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Silicon-containing Isocyanates

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Methods of preparation, properties, and prospects for the application of silicon-containing isocyanates are surveyed. In the Review these compounds are divided into two classes—isocyanatosilanes and "*C*-functional" organosilicon isocyanates—because of the substantial differences in their properties and methods of preparation. Not only monomeric compounds but also oligomeric and polymeric products containing silicon and one or more isocyanato-groups are considered. The Review covers papers that appeared up to the end of 1971 and to some extent at the beginning of 1972. A list of 304 references is included.

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I. INTRODUCTION

The importance of organic isocyanates in theoretical and applied chemistry is well known, and progress in this field has been surveyed repeatedly [1-5]. The chemistry of organosilicon isocyanates began to be developed intensively only during the past decade, and their applied importance is continually increasing. Organosilicon isocyanates can be divided into two fundamentally different classes: the first comprises compounds containing the isocyanato-group directly attached to the silicon atom; and the second class includes isocyanato-alkyl, -aryl, -alkoxyl and other derivatives of silicon in which the isocyanato-group is separated from the silicon atom by some other group of atoms. Isolated data on the first type of compounds will be found in a review [6] on the pseudohalides of elements of Groups IIIb and IVb and in two papers [7,8]. However, most of the information on either type of silicon isocyanates has not been specially summarised. The present Review is an attempt to fill this gap.

II. COMPOUNDS CONTAINING AN ISOCYANATO-GROUP ATTACHED TO THE SILICON ATOM

1. Methods of Preparation

(*a*) Exchange between halogenosilanes and metal cyanates

A general method for the preparation of isocyanatosilanes is the double decomposition of halogenosilanes and metal cyanates [9-58]. This reaction has been used to prepare isocyanatosilanes of general formula $R_nSi(NCO)_{4-n}$, where $n = 1-3$ and R = Alk, Ar, OAlk, Hal, etc.

Although isocyanatosilanes are best obtained from bromosilanes, the more readily available chlorosilanes are often used. With iodosilanes yields are lower and the final products are less pure. Fluorosilanes do not undergo this reaction [27]. Replacement of the halogen by an isocyanato-group is effected by passing the vapour of the halogenosilane over the cyanate salt [29,30], in the melt [32], in an aprotic liquid organic solvent, or in the absence of a solvent [27,56].

The silver, mercury, lead, copper, tin, zinc, antimony, and thallium salts are generally employed for the double decompositions [27,33,34,43,44,47]. The use of freshly prepared salts taken in excess normally improves the yield [19,42,43,47]. The reaction of halogenosilanes with potassium and sodium cyanates is considerably more difficult. For example, silicon tetraiodide has not reacted with potassium cyanate at 20°C after twelve days [30], and the prolonged heating of silicon tetrachloride with potassium and sodium cyanates gives a low yield of silicon tetraisocyanate [9,45]. Satisfactory yields of this product are obtained when silicon tetrachloride vapour is passed over the finely ground or molten salts of alkali or alkaline-earth metals at temperatures above 200°C. [45] Trimethylsilyl isocyanate has been obtained under similar conditions [34,57].

Isocyanatosilanes have recently been obtained in high yields by the reactions of chlorosilanes with potassium and sodium cyanates in liquid sulphur dioxide [35], and also with the lithium salt in benzene [36]. The most complete series of compounds $R_nSi(NCO)_{4-n}$ have been obtained with R = Alk and C_6H_5. [12,18,19] Isocyanatosilanes having a vinyl, phthalocyanine, alkoxyl, aroxyl, or organosilyl group attached to the silicon atom are obtained by the same scheme as are alkyl and aryl derivatives [14,18,31,35,37,38,41,49].

In the preparation of silicon tetraisocyanate from the tetrachloride and silver cyanate the reaction takes place step by step and is accompanied by partial hydrolysis of the reaction products [10,17]. In this way the compounds

$$Cl_3SiNCO,\quad Cl_2Si(NCO)_2,$$

$$Si(NCO)_4;\ (OCN)_3SiOSi(NCO)_3 \text{ and } (OCN)_3SiOSi(NCO)_2OSi(NCO)_3$$

were isolated.

