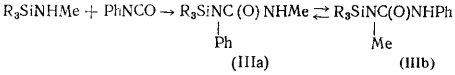


(2)

Depending on the solvent and the nature of the groups at the silicon and nitrogen atoms, the equilibrium can be displaced towards one of the isomers.

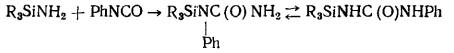
The occurrence of silyl–proton exchange was also confirmed by a study of the products of the addition of optically active *N*-(methylphenyl-α-naphthylsilyl)methylamine to phenyl isocyanate[73,74]. It was shown that the reaction proceeds with retention of the configuration at the silicon atom (its stereospecificity is greater than 90%) and the resulting optically active silylurea (IIIa) undergoes rapid racemisation in tetrahydrofuran (THF) solution and slow racemisation in benzene solution, the latter being greatly accelerated on heating§.

After compound (IIIa) has been allowed to stand for many hours, its ^{1}H NMR spectra show that it has been converted into (IIIb) as a result of the intermolecular exchange of the Me_3Si groups:



where R_3Si = (c-$C_{10}H_7$)(C_6H_5)(CH_3)Si.

In view of the possibility of the silyl–proton exchange in silylurea, one cannot rule out the possibility that the above anomalous reaction (in the series of reactions of isocyanates with aminosilanes) with primary aminosilanes[62,66,70] in reality involves the Si–N bond and not the N–H bond, the final reaction product being formed as the result of the fast intermolecular or intramolecular silylation of the *N*-phenyl-*N*-trimethylsilylurea produced initially, which is in the present case facilitated by the presence of the free NH_2 group:



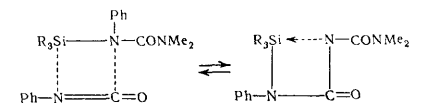
N-Silylureas formed on interaction of equimolar amounts of isocyanate and aminocyanate (or silazane) can readily enter into further reaction with the excess isocyanate and, depending on whether the urea contains only Si–N bonds or both Si–N and N–H bonds, the reaction proceeds in different ways. Silylureas without N–H bonds, obtained from tertiary silylamines R_2NSiMe_3, react with isocyanate in the same way as the initial silylamines, i.e. with migration of the triorganosilyl group to the nitrogen atom of the isocyanate. High yields of the corresponding silyl derivatives of biurets are then formed[36,57,63–65]:



The same compounds can be obtained also when an excess of isocyanate reacts directly with tertiary silylamines[63].

When silylbiurets are heated (for example in the course of their distillation), they decompose into the initial components[57], so that, depending on the temperature conditions, the compounds can be in equilibrium with the initial silylurea and isocyanate, the equilibrium can be established several times but does not result in racemisation[74].

A mechanism similar to that for the reaction of isocyanates with aminosilanes was proposed for the formation of silylbiurets and the reverse reaction involving the elimination of the isocyanate[74]:



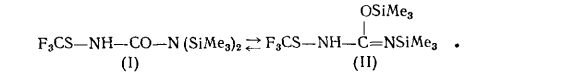
The Si–N bond in silylbiurets is more resistant to hydrolysis than in silylureas and further reaction involving this bond with the excess isocyanate does not proceed or proceeds with difficulty[57]. Fink explains this finding by

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‡ According to Haas's data[68,69], the reaction of trifluoromethylsulphenyl isocyanate with HMDS also involves the cleavage of the N–H bond and not the Si–N bond:

$$(Me_3Si)_2NH + F_3C(S)NCO \rightarrow F_3C(S)NHC(O)N(SiMe_3)_2\ .$$

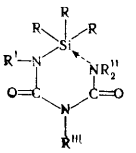
Although the ^{1}H NMR spectrum of the resulting urea has two kinds of resonances due to the Me_3Si groups, like *NN*-bis-silylamides, the authors attribute this to the hindered rotation about the C–N bond and believe that the product has structure (I) and not (II):



This conclusion was also confirmed by infrared spectroscopic data.

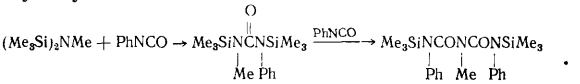
§ Kaufmann et al.[74] showed for the 1 : 1 adduct of PhNCO and the optically active silylamine (α-$C_{10}H_7$)(C_6H_5)(CH_3)SiN.$(CH_3)_2$ that silylureas without N–H bonds do not racemise.

the stabilisation of the molecule due to intramolecular coordination with formation of the following stable cyclic structure[57,64]:

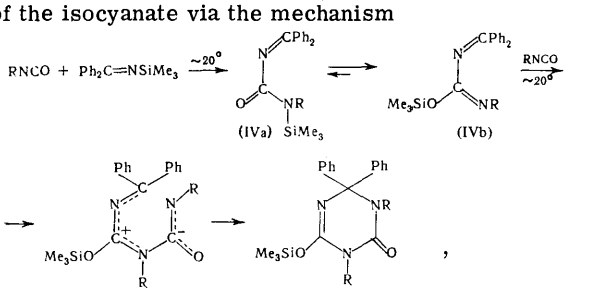


Since these compounds regenerate free isocyanate on heating and exhibit all the reactions characteristic of the isocyanate group, they have been patented as "latent" isocyanates, which are less susceptible to hydrolysis and are less volatile than free isocyanates[64].

Silylureas without N–H bonds, formed from *N*-alkylsilazanes, react with isocyanates via the same mechanism as tertiary silylamines[52,53,62,63,66]:

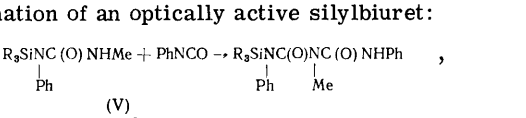


The interaction of isocyanates with diphenylmethylene-*N*-trimethylsilylamine proved to be specific[75]. For a 1 : 1 reactant ratio, the reaction proceeds selectively with cleavage of the Si–N bond to give silylureas, but, in the presence of an excess of the isocyanate, the products are not silylbiurets, as usually happens, but triazinone derivatives. The authors[75] explain this by 1,4-cycloaddition of the isomeric (imide) form of silylurea (IVb) to the C–N bond of the isocyanate via the mechanism

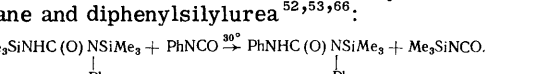


where R = Me, Ph, or PhC(O). This reaction confirms the possibility of the existence of silylureas in the isoamide form. The occurrence of the tautomeric equilibrium (IVa) ⇌ (IVb) has also been confirmed by a study of the temperature-induced changes in the ^{1}H NMR spectrum of compound (IV).[75]

The mode of reaction involving ureas containing both Si–N and N–H bonds has been studied inadequately, in many cases not at all owing to the instability of the addition products. Thus, according to the data of Kaufmann et al.,[73] when an excess of isocyanate is allowed to react with the optically active silylurea (V), the reaction involves the N–H bond with retention of the configuration and the formation of an optically active silylbiuret:



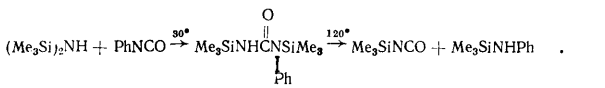
However, in the case of the silylurea containing the N–H bond and obtained from HMDS and PhNCO (1 : 1), further reaction with a second isocyanate molecule under the same mild condition leads to the formation of isocyanatotrimethylsilane and diphenylsilylurea[52,53,66]:



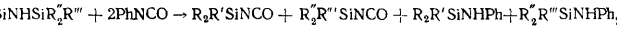
The same products were isolated also after the direct interaction of HMDS with PhNCO in proportions of 1 : 2.[52,63,66]

At an elevated temperature the composition of the products of the reaction of aminosilanes with isocyanates is as a rule anomalous, which is evidently due to the thermal instability of the intermediate silylureas, their tendency towards tautomeric transformations, and a number of other factors.

Thus at about 120°C HMDS reacts with PhNCO to form Me_3SiNCO and $PhNHSiMe_3$.[61,66] Since the same products are formed on heating *N*-phenyl-*NN'*-bis(trimethylsilyl)urea to 120°C,[61] the reaction evidently proceeds via the intermediate formation of this compound:

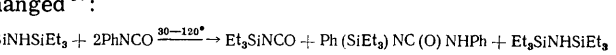


Other hexaorganodisilazanes, with the exception of hexaethyldisilazane, react similarly with PhNCO at elevated temperatures, silazanes containing different groups at the silicon atoms forming two isocyanates and two triorganosilylamines in approximately equal amounts[67]:

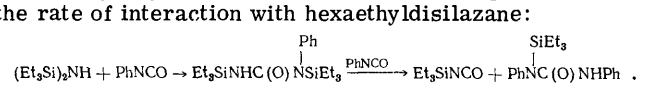


where R and R'' = Me or MeO and R' and R''' = Me, MeO, or Ph. The nature of the organic group linked to the silicon atom does not have a significant influence on the course of this reaction.

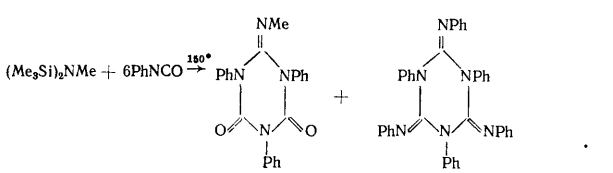
Hexaethyldisilazane reacts differently with PhNCO. Regardless of the temperature conditions, the interaction of equimolar amounts of the reactants leads to the formation of Et_3SiNCO and *NN'*-diphenyl-*N'*-triethylsilylurea, half of the silazane taken for the reaction remaining unchanged[67]:



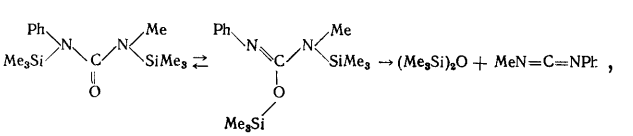
The authors[67] explained this course of reaction by the fact that the rate of interaction PhNCO with *N*-phenyl-*NN'*-bis(triethylsilyl)urea formed in the first stage is faster than the rate of interaction with hexaethyldisilazane:



The reaction of isocyanates with *N*-alkylated disilazanes at elevated temperatures is unusual. For example, Itoh et al.[76] showed that heptamethyldisilazane reacts with an excess of PhNCO to form the triazine derivatives (VI) and (VII):

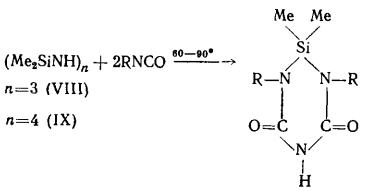


They suggest that the formation of (VI) is due to the β-elimination of the iso-form of the initial silylurea (1 : 1 adduct) to give methylphenylcarbodiimide:



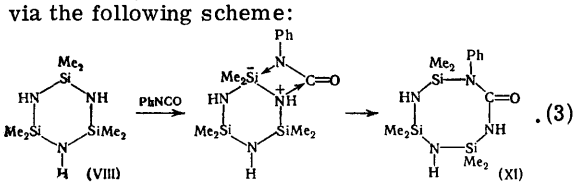
which then undergoes a cyclisation reaction with two molecules of PhNCO to give compound (VI). The formation of compound (VII) can be accounted for in two ways: (1) the 1 : 2 adduct of heptamethyldisilazane with PhNCO undergoes a similar decomposition (with decarboxylation) to diphenylcarbodiimide, which then trimerises and (2) PhNCO is decarboxylated with subsequent trimerisation of the resulting diphenylcarbodiimide.

Fink showed [56,77,78] that the interaction of organic isocyanates with cyclic silazanes proceeds in the same way as the interaction with silylamines via the Si–N bond, while in the presence of the N–H bond the latter is not involved in the reaction. Thus the cyclosilazanes (VIII) and (IX) react vigorously with organic isocyanates, forming derivatives of 1,3,5-triaza-2-silacyclohexanediones [56,77,78], which are cyclic analogues of silylbiurets:

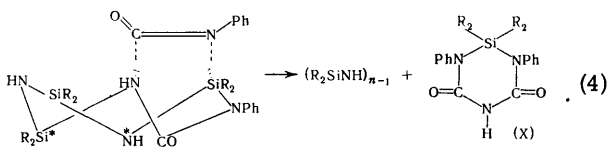


The structures of the compounds obtained were demonstrated by hydrolysis (when R = Ph, 1,5-diphenylbiuret is formed), ^{1}H NMR spectra, and X-ray diffraction [79].

According to the proposed reaction mechanism [56,77], there is initially a cycloaddition to the Si–N bond of the silazane via the following scheme:

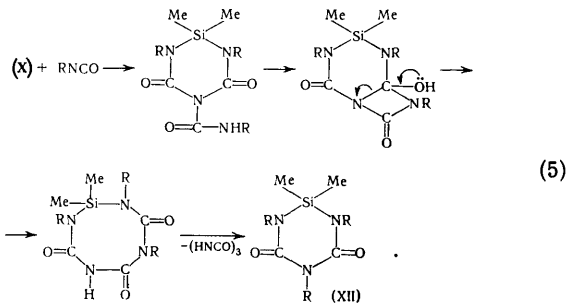


The heterocycle (XI) formed can react further in two ways: by combining with another molecule of PhNCO via the Si–N bond adjoining the PhN–Si group or it can react via Scheme 4, where the transannular interaction between the Si* and N* atoms lead to ring contraction and the elimination of cyclosilazane:



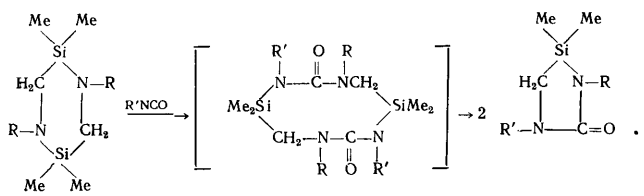
When an excess of the isocyanate (in relation to two moles of PhNCO per Me_2SiNH structural unit) is used, the number of moles of compound (X) formed is inconsistent with the theoretical value. Depending on the ratio of the initial reactants and the type of silazane, a greater or smaller amount of unidentified product is formed, which has been interpreted as supporting a stepwise reaction involving the Si–N bonds of the silazane, since the formation of such products on simultaneous reaction via all the Si–N bonds could not be explained.

At an elevated temperature (120–160°C) further reaction of the isocyanate with 1,3,5-triaza-2-silacyclohexanediones (X) or the direct reaction of cyclosilazanes with a large excess of the isocyanate leads to the formation, via a stage in which unstable macrocyclic compounds are produced, of 1,3,5-trisubstituted derivatives of 2,2-dimethyl-1,3,5-triaza-2-silacyclohexanediones (XII) [56,77]. The reaction can be regarded as cycloaddition to the RNSi–N bond in accordance with Eqn. (3) or as transacylation by the isocyanate [reaction (5)] via the formation of an eight-membered ring with subsequent elimination of cyanuric acid:



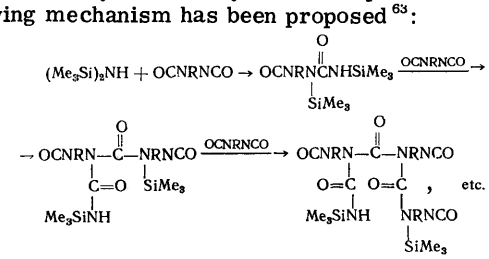
The use of an excess of diisocyanate in this reaction leads to compounds (XII) with free NCO groups [56,80,81] [for example, R-3-NCO-4-MeC_6H_3, $-(CH_2)_6NCO$, or $-C_6H_4CH_2C_6H_4NCO$ respectively for *p*-tolylene, hexamethylene, and diphenylmethylene diisocyanates].

Cyclic aminosilanes, derived from the recently discovered heterocyclic 2,5-disilapiperazine system [82], react vigorously with isocyanates to form five-membered silacycloureas. Ten-membered products resulting from the insertion of two molecules of isocyanate, which rearrange to five-membered rings by virtue of the ease of the transannular interactions between the Si and N atoms, are evidently formed in the first stage [82]:

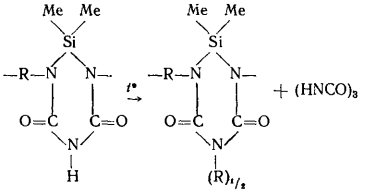


Reactions with di-isocyanates. The reactions of organoaminosilanes and silazanes with diisocyanates proceed similarly to the reactions with these compounds with monoisocyanates and lead to the formation of monomeric or polymeric silylureas and silylbiurets depending on the conditions, the reactant ratio, and the functional groups in the aminosilane [63,66,78,83–87], aromatic diisocyanates being more reactive than aliphatic diisocyanates [66].