Partly halogenated silanes are also used for the preparation of isocyanatosilanes [13,59]: e.g.

$$2SiHCl_3 + 8AgOCN \rightarrow 2Si(NCO)_4 + 6AgCl + 2Ag + H_2$$

Finally, it is noteworthy that isothiocyanato- and mercapto-groups can also be replaced by the isocyanato-group [11,27]:

$$Cl_3SiSH + 4AgNCO \rightarrow Si(NCO)_4 + AgSH + 3AgCl$$

$$Me_2Si(NCS)_2 + 2AgNCO \rightarrow Me_2Si(NCO)_2 + 2AgSCN$$

(*b*) Aspects of exchange reactions

Eaborn arranged organosilicon compounds in what he termed "conversion series", characterising their capacity for irreversible transformation on reaction with metal

salts. With the triethylsilyl derivatives, for example, the series is (R = C_2H_5) [26,27,60]

$$R_3SiI \xrightarrow{Ag_2S} (R_3Si)_2S \xrightarrow{AgBr} R_3SiBr \xrightarrow{NaH} R_3SiH \xrightarrow{AgCN} R_3SiNC \rightarrow$$
$$\xrightarrow{AgCl} R_3SiCl \xrightarrow{AgSCN} R_3SiNCS \xrightarrow{AgNCO} R_3SiNCO \xrightarrow{KOAc} R_3SiOC(O)Me \rightarrow$$
$$\xrightarrow{H_2O} (R_3Si)_2O \xrightarrow{\text{heavy-metal fluorides}} R_3SiF$$

Hence it follows that isocyanatosilanes cannot be obtained from acyloxysilanes, siloxanes, and fluorosilanes. Analogous conversion series have been established for methylsilanes $(CH_3)_3SiX$, dialkyl(and aryl)silanes R_2SiX_2 [23,27], and salts of other metals—mercury, tin, antimony, cadmium, zinc, and copper.

Under the conditions of a heterolytic reaction mechanism the factor determining the sequence of compounds in conversion series is probably the affinity of the various functional groups for the silicon atom, although other factors are also important. This conclusion is supported by the coincidence of the conversion series with the sequence of compounds in order of increasing energy of the ionic Si–X bonds (X = I, S, Br, etc.) [27].

On the other hand, Anderson showed [24,60-66] that silicon; germanium, and phosphorus isocyanates undergo exchange reactions with compounds of elements in the middle of the Periodic System provided that the most volatile component is removed from the reaction mixture. Such sequences of conversion of some compounds into others were termed "volatility series". Examples of such reactions are

$$Me_2Si(NHPh)_2 + Ph_2Si(NCO)_2 \rightarrow Me_2Si(NCO)_2 + Ph_2Si(NHPh)_2$$
$$Et_3GeOSO_2R + Ph_3SiNCO \rightarrow Et_3GeNCO + Ph_3SiOSO_2R$$

In the triethylsilyl series the conversions

$$Et_3SiNHPh \rightarrow Et_3SiNCS \rightarrow Et_3SiI \rightarrow Et_3SiNCO \rightarrow Et_3SiBr \rightarrow Et_3SiCl$$

are possible. It must be noted that the sequences of exchange reactions in "conversion series" and "volatility series" often do not coincide.

(*c*) Reactions of organosilicon compounds with isocyanic acid

The original attempts to use isocyanic acid to replace chlorine atoms in chlorosilanes by the isocyanato-group were unsuccessful, in spite of the use of aluminium, zinc, iron, and mercury chlorides as catalysts [11,34]. It was found, however, that isocyanatosilanes are easily formed if the hydrogen chloride liberated is bound by tertiary amines or by amides of carboxylic acids [37,67,68]:

$$R_nSiCl_{4-n} + (4-n)HNCO + (4-n)R'_3N \rightarrow R_nSi(NCO)_{4-n} + (4-n)R'_3N \cdot HCl$$

The reaction must be conducted in the presence of a slight excess of chlorosilanes, which stabilise isocyanic acid and isocyanatosilanes [68]. Alkoxy- and aryloxy-isocyanatosilanes have been obtained by this method [69]. According to patent claims [70] silanols, e.g. triphenylsilanol, can be used as initial compounds in the reaction with isocyanic acid. In view of the ready availability of isocyanic acid, obtained by the pyrolysis of cyanuric acid or urea, its use for the preparation of isocyanatosilanes is extremely promising.