It has not been possible to achieve the reaction between hexamethylene diisocyanate and HMDS [63]. At 30–35°C there is no interaction and at 80°C the diisocyanate polymerises. Under these conditions, HMDS is completely recovered from the reaction. When an excess of the diisocyanate (up to tenfold) is used, a polyisocyanate is also formed. Evidently at elevated temperatures HMDS behaves merely as a catalyst for this process. The following mechanism has been proposed [63]:

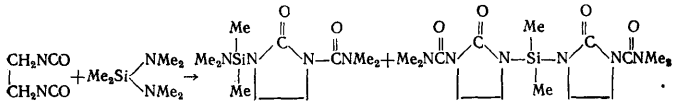


The reaction of hexamethylcyclotrisilazane with diisocyanates at 110°C leads to the formation of transparent, elastic, linear polymers with structural units (XIII), which decompose on heating above 110°C with elimination of cyanuric acids, giving cross-linked polymers with the structural units (XIV), exhibiting a high resistance to the action of acids[77]:



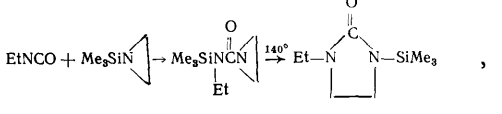
(XIII) (XIV)

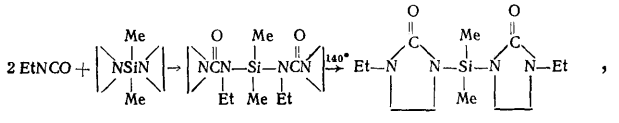
An interesting reaction with formation of cyclic silylurea derivatives (*N*-silylimidazolidinones) was discovered by Scherer and Schmidt[88]:



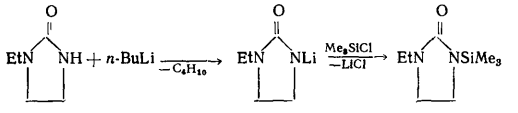
(70%) (20%)

According to the data of the same workers[89], derivatives of *N*-silylimidazolidinone can be obtained also in a different way: by a thermal rearrangement with the expansion of the rings of the silylureas formed in the reaction between monoisocyanates and *N*-silylaziridines:

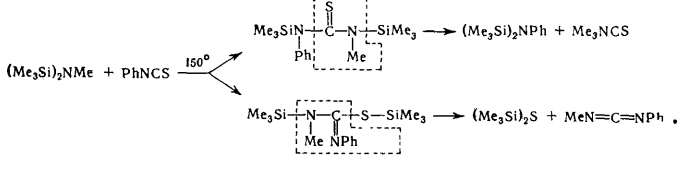




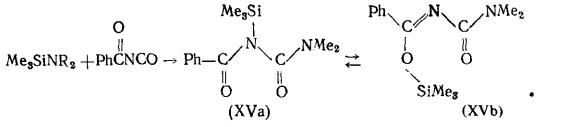
or via the lithio-derivative of imidazolidinone:



Reactions with isothiocyanates. The addition of silylamines and silazanes to isothiocyanates[53-55,57,61,62,66,74,90] proceeds via the same mechanism as the addition to isocyanates but much less vigorously[66,90] and leads to the corresponding organosilicon thiourea derivatives. It has been shown for the reaction of hexamethyldisilazane with PhNCS[90] that, in contrast to isocyanates, under severe conditions there is a possibility of addition not only to the C=N but also the C=S bond, which has been confirmed by the composition of the decomposition products of the intermediates:

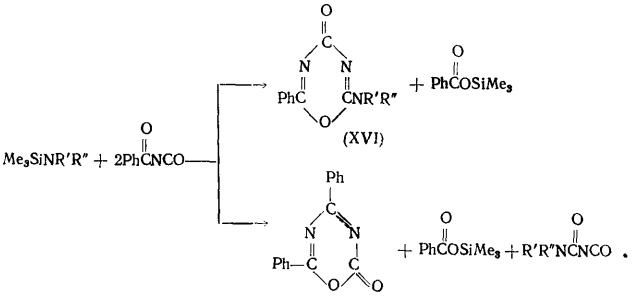


Reactions with acyl isocyanates. A characteristic feature of the reaction of aminosilanes with acyl isocyanates consists in the ability of the latter to be involved not only in 1,2- but also in 1,4-addition. Thus the reaction of dialkyl-*N*-trimethylsilylamines and benzoyl isocyanate in proportions of 1 : 1 gives a high yield of *NN*-dialkyl-*N'*-benzoyl-*N'*-trimethylsilylurea (1,2-addition), which is believed to be involved in the tautomerism (XVa) ⇌ (XVb) on the basis of ^{1}H NMR data[91-93]:



(XVa) (XVb)

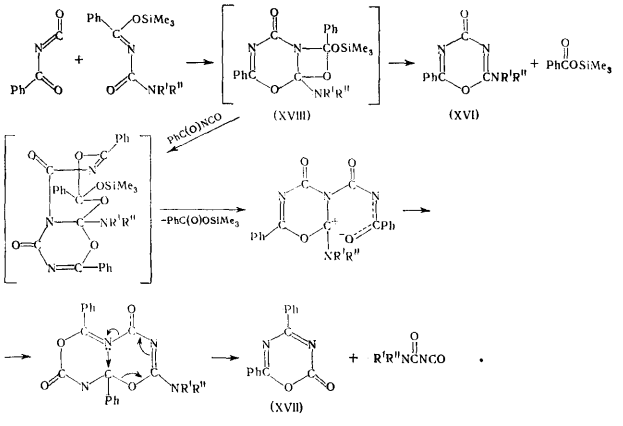
When a second acyl isocyanate molecule acts on the resulting urea or the silylamine reacts with two moles of the acyl isocyanate, the products are (in contrast to the reaction with isocyanates) derivatives of oxadiazinone [(XVI) and (XVII)], benzoyloxytrimethylsilane, and *NN*-dialkylcarbamoyl isocyanate and not silylbiurets:



(XVI)

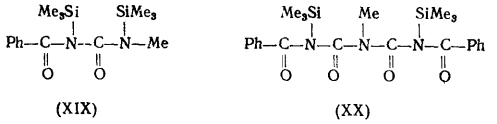
(XVII)

This reaction is regarded as proof of the existence of the iso-form of silylurea. The formation of the oxadiazinones (XVI) and (XVII) can be accounted for by the 1,4-addition of precisely this form of silylurea to benzoyl isocyanate[91,92]. The reaction mechanism evidently includes the formation of an unstable 1 : 1 adduct (XVIII) and its subsequent reactions via the following mechanism[91,92]:



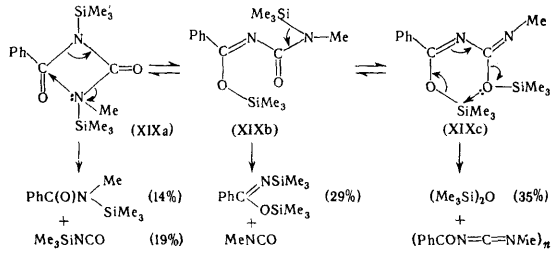
(XVIII) (XVI) (XVII)

In contrast to dialkyl-*N*-(trimethylsilyl)amines, heptamethyldisilazane $(Me_3Si)_2NMe$ forms with benzoyl isocyanate 1 : 1 (XIX) or 1:2 (XX) adducts depending on the reactant ratio[93]:

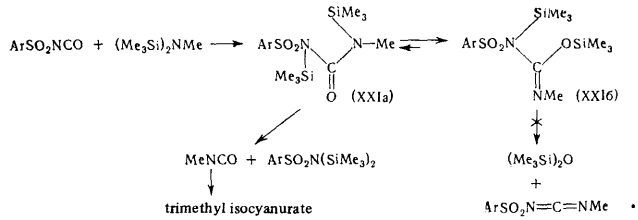


(XIX) (XX)

According to ^{1}H NMR data, the adduct (XIX) is a mixture of at least two isomers and the composition of the products formed on its pyrolysis indicates the possibility of the existence of three isomers of (XIX)[93]:



Reactions with sulphonyl isocyanates. Sulphonyl isocyanates react with aminosilanes (in proportions of 1 : 1) to give a quantitative yield of *N*-silyl-substituted sulphonated ureas, among which the main species is the carbonyl form (XXIa)[94]. This is confirmed by infrared spectroscopic and ^{1}H NMR data and also by the composition of the products of the pyrolysis of the compounds in which an organic isocyanate (or its trimer) and *NN*-bis(trimethylsilyl)sulphonamide are formed, in contrast to the pyrolysis of the analogous adducts of isocyanates and aminosilanes:

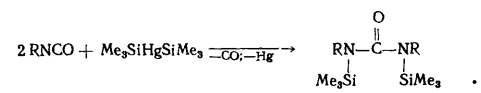


In conclusion of this section, one may note that, apart from the direct interaction of aminosilanes with isocyanates, *N*-silylureas are also formed in the reaction of aminosilanes with carboxylic acid azides[95]. At a low temperature in the presence of catalytic amounts of $AlCl_3$ or close to the decomposition temperature of the azide, this reaction proceeds as a double decomposition with formation of silyl azides and acid amides:

$$RC(O)N_3 + Me_3SiNR'R'' \rightarrow Me_3SiN_3 + RC(O)NR'R''$$

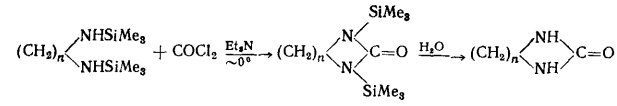
When this temperature is exceeded, the acid azide decomposes with liberation of the isocyanate, which then reacts further with the silylamine present to give a silylurea. In particular, high yields of trimethylsilyl-substituted derivatives of *N*-butyl-*N'*-phenyl- and *N*-benzyl-*N'*-phenylureas were obtained in this way (the position of the silyl residue in the ureas was not determined).

The interaction of isocyanates with bis(trimethylsilyl)-mercury in hexametapol yielded bissilylureas[96]:

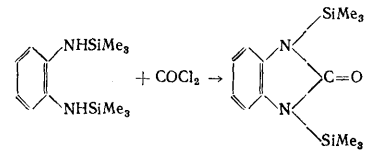


e. Other Methods of Synthesis

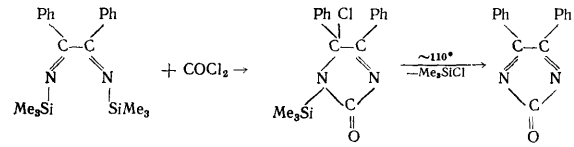
Birkofer et al.[38] showed in 1960 that cyclic derivatives of silylurea are formed in 60–75% yield in the reaction of phosgene with bissilyl-substituted tri- and tetra-methylenediamines in the presence of triethylamine. In the hydroxysis or methanolysis of these compounds organic derivatives of urea, which could not be synthesised by direct phosgenation of $\omega\omega'$-diamines, were obtained in quantitative yields:



Under the same conditions, *NN'*-bis(trimethylsilyl)-*o*-phenylenediamine reacts with $COCl_2$ to give *NN*-bis(trimethylsilyl)benzimidazol-2-one[38]:



while benzylbis(trimethylsilyl)imine is converted at −10°C into the thermally unstable silylimidazoline[97], which decomposes on heating to 4,5-diphenylimidazol-2-one:



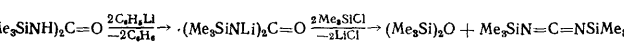
In contrast HMDS reacts with phosgene mainly according to the mechanism

$$6(Me_3Si)_2NH + 3COCl_2 \rightarrow 2(Me_3Si)_2NH + 5Me_3SiCl + 3Me_3SiNCO + NH_4Cl$$

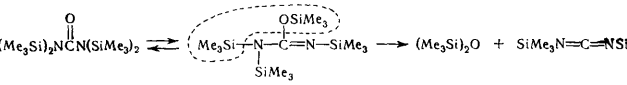
and not to give silyl-substituted ureas as might have been expected[18]. The interaction of metallated HMDS with $COCl_2$ also did not lead to the formation of the expected tetrasilylurea[18,98,99]. The stable bis(trimethylsilyl)carbodiimide and hexamethyldisiloxane were isolated as the main products of this reaction, the mechanism of which the authors were unable to elucidate:

$$2(Me_3Si)_2NNa + COCl_2 \rightarrow 2NaCl + (Me_3Si)_2O + Me_3SiN{=}C{=}NSiMe_3$$

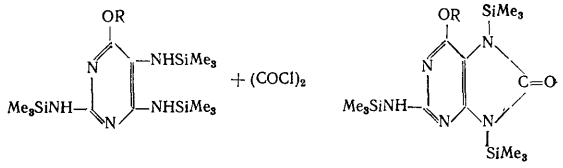
The attempts to obtain tetrasilylurea via the lithio-derivative of bis(trimethylsilyl)urea were also unsuccessful[98,99]. Despite the formation of lithium chloride, the same products were isolated from the reaction mixture:



Tetrasilylureas are nevertheless evidently formed as intermediates in these reactions, but, owing to their thermal instability, they decompose to the above compounds. Bearing in mind the tendency of *N*-silylureas (and silylamides in general) to undergo tautomerism and also the thermal instability of the compounds with the Si–N–C–X bond system (X = electronegative groups) observed previously[7,100], the following mechanism of the decomposition reaction appears to be most likely:



On treatment with oxalyl chloride, 2,4,5-tris(trimethylsilylamino)pyrimidines form compounds with a urea moiety in the ring system—silylpurines[101]:



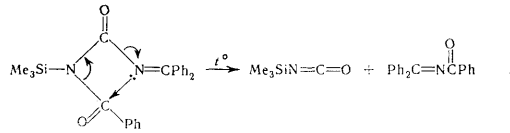
2. PHYSICAL PROPERTIES

Depending on the substituents at the silicon and nitrogen atoms, *N*-silylureas are liquid, oily, or crystalline substances, which are in most cases readily soluble in acetone, carbon tetrachloride, chloroform, ether, dioxan, and THF and more sparingly soluble in benzene, toluene, xylene, and petrol[18,41,53,66]. Their solubility in petroleum ether is as a rule low. Partly nitrogen-substituted derivatives, such as $Si(NHCONHPh)_4$ and $(OCN)_2Si(NHCONHPh)_2$, do not have distinct melting points and like urea are sparingly soluble in organic solvents.[41] Crystalline products sublime on heating *in vacuo*, and this can be used for their purification[18,41,53].

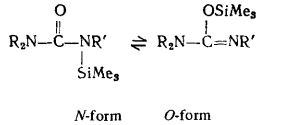
The thermal stability of *N*-silylureas was not specially studied, but it evidently varies within wide limits and depends mainly on the structure and the presence of secondary impurities. Thus the compounds $Me_3SiNHC(O)NPh_2$ and $Me_2Si(NHCONPh_2)_2$ decompose fully at about 250°C to isocyanatosilane and diphenylamine. This reaction was proposed for the synthesis of isocyanatosilanes[6]. On heating urea with HMDS at 90–110°C in the presence of $(NH_4)_2SO_4$, Me_3SiNCO is formed in a yield in excess of 90%, which is also evidence for the thermal instability of the intermediate silylurea.

On the other hand, the compound $Me_3SiNHC(O)NEt_2$ is stable in the absence of moisture up to 300°C and $Me_3SiNHC(O)NBu_2$ and $Me_3SiNHC(O)NMe_2$ merely sublime on heating to 220°C.[41] On the other hand, according to the data of other workers[18], in the presence of HMDS the complete decomposition of the latter compound to Me_3SiNCO and Me_2NH occurs already at the boiling point of HMDS (about 126°C).

Tetrakis(trialkylsilyl)ureas could not be obtained, probably owing to their thermal instability[98,99]. The decomposition of *N*-acyl-*N*-silylureas on heating proceeds with formation of isocyanatosilane and *N*-(diphenylmethylene)benzamide[75]:



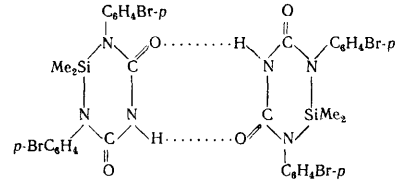
By analogy with *N*-trimethylsilylamides of carboxylic acids, which are capable of amide–isoamide tautomerism involving the Me_3Si group[30], Klebe et al.[53] suggested the possibility of the same type of tautomerism also for silicon-containing ureas:



N-form *O*-form

Comparison of the infrared and ultraviolet spectra of the compounds[11,18,41,52,56,61–63,66,70,102] with those of model molecules does not, however, allow unambiguous conclusions in this respect. All the compounds have absorption bands in the range 1500–1700 cm^{-1}, characteristic of secondary and tertiary amides. The study of a number of *N*-organosilyl-*N'*-phenylureas[70] showed that in the solid state they apparently contain only hydrogen-bonded N–H groups, while in solution there exist also associated N–H groups, to which the 3413 and 3517 cm^{-1} bands correspond. The 3413 cm^{-1} band was assigned to the phenyl–NH group and the 3517 cm^{-1} band to the silyl–NH group. The 3280, 3323, 3324, 3341, and 3349 cm^{-1} bands, observed in the spectra of suspensions of these compounds, were assigned respectively to bound phenyl–NH and silyl–NH groups. The comparatively high stretching vibration wavenumbers of the free NH group and their appreciable displacement on passing from solutions to suspensions (from 176 to 194 cm^{-1} for various substituents at the silicon atom), demonstrates the amphoteric nature of the silyl–NH group and the greater mobility of its proton compared with that of the phenyl–NH group (the corresponding shift is 133 cm^{-1}). One of the explanations of this finding involves the participation of the lone electron pair of the nitrogen atom in the formation of a bond with silicon and hydrogen, the degree of involvement of this pair depending on the nature and strength of the intermolecular interaction. In the formation of a hydrogen bond the lone electron pair is probably located at the silicon–nitrogen bond[70].

According to X-ray diffraction analysis, the molecules of 2,6-di(*p*-bromophenyl)-1,1-dimethyl-1-sila-2,4,6-triazacyclohexanedione (the product of the reaction of the *p*-bromophenyl isocyanate with HMDS) are dimerised in the crystal by hydrogen bonding[79]:



The spectra of silylureas obtained by the interaction of Et_2NSiMe_3 or silazanes with phenyl isocyanate do not contain the intense band due to the stretching vibrations of the silicon–nitrogen band, which is observed in the spectra of the initial compounds at 925 and in the range 900–950 cm^{-1} respectively. Its disappearance is explained by the fact that the corresponding vibration in silylureas is no longer characteristic and is not observed in the same part of the spectrum[63]. Other workers assign the bands at 850, 848, and 840 cm^{-1} to the ν_{as} vibrations of the Si–N bond in $(Me_3SiNH)_2CO$, $(Me_3Si)_2NC(O)NHPh$, and $Si(NHCONH_2)_4$ respectively[18].