(*d*) Disproportionation

Many observations have been made of the formation of isocyanatosilanes by disproportionation [10,71-79]:

$$Si(NCO)_4 + Si(NCS)_4 \rightarrow SCNSi(NCO)_3$$
$$Si(NCO)_4 + SiCl_4 \rightarrow Cl_3SiNCO + Cl_2Si(NCO)_2 + ClSi(NCO)_3$$
$$Si(NCO)_4 + SbF_3 \rightarrow F_3SiNCO + F_2Si(NCO)_2 + FSi(NCO)_3$$

However, isolation of the reaction products is extremely difficult owing to their tendency to symmetrisation. This applies especially to compounds of the type $XSi(NCO)_3$ (where X = Cl, OCH_3, F) [10]. Compounds of types $(CH_3)_nSi(NCO)_{4-n}$ and $(CH_3)_nSiCl_{4-n}$ ($n \geq 1$) exhibit a tendency to disproportionate only about one-thousandth of that shown by silicon tetraisocyanate and the tetrachloride or tetrabromide [10,72-74].

A quantitative study by means of proton magnetic resonance spectroscopy of the exchange of isocyano, isocyanato, and isothiocyanato for chloro, bromo, alkoxyl, alkylthio, etc. in mono- and di-methylsilanes [75-77] showed that, with rare exceptions [75], the position of equilibrium conforms to a random distribution. Equilibrium constants have been determined for several exchange reactions [75-77,80].

Disproportionation has found application only in the preparation of fluoroisocyanatosilanes.

(*e*) Other methods of preparation of isocyanatosilanes

Besides the above general methods there are several specific reactions one of whose products is a compound containing an Si–NCO fragment. Gilman et al. [46] obtained triphenylsilyl isocyanate by the reactions

$$Ph_3SiCl + \begin{matrix} Na \\ \diagdown \\ NCOOEt \\ \diagup \\ H \end{matrix} \rightarrow Ph_3SiNCO + EtOH + NaCl$$
$$Ph_3SiCl + NH_2CONH_2 \xrightarrow{Cu} Ph_3SiNCO + NH_4Cl$$

Goubeau and Paulin [34] prepared trimethylsilyl isocyanate and dimethylsilylene di-isocyanate by the reaction of urea at 240–320°C with trimethylchlorosilane and dimethyldichlorosilane respectively, the yield in the latter case being 5–10%.

Pump and Rochow [81] showed that trimethylsilyl isocyanate is formed in the thermal decomposition of silicon derivatives of carbamic acid:

$$ROC(O)Cl + NaN(SiMe_3)_2 \rightarrow RO-\overset{\overset{N-SiMe_3}{\|}}{C}-OSiMe_3 \rightarrow Me_3SiNCO + Me_3SiOR$$

The reaction of carbon dioxide with bistrimethylsilylsodamide obviously has a similar mechanism, via trimethylsilyl isocyanate as an intermediate product [82]. The formation of this isocyanate has been observed also in the reaction of carbonyl chloride with hexamethyldisilazane [83-85] and in the interaction of technical calcium or barium cyanamide with trimethylchlorosilane in a lithium chloride–sodium chloride melt at 400°C [86].

Zhinkin and his coworkers [87-92] suggested an interesting route for the preparation of isocyanatosilanes:

$$(Me_3Si)_2NH + PhNCO \rightarrow PhNHC(O)N(Ph)SiMe_3 + Me_3SiNCO$$
$$Me_3SiNHC(O)N(Ph)SiMe_3 \xrightarrow{120°C} Me_3SiNCO + Me_3SiNHPh$$

Unsymmetrical organodisilazanes yield two isocyanatosilanes and two aminosilanes in this reaction [92]. Mono-, di-, and tri-isocyanatomethylsilanes, as well as isocyanatosilanes containing unsubstituted hydrogen, have been obtained by the pyrolysis of *N*-silylated ureas [94-96]:

$$Me_nSi(NHCONPh_2)_{4-n} \rightarrow Me_nSi(NCO)_{4-n} + (4-n)\,Ph_2NH$$

$$NH_2CONH_2 + (HSiMe_2)_2NH \rightarrow HSiMe_2NCO + NH_3$$

$$NH_2CONH_2 + (Me_3Si)_2NH \rightarrow Me_3SiNCO + NH_3$$

$$(PhNH)_2CO + (Me_3Si)_2NH \rightarrow Me_3SiNCO + Ph_2NH$$

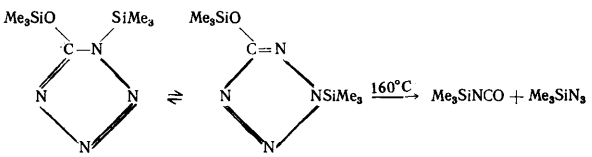
Silyl isothiocyanates are readily formed by the action of sulphur on silicon isocyanides [97,98]. Nevertheless, mild oxidation of the latter with mercury(II) oxide or silver(I) oxide does not yield isocyanatosilanes but products in which the silicon–nitrogen bond has been ruptured [7,56,98]. Strong oxidants (lead dioxide, manganese dioxide, and sodium peroxide) react with trialkylsilyl isocyanides only on heating, but formation of isocyanatosilanes has not been reported at all [52,99,100].