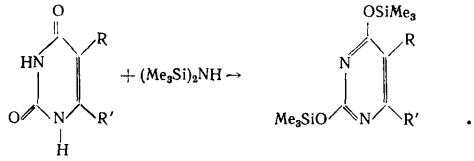
The infrared spectrum of tetraureidosilane $Si(NHCONH_2)_4$ has an absorption band at 2175 cm^{-1}, which is the most intense in the sublimate formed on heating the urea *in vacuo* at 160°C. It is assigned to the ν_{as} stretching vibrations of the N=C=N group, the formation of the latter being explained by partial decomposition via the reaction[18]

$$Si(NHCONH_2)_4 \rightarrow 4H_2O + Si(N{=}C{=}NH)_4 .$$

The ^1H NMR spectra of a number of silylureas have been published[52,66,73,75,89,92–94]. The study of the nature of the Me_3Si signal as a function of temperature showed that in the case of a number of silylureas, for example $Me_3SiN(Me)C(O)NMe_2$ and $PhSO_2N(SiMe_3)C(O)NMe_2$, the

signal due to the protons of this group does not split at low temperatures[92]. This is evidence for the absence of appreciable tautomerism or for the presence of a mixture of *O*- and *N*-forms with their very rapid interconversion even at low temperatures. On the other hand, the signal for other compounds, for example $PhC(O)N(SiMe_3)C(O)NR_2$ [76,92] and $Ph_2C{=}NC(O)N(SiMe_3)R$ [75] splits into two at temperatures below −43°C, which has been interpreted as supporting the 1,3-transfer of the Me_3Si group, i.e. the presence of the *O*-silyl form of ureas (amide–isoamide tautomerism). As already mentioned above, the formation of the isoamide form is also indicated by a number of chemical reactions of silylureas[75,76,92].

The presence of only the *O*-form has been established for certain cyclic silylureas. For example, silylation of uracil derivatives with HMDS results in the formation of silyl derivatives which have the structure of siloxypyrimidines and not *N*-silyluracils[23,103]:



3. CHEMICAL PROPERTIES

The majority of silylureas are unstable with respect to hydrolysis[18,41,52,55,57,61–63,66,68,69,73,95,104] and readily deliquesce in moist air[66]. They are hydrolysed with dissociation of the Si–N bond and the formation of organosilanols (or organosiloxanes) and organic urea derivatives[41,68,73,75,95]:

$$2\,Me_3SiNHC(O)NR_2 + H_2O \rightarrow (Me_3Si)_2O + 2H_2NC(O)NR_2 \quad .$$

On the other hand, in contrast to asymmetric ureas, *NN'*-bis(trimethylsilyl)urea is hydrolysed by water with considerable difficulty[18]. According to the authors, electron density is in this case redistributed in the direction which lowers the double bond character of the linkage between the Si and N bonds and this ultimately reduces the susceptibility of the silicon atom to nucleophilic attack. Incidentally, one cannot rule out the possibility that hydrolysis is slow because the reaction takes place in a heterogeneous medium owing to the sparing solubility of the silylurea in water.

N-Silylureas, particularly aromatic derivatives, are powerful silylating agents, like carboxylic acid silylamides[22,25,26,36]. Their reactions with amines and hydroxy-compounds are rapid even at room temperatures and lead to the quantitative formation of the corresponding silyl derivatives with removal (or in some cases without removal) of one of the components of the equilibrium mixture. For example, $Me_3SiN(Ph)CONHPh$ and *NN'*-dimethylurea are completely converted after 1 min at 20°C[22]:

$$Me_3SiN(Ph)CONHPh + MeNHCONHMe \rightarrow Me_3SiN(Me)CONHMe + PhNHCONHPh \quad .$$

Experiments with compounds containing an active hydrogen atom at a carbon atom (acetylacetone, nitromethane, and malononitrile) showed that these too are capable of undergoing the silyl–proton exchange with silylureas[22].

Alcoholysis

When silylureas are treated with an alcohol, solvolysis takes place with formation of alkoxysilanes and organic urea derivatives[25,88,89,105], for example:

$$Me_3SiNHCNMe_2 + EtOH \rightarrow Me_3SiOEt + H_2NCNMe_2 \quad .$$

The methanolysis of optically active silylureas and biuret is accompanied, with rare exceptions[74], by the reversal of the configuration at the silicon atom[73], which indicates an S_N2 mechanism for this reaction:

$$(+)\text{-}R_3Si^*NCONHMe + MeOH \rightarrow (+)\text{-}R_3Si^*OMe + PhNHCONHMe \quad ,$$

$$(-)\text{-}R_3Si^*NCONCONHPh + MeOH \rightarrow (+)\text{-}R_3Si^*OMe + PhNHCONCONHPh \quad ,$$

where $R_3Si^* = (\alpha\text{-}C_{10}H_7)PhMeSi^*$.

Aminolysis

The compounds readily enter into a reversible reaction with amines, which is fully displaced to the right owing to the sparing solubility of the resulting urea or biuret derivatives, and, like alcoholysis, is accompanied by the reversal of the configuration[73].

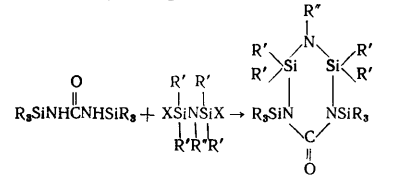
$$(+)\text{-}R_3Si^*NCONHMe + Me_2NH \rightleftarrows (+)\text{-}R_3Si^*NMe_2 + PhNHCONHMe \quad .$$

Silylureas react with acids according to the mechanism[74]:

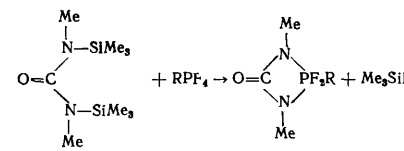
$$R_3SiNCNMe_2 + PhCOOH \rightarrow R_3SiOCPh + PhNHCNMe_2 \quad .$$

Kaufmann et al.[74] showed that, in contrast to silylamines and *N*-silylthioureas, the Si–N bond in silylureas is not cleaved under the influence of *p*-nitrobenzoyl chloride.

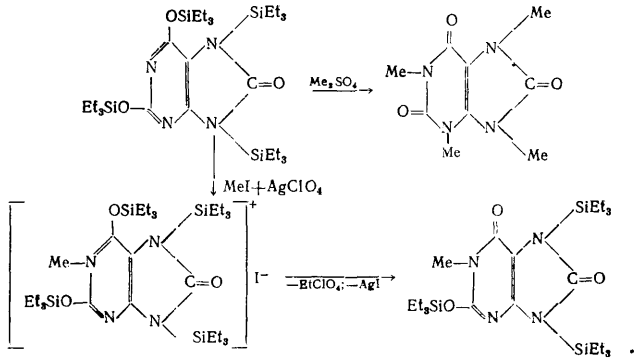
1,3-Dihalogenosilazanes react with *NN*-bis(trimethylsilyl)ureas to form cyclic products[106]:



When acted upon by fluorophosphoranes, asymmetric disilylureas form fluorophosphadiazetidinediones with cleavage of the Si–N bond[107]



Silyl derivatives of uric acid react with dialkyl sulphates or methyl iodide to form alkyl derivatives of uric acid[101]:



4. APPLICATIONS

The interest in silylureas is due to their ability to form compositions which are self-hardening at the normal temperature, their high silylating activity, and many other valuable properties.

According to patent data, monomeric *N*-triorganosilylureas are effective agents for the treatment of fabrics, paper, leather, and non-fibrous materials (for example, cellophane) in order to make them hydrophobic and creaseless, to reduce their brittleness, and to improve other characteristics[5,17]. *N*-Silylureas can be used in the synthesis of plastics[54], lubricating oils, and hydraulic liquids[36,65], for the stabilisation of poly(vinyl chloride)[42], as vulcanisers for the cold-hardening of polysiloxanes[108], and for other purposes[109,110]. Some of these compounds exhibit pharmacological and pesticidal properties[17,36,54,65,-111,112]. Silylureas with unsaturated groups in the molecule have been patented in connection with the synthesis of block copolymers and the vulcanisation of polyorganosiloxane elastomers[72].

The polysilylureas formed when isocyanatosilanes react with polyamines can be thermoplastic or thermoreactive, depending on the type of the initial reactants; they have been suggested for the formation of moulded articles, laminated materials based on fibreglass, and for many other purposes[43,113-115]. Polysilylurea films have a high breakdown voltage and tensile strength[83,85].