Heating trimethylsilyl isoselenocyanate in dry air gives selenium, trimethylsilyl isocyanate, and trimethylsilyl cyanide [52].

A peculiar type of exchange occurs in the reaction between chlorosilanes and chlorine isocyanate [95]:

$$R_3SiCl + ClNCO \rightarrow R_3SiNCO + Cl_2$$

Finally, trimethylsilyl isocyanate has been obtained by the pyrolysis of a mixture of tautomeric forms of 1-hydroxy-*NO*-bistrimethylsilyltetrazole [101]:



2. Structure and Properties of Isocyanatosilanes

(*a*) Physical properties

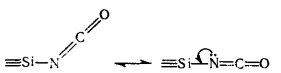
Pseudohalide groups are polyatomic, linear, electronegative, and able to develop a negative inductive effect along a bond with a metal. All these properties are exhibited by isocyanato-groups in silanes. Nevertheless, in contrast to organic isocyanates, the proximity of the isocyanato-group to a silicon atom having vacant *d*-orbitals may produce special structural features connected with the ability of the isocyanato-group to be conjugated by means of its π-system or its donor atoms (nitrogen or oxygen). These peculiarities may be represented by the structural isomerism

$$\underset{\text{isocyanate form}}{Si{-}N{=}C{=}O} \rightleftharpoons \underset{\text{siloxynitrile form}}{Si{-}O{-}C{\equiv}N}$$

and by the partly double-bond character of the silicon–nitrogen bond, as a consequence of which the Si–N=C=O unit should be spatially linear.

The isocyanate form is generally accepted, although problems of the three-dimensional structure of the molecules, and in particular linearity of the Si.N:C:O system, have still been inadequately studied. Preference has been given to the iso-structure on the basis of molecular refractions, infrared, Raman, nuclear magnetic resonance, and mass spectra, and also the observed analogy in properties between isocyanatosilanes and the thermodynamically more stable (relative to the isomeric cyanic esters) organic isocyanic esters.

Spectral data for trimethylsilyl isocyanate [99], compounds $(C_6H_5O)_nSi(NCO)_{4-n}$ (n = 1–3) [103,104], trichlorosilyl isocyanate [104], and several other isocyanates and isothiocyanatosilanes [37,49,105-115] confirm their iso-structure. The infrared spectra of isocyanatosilanes contain bands corresponding to the characteristic stretching vibrations ν_{sym}^{NCO} = 1475–1325, ν_{asym}^{NCO} = 2290–2190, and δ_{Si-NCO} = 616, 606 cm^{-1}. [37,99,102-105,116-118] Vibrations of the Si–NCO bond are probably responsible also for bands around 2381 and 1972–2000 cm^{-1} [117,118]. In the series of compounds $(CH_3)_nSi(NCO)_{4-n}$, moreover, the ν_{sym}^{NCO} frequency increases with n; the intensity and the width of the infrared bands remain typical of organic isocyanates [99,116,119-121]. The probable reason is $p \rightarrow d$ interaction between silicon and nitrogen atoms, which governs the multiplicity of the Si–NCO bond and the appearance of the resonance structures [116]



The infrared and Raman spectra of silyl isocyanate [122], trichlorosilyl isocyanate, and chlorosilylidyne tri-isocyanate are consistent with this hypothesis, and agree well with the formal charge distribution in silyl isocyanate and the octet rule [123].

The carbon-13 nuclear magnetic resonance spectra show that all the carbon atoms in silicon tetraisocyanate are of the same type [119]. According to the proton magnetic resonance spectra protons of only one type are present in silyl isocyanate and isothiocyanate and in disilylcarbodiimide [48]. The infrared and Raman spectra of the tetraisocyanate in the range 4000–80 cm^{-1} are very simple, which indicates that the molecule is highly symmetrical, and corresponds to a tetrahedral model [116,119,120].