Polysilylureas obtained from organic polyisocyanates and silylamines have many valuable properties. Polymeric materials of this kind can be used to synthesise elastomers[116], fibres, and films[117] and for other purposes[87,118]. The susceptibility of the Si–N bond to hydrolysis does not preclude their employment since, on being acted upon by atmospheric moisture, the film is only partly hydrolysed on the surface and the liberated siloxane plasticises the material.

The polyureidosilazanes, obtained when linear or cyclic silazanes are treated with organic polyisocyanates, adhere effectively to metals, glass, and rubber, are resistant to the action of water, organic solvents, acids, and alkalis, and have satisfactory dielectric and other properties[78,86,119].

Monomeric and polymeric silylbiurets[64,65,84,120] have been patented as antifoaming and anti-ageing agents, as agents accelerating vulcanisation, and as plasticisers and herbicides.

III. SILYLISOUREAS

Silylisoureas were obtained for the first time in 1968 by the reaction of cyanic acid esters with aminosilanes or silazanes[121,122]. This reaction proceeds mainly similarly to the reaction of aminosilanes with isocyanates, i.e. with cleavage of the Si–N bond and addition to the multiple bond of the cyanate. However, in contrast to isocyanates, cyanic acid esters can also enter into an exchange reaction involving the Si–N bond of the aminosilane similar to the Brown cleavage reaction. Dialkylaminosilanes are known[123] to enter into a similar reaction with bromocyanogen, forming bromosilane and dialkylcyanamide. When there is a possibility of competing reactions involving the Si–N and N–H bonds, as happens in the case of secondary aminosilanes, the Si–N bond is cleaved first. The interaction of cyanates with various types of aminosilanes is to some extent specific.

The reaction of cyanic acid esters with dialkyl-*N*-trimethylsilylamines in 1:1 proportions results in the quantitative yield of *NN*-dialkyl-*N'*-trimethylsilylisoureas[121]:

$$ROC{\equiv}N + R'_2NSiMe_3 \rightarrow ROC(=NSiMe_3)NR'_2 ,$$

where R = aryl and R′ = alkyl. The same compounds can be obtained by the silylation of *NN*-dialkylisoureas with chlorotrimethylsilane[121].

When the resulting isourea is acted upon further by the cyanate, the products are 2-dialkylamino-4,6-diaryloxy-*s*-triazines and aryl trimethylsilyl ethers:

$$ROC(=NSiMe_3)NR'_2 + 2ROC{\equiv}N \rightarrow \text{2-dialkylamino-4,6-diaryloxy-}s\text{-triazine} + Me_3SiOR .$$

Thus, in contrast to isocyanates, cyanic acid esters do not form 1:2 adducts with dialkyl-*N*-trimethylsilylamines, since the first stage of this reaction is an addition process and the second is a process of the type of the Brown reaction.

The reaction of alkyl-*N*-trimethylsilylamines with aryl cyanates in proportions of 1:1 results in the initial formation of *N*-alkyl-*O*-aryl-*N'*-trimethylsilylisourea (possibly in a mixture with its isomeric form). However, these compounds cannot be isolated, since under the influence of the cyanate they are immediately converted into *N*-alkyl-*O*-aryl-*N'*-cyanoisoureas with elimination of the Me_3Si group:

$$RNHSiMe_3 + ArOCN \rightarrow \left[ArO{-}C(=NR){-}NHSiMe_3 \rightleftarrows ArO{-}C(NHR){=}NSiMe_3 \right] \xrightarrow{ArOCN} ArO{-}C(NHR){=}N{-}CN + ArOSiMe_3 .$$

In addition, phenol, carbodiimide, and polymerisation products of the latter are formed in small amounts.

The reaction with HMDS proceeds similarly. In this case too it was impossible to isolate the 1:1 adduct, which is converted under the influence of ArOCN into *O*-aryl-*N*-cyano-*N'*-trimethylsilylisourea. At an elevated temperature a silylated cyanoguanidine is formed in addition. The reaction can be represented as follows:

$$ArOCN + (Me_3Si)_2NH \rightarrow \left[ArO{-}C(=NSiMe_3){-}NHSiMe_3 \right] \xrightarrow[ArOSiMe_3]{ArOCN} \left[ArO{-}C(NHSiMe_3){=}N{-}C{\equiv}N \right] \rightleftarrows \left[ArO{-}C(=NSiMe_3){-}NH{-}C{\equiv}N \right] \rightleftarrows \left[ArO{-}C(=NSiMe_3){-}N{=}C{=}NH \right] .$$

On the other hand, the reaction of methyl-*NN*-bis(trimethylsilyl)amine with ArOCN (in proportions of 1 : 1 or 1 : 2) is of the double addition type with formation of the 1 : 2 adduct—the diaryl ester of N^2-methylimino-N^1N^3-bis(trimethylsilyl)carbamic acid. Only in the presence of an up to sixfold excess of the cyanate are the Me_3Si groups exchanged for CN with formation of the diaryl ester of N^1N^3-dicyano-N^2-methyliminocarbamic acid, which tends to polymerise:

$$(Me_3Si)_2NMe + 2PhOCN \rightarrow \begin{matrix} PhO-C=NSiMe_3 \\ | \\ Me-N \\ | \\ PhO-C=NSiMe_3 \end{matrix} \xrightarrow[-PhOSiMe_3]{+PhOCN} \begin{matrix} PhO-C=N-CN \\ | \\ Me-N \\ | \\ PhO-C=N-CN \end{matrix} .$$

Silylisoureas are colourless viscous oils, which can be distilled without decomposition in a high vacuum. Their infrared spectra contain intense bands in the ranges 1745–1755 and 1685–1698 cm^{-1}, which are characteristic of the stretching vibrations of the double bond of the silylated imido-group $\rangle C{=}NSi\langle$.

At high temperatures (for example under the conditions of gas-chromatographic analysis) the silylisoureas decompose via the mechanism

$$RO-\underset{\underset{NR'_2}{|}}{C}=N-SiMe_3 \xrightarrow{t^\circ} ROSiMe_3 + R'_2N-C\equiv N .$$

On treatment with alcohols or on prolonged standing in air, they are desilylated to organic isoureas. The reaction with acid chlorides also proceeds with the cleavage of the Si–N bond and the formation of acyl isoureas and chlorosilanes[121].

IV. CARBOFUNCTIONAL ORGANOSILICON DERIVATIVES OF UREA

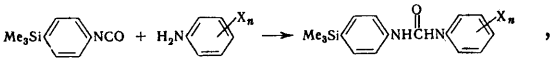
1. METHODS OF SYNTHESIS

Silicon-containing derivatives in which the urea moiety and the silicon atoms are separated by a group of atoms have been less thoroughly investigated. The majority of the methods for their preparation reduce mainly to the familiar procedures of organic chemistry for the synthesis of alkyl (or aryl)-substituted urea derivatives (isocyanate condensation transamination, and other reactions) and are based on the employment as the starting materials of the corresponding isocyanates and amines or compounds containing an amino-group.

a. Isocyanate Condensation Reactions

Two versions of isocyanate condensation via a combination of organic and organosilicon starting materials are possible: (1) the interaction of carbofunctional organosilicon isocyanates with organic or organosilicon amines and (2) the interaction of organic isocyanates with carbofunctional silicon-containing amines.

Until 1959, the first reaction was illustrated by only one example[124]:



where X = Cl, MeO, EtO, or H and n = 1 or 2.

A wide variety of both mono- and di-silyl-substituted ureas became available recently after the development of convenient methods for the preparation of carbofunctional organosilicon isocyanates[125]. In particular, the first and simplest representatives of aliphatic silicon-containing ureas $R_3Si(CH_2)_nNHCONH_2$ [7,126–130] and also ureas with a disiloxane bond of the type $[H_2NCONH(CH_2)_nSiMe_2]_2O$ [6,7] were obtained recently from these compounds.

Carbofunctional organosilicon isocyanates as a rule react exothermically with amines to form the corresponding urea derivatives in virtually quantitative yields [6,7,126,127,130–136]:

$$R_3Si(CH_2)_nNCO + Bu_2NH \rightarrow R_3Si(CH_2)_nNHC(=O)NBu_2 ,$$

where R = Me, Et, or Ph and n = 1 or 3.

ω-Isocyanatoalkylsilanes with an NCO group in the γ-position are more reactive than α-isocyanatoalkylsilanes[130,135].

When isocyanates react with hydrazine and its derivatives, silylsemicarbazides are formed[134,137,138]:

$$[OCN(CH_2)_3SiMe_2]_2O + R_2NNH_2 \rightarrow [R_2NNHC(=O)NH(CH_2)_3SiMe_2]_2O,$$

and the reaction with aminoethers gives a high yield of carbamidoiminoethers[139]:

$$RC(=NH)OEt + p\text{-}HMe_2SiC_6H_4NCO \rightarrow RC(=NC(=O)NHC_6H_4SiMe_2H\text{-}p)OEt .$$

Organosilicon isocyanates react just as easily with acid hydrazides to form the compounds $R_3Si(CH_2)_n$. .NHCONHNHCOAr.[130]

The interaction with acid amides is more difficult[130]. For example, benzamide and sulphonamides form the substituted ureas $R_3Si(CH_2)_nNHCONHCOPh$ and $R_3Si(CH_2)_n$. .$NHCONHSO_2Ar$ only after prolonged heating with isocyanate in dimethylformamide (DMF) in the presence of triethylamine as the catalyst.

Symmetrical silicon-containing ureas have been obtained on heating carbofunctional organosilicon isocyanates with water in DMF[140]:

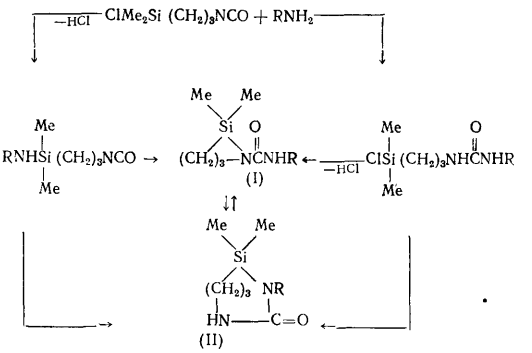
$$R_3Si(CH_2)_nNCO + H_2O \rightarrow [R_3Si(CH_2)_nNHCOOH] \xrightarrow{-CO_2} R_3Si(CH_2)_nNH_2 \xrightarrow{R_3Si(CH_2)_nNCO} R_3Si(CH_2)_nNHC(=O)NH(CH_2)_nSiR_3,$$

where R = Me, Et, or Pr and n = 1 or 3. In the presence of an excess of water an organosilicon amine is formed in this reaction.

In contrast to the reactions with amines and alcohols, where α-isocyanatomethylsilanes have a reduced reactivity compared with γ-isocyanatoalkylsilanes, in the reaction with water these compounds have virtually the same reactivities[140]. Evidently the overall electropositive effect of the R_3SiCH_2 group in α-isocyanates is manifested in two ways: on the one hand, the electrophilicity of the carbonyl carbon atom is reduced and the rate of reaction of the isocyanate with water is diminished and, on the other, the basicity of the resulting amine is enhanced, as a result of which the rate of the secondary reaction (the reaction with the isocyanate) rises.

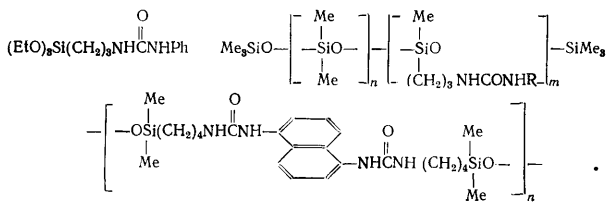
Isocyanates with other reactive groups or atoms at the silicon atom can interact with amines via these groups too. Thus the reaction of $ClMe_2Si(CH_2)_3NCO$ with an excess of a

primary amine results in the formation of 1-alkylcarbamido-1-aza-2-silacyclopentanes (I), which are in a state of tautomeric equilibrium with 1,3-diaza-4-silacycloheptan-2-ones (II)[7,141]:

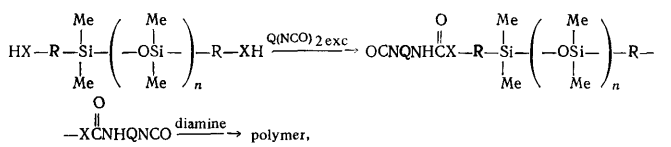


The reactions of organosilicon diisocyanates with diamines, hydrazines, and dihydrazides yielded respectively polysilylureas[142-144], polysilylureylenes[142,145], and polyacylsemicarbazides[146,147].

The reaction of organic isocyanates with carbofunctional organosilicon amines has been little investigated, although it has been shown for the synthesis of monomeric, oligomeric, and polymeric ureas that it is of a general type[148-151]. In particular, compounds having the following formulae have been obtained:



A number of oligomeric and polymeric compounds containing in the chain alternating siloxane, urethane, and urea units have also been synthesised by the isocyanate condensation reaction using organic diisocyanates[150,151]:



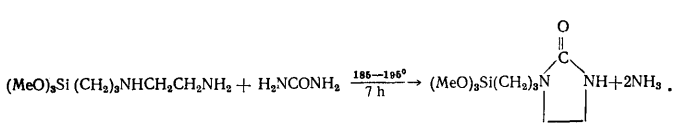
where R and Q = alkylene or arylene and X = O or NH.

b. Transamination Reactions

Silicon-containing ureas are formed in satisfactory yields on prolonged heating of high-boiling organosilicon amines with the urea[152]:

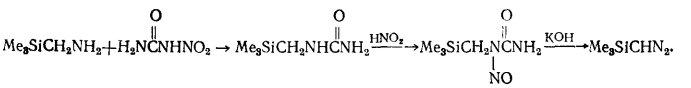
$$2\,(EtO)_3Si\,(CH_2)_3NH_2 + H_2NCONH_2 \xrightarrow[7.5\ h]{185^\circ} [(EtO)_3Si\,(CH_2)_3NH]_2CO + 2NH_3.$$

When organosilicon diamines are used in the reaction, cyclic silylureas are formed[153,154]:



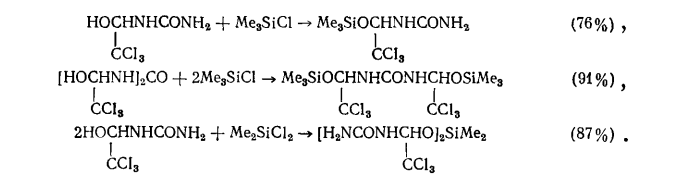
Hydrolysis of such cyclic or linear compounds with alkoxy-groups at the silicon atom leads to the formation of polysiloxanes with urea units in the side chain. Copolymers of these compounds with silanes and siloxanes containing hydrolysable groups at the silicon atom have also been obtained[153,154].

Using the transamination reaction, Seyferth and coworkers[155,156] synthesised *N*-nitroso-*N*-trimethylsilylurea, which is a convenient starting material for the synthesis of the unusually stable trimethylsilyldiazomethane. The synthesis was carried out in accordance with a scheme similar to that used in the synthesis of a diazomethane from *N*-methyl-*N*-nitrosourea:



c. Silylation of Urea Derivatives

When the products of the condensation of chloral with urea are acted upon by chlorosilanes in the presence of an excess of pyridine, high yields of siloxyureas are formed[157]:



Similar derivatives were obtained by treating mono- and di-(hydroxymethyl)ureas with chlorotrimethylsilane and triethylamine[104]. A study of the reaction of mono(hydroxymethyl)urea with Me_3SiCl has shown that, even for an equimolar reactant ratio, Me_3SiCl reacts with the hydrogen atoms of both OH and NH_2 groups:

$$H_2NCONHCH_2OH + Me_3SiCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Me_3SiNHCONHCH_2OSiMe_3 \qquad (39\%).$$

When Me_3SiCl is allowed to react with di(hydroxymethyl)-urea, only the hydrogen atoms in the hydroxy-groups are substituted:

$$O{=}C\,(NHCH_2OH)_2 + 2Me_3SiCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} O{=}C\,(NHCH_2OSiMe_3)_2 \qquad (44\%).$$

Silylation of the hydroxymethyl groups in *NN'*-di(hydroxymethyl)urea proceeds readily also when the latter is acted upon by HMDS, *N*-trimethylsilylacetamide, *NO*-bis(trimethylsilyl)acetamide, diethyl-*N*-trimethylsilylamine, and dimethyl-*N*-trimethylsilylamine at about 35°C in acetone, pyridine, or ethyl acetate, dialkyl-*N*-trimethylsilylamines being the most effective silylating agents[158]. This reaction has been used to silylate the products of the condensation of urea with formaldehyde in order to decompose intramolecular and intermolecular hydrogen bonds in aminoplastics, which leads to the formation of products soluble in organic solvents to which gel-chromatographic research techniques are applicable[158].

According to Kreshkov et al.,[159] the hydroxy-groups in urea-formaldehyde resins can react with alkoxysilanes, probably via the following mechanism:

By combining urea-formaldehyde resins with polyethoxypolysiloxanes, silicon-modified polymers were obtained using this procedure[159].

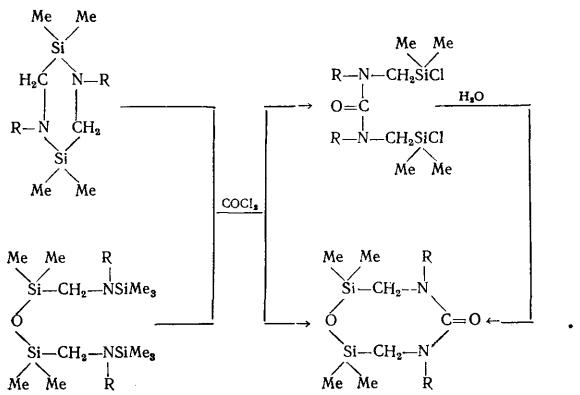
d. Other Reactions

Montgomery[160,161] synthesised symmetrical silicon-containing derivatives by heating aminoalkylsilanes with carbonyl sulphide in an autoclave:

$$PhMe_2SiCH_2NH_2 + COS \xrightarrow[4\ h]{100^\circ;\ 91\ atm} [PhMe_2SiCH_2NH]_2CO + H_2S\ ,$$

$$Me_3SiOSi(Me)_2CH_2NH_2 + COS \xrightarrow{100^\circ;\ 8.6\ atm} [Me_3SiOSi(Me)_2CH_2NH]_2CO + H_2S\ .$$

Linear and cyclic compounds were obtained by treating piperazine rings with phosgene and by synthesis from *N*-silylated α-diamines of the disiloxane series[162]:



When urea is acylated with the chlorides of organosilicon acids, the products are acylureas with a silicon atom in the acyl residue[163,164].

A number of other methods known only in organic chemistry can be used to synthesise organosilicon ureas. In particular, ureas are formed when carbofunctional organosilicon amines are treated with carbamoyl chlorides[6,7]:

$$Me_3SiCH_2NH_2 + Ph_2NC(O)Cl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Me_3SiCH_2NHCNPh_2 \qquad (62\%)$$

and on oxidising the corresponding amines with lead tetraacetate in the presence of an amine[6,7]:

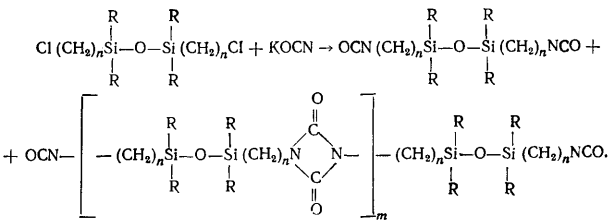
$$Me_2EtSi(CH_2)_3CNH_2 \xrightarrow[DMF]{Pb(OAc)_4} [EtMe_2Si(CH_2)_3NCO] \xrightarrow{AllNH_2} Me_2EtSi(CH_2)_3NHCNHAll.$$

A number of cyclic urea analogues having the structure of uretidinediones were obtained by the reaction of halogenoalkylsilanes with metal cyanates in DMF. The formation of these compounds is due to the dimerisation of the isocyanates, which are the primary reaction products, under the influence of the cyanate salt[165-167]:

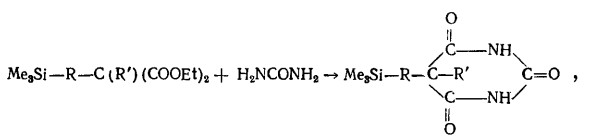
$$R'R_2Si(CH_2)_nCl \xrightarrow[-MCl]{MOCN} [R'R_2Si(CH_2)_nNCO] \rightarrow R'R_2Si(CH_2)_nN(CO)N(CO)(CH_2)_nSiR_2R'\ ,$$

where R and R′ = Me, Et, or Ph, n = 1 or 3, and M = K or Na.

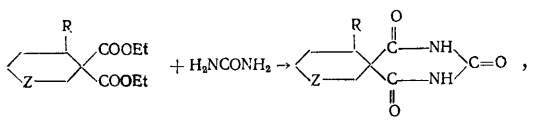
When bishalogenoalkylsilanes are used in this reaction, the analogous oligomeric compounds are formed:



Silicon-containing uretidinediones were obtained in low yields also by treating carbofunctional organosilicon amines with phosgene[7]. Finally, silyl-substituted barbiturates were obtained by the condensation of urea with organosilyl malonates[168,169]:



where R = $-CH_2-$ and R′ = H, Me, or allyl[168] or R = $-C_6H_4-$ and R′ = H or Et[169], and with spirobarbiturates[170]:



where Z = $SiMe_2$ or CH_2SiMe_2 and R = H, Me, or Et.

2. PROPERTIES

Carbofunctional organosilicon ureas are colourless viscous liquids or crystalline substances. Some decompose appreciably on vacuum distillation[171]. They are readily soluble in benzene, acetone, and DMF and are insoluble in water and petroleum ether[130,171].

Silicon-containing acylureas and semicarbazides are crystalline substances soluble in DMF and alcohol and sparingly soluble or insoluble in water, benzene, and carbon tetrachloride[130].

The infrared spectroscopic data for silylureas[6,7,130,132,133,141,142,172], silylsemicarbazides[137], and silylpolyacylsemicarbazides[146] agree well with the amide structure of these compounds. The characteristic absorption bands of the C=O group (amide band I) in the infrared spectra of asymmetric ureas of the type $R_3Si(CH_2)_nNHCONR_2$ are in the region of 1630 cm^{-1}.[130] The analogous bands in the spectra of polysilylureas are at 1650 cm^{-1}.[132]

An appreciable decrease of the carbonyl absorption wavenumber (1690 cm^{-1}) has been observed for uretidinediones (cyclic compounds) $R_3Si(CH_2)_nNC(O)N(CO)(CH_2)_n$. .$SiR_3$ compared with compounds of analogous structure but without silicon (1780–1790 cm^{-1}). A similar decrease of the C=O vibration wavenumber is known to occur in the spectra of organosilicon ketones $R_3Si(CH_2)_nC(O)Me$. Evidently, in this case there is an appreciable decrease of the amount of double bond character of the linkage joining the carbonyl group owing to the intramolecular coordination of its oxygen atom to silicon[165]. The bond formed is fairly stable, as shown by the constancy of the extinction coefficient of the C=O band when the concentration of the substance is reduced from 0.1 to 0.0001 M.

NMR data for a number of silylureas have been published[7,141].

When organosilicon ureas are pyrolysed, an isocyanate and an amine are formed, as from their hydrocarbon analogues[6]:

$$Me_3SiCH_2NHC(=O)NPh_2 \xrightleftharpoons{250\div300^\circ} Me_3SiCH_2NCO\,(70\%) + Ph_2NH.$$

3. APPLICATIONS

Carbofunctional organosilicon ureas are of interest primarily for the preparation of modified polymeric materials. The study of various types of polymers (polyamides, polyimides, etc.) has shown[173] that the introduction of, for example, polysiloxane units into the organic polymeric chain in an amount of 3–5% entails a number of significant changes in the properties (a decrease of the yield temperature, an improvement in solubility and dielectric parameters) and makes polymeric materials hydrophobic and resistant to hydrolysis. When a large number of siloxane units (from 15 to 20%) are introduced, there is in addition an appreciable improvement in thermal stability.

The foregoing applies equally to carbofunctional organosilicon materials in which the organic and organosilicon fragments are linked chemically. Polymeric materials of this kind have been proposed for the preparation of coatings, resins for laminated plastics, stable water-repellent impregnation for cotton and paper fabrics[152,153], and self-vulcanising rubbers[174]. Monomeric and polymeric silylureas can be used as adhesives[152–154,175–177], antifoaming agents[160,161], auxiliary substances in the synthesis of glass fibre-reinforced plastics[135,178,179], surface-active substances[149,175,176,180], hardening agents for epoxy-resins[181], and other purposes[149,151–154,178,180,182–187]. Some of these compounds exhibit physiological activity[163,164,168–170,188].

Silicon-carbamide polymeric materials, obtained by the copolymerisation of urea-formaldehyde prepolymers with organosilicon polymers or oligomers[159,189], have been proposed for the preparation of varnish films, adhesives, cast articles, and laminated plastics with better dielectric parameters and improved thermal stability and water resistance compared with the usual urea-formaldehyde materials. Silyl ethers of hydroxymethyl derivatives of urea have been recommended for the preparation of rubbers which undergo self-cross-linking under the influence of moisture[190,191] and as intermediates in the preparation of medicines, textiles, and resins[192].

The use of compositions of monomeric or polymeric organic urea derivatives with silicon-containing compounds (components not linked chemically) is also a promising application[193–225]. For example, the introduction of 0.05–5% of urea, diphenylurea, or tolylurea into a vulcanisate improves the thermal stability of silicon elastomers[203]. The compositions are used to treat textiles in order to make them hydrophobic and crease-resistant[195,219,221,223,225], to improve the water resistance of aminoplastics[208], to bind polyurethanes to the support[213], as coatings[220,222], adhesives[215], lubricants[214,218], and binders for articles made of fibreglass[140], and for many other purposes.

Studies on the use of organosilicon products as auxiliary substances in the manufacture of various urea-based materials are also noteworthy[201,206,226]. Urea and its derivatives can be used in their turn as auxiliary products in the preparation of silicon-containing compounds, for example as ligands which reduce the activity of platinum catalysts in the addition of hydropolysiloxanes to olefinic silicones[227] and as solvents in the reduction of halogenosilicones with sodium hydride[228–230].

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