Electron diffraction examination of silyl isocyanate [124], trimethylsilyl isocyanate [125], silicon tetraisocyanate [126], chlorosilylidyne tri-isocyanate, dichlorosilylene di-isocyanate, trichlorosilyl isocyanate [127], and trifluorosilyl isocyanate [128] shows that the Si–N–C angles are smaller than 180°, being respectively 151.7 ± 1.2°, 154 ± 2° (150 ± 3°), 146.4°, 145.0°, 136.0°, 138.0°, and 160.7 ± 1.2°. The results no longer correspond to a rigid model (of symmetry D_{2d}) but to a model with free rotation about the silicon–nitrogen bond (symmetry C_{3v} [125]), and indicate the absence of appreciable double-bond character. In the Reviewers' opinion, however, a final conclusion on this matter is premature.

Mass-spectroscopic investigation of the tetraisocyanate reveals the formation of a molecular ion $Si(NCO)_4^+$. [129]

Isocyanatosilanes, other than the gaseous silyl and trifluorosilyl isocyanates, are colourless liquids or solids with an acrid smell. The odour of triethylsilyl isocyanate recalls that of camphor [12].

The boiling points of compounds R_3SiX vary with the nature of X in the sequence [61] Cl < Br = NCO < I < NCS < < NHC_6H_5.

Several alkyl- and aryl-isocyanatosilanes exhibit a tendency to supercooling [11]. Members of the series $(CH_3)_nSi(NCO)_{4-n}$ (n = 1–3), on the other hand, have sharp melting points. Isocyanatosilanes burn readily in air, dissolve well in organic solvents [17,71], and are mostly thermostable compounds [16]. Their stability is greater the lower the electronegativity of other substituents attached to the silicon atom [130], and is sharply diminished by contamination with silver cyanate, cyanic acid, diborane, or triethyl phosphine [29].

The values of the Trouton constant suggest that there is little or no association of isocyanatosilanes in the liquid state [18,19,29].

(v) Chemical properties

The pseudohalide character of the NCO group in isocyanatosilanes is shown in their ability to react with proton-containing compounds, either with replacement of the isocyanato-group [6]

$$R_3SiNCO + H{-}X \rightarrow R_3SiX + HNCO$$

or with addition of the elements of H–X at the double bond in the isocyanato-group

$$R_3SiNCO + H{-}X \rightarrow R_3SiNHC(O)X$$

Hydrolysis. All isocyanatosilanes, on treatment with water, are hydrolysed to silanols and isocyanic acid. Qualitative observations show that the rates and the heats of hydrolysis of the compounds $Alk_nSi(NCO)_{4-n}$ fall with increase in n [12,19]. The stability of triphenylsilyl and triethylsilyl isocyanates towards water is due to their poor solubility, since they are rapidly hydrolysed on the addition of alcohol, acetone, or dioxan [12,20,27,46]. The isocyanatosilanes $Cl_nSi(NCO)_{4-n}$, $F_nSi(NCO)_{4-n}$, and $(OCN)_3Si.O.Si(NCO)_3$ undergo vigorous hydrolysis with the evolution of heat [12,71,73]. Silicon tetraisocyanate forms products of partial hydrolysis when insufficient water is used [17]. Methoxy- and phenoxy-isocyanatosilanes hydrolyse at a moderate rate. The ease of hydrolysis of isocyanatosilanes in comparison with silicon pseudohalides of the same type places them in the sequence—$R_3SiNCO < R_3SiNCS < R_3SiNC$ [27].

The reaction of isocyanatosilanes with water is used for the quantitative determination of the isocyanato-group [12,16,27,71]. However, more reliable results are obtained by the Dumas determination of nitrogen [12,17–19].

Reactions with alcohols. A detailed study of the alcoholysis of isocyanatosilanes was made in work [34] which confirmed earlier results obtained by Forbes and Anderson [11,18,71] on the formation of alkoxysilanes and the corresponding urethanes. This showed that increase in the size and in the degree of branching of the radical, either in the silane or in the alcohol, leads to a fall in the rate of alcoholysis [34,46]. The two schemes

$$R_3SiNCO + R'OH \begin{cases} \xrightarrow{1} R_3SiOR' + HNCO \xrightarrow{R'OH} H_2NC(O)OR' \\ \xrightarrow{2} R_3SiNHC(O)OR' \xrightarrow{R'OH} R_3SiOR' + H_2NC(O)OR' \end{cases}$$

were suggested [34] to explain the course of the reaction. In the first stage of interaction with an aqueous alcohol, isocyanic acid is formed, and can be titrated [12]. Nevertheless, its presence was not detected in the reaction with an anhydrous alcohol [34].

Considerable doubt must attach to the reported [131] preparation of urethanes containing a silicon–nitrogen bond by heating dibutylsilylene di-isocyanate with higher alcohols and glycols, in view of the lack of adequate characterisation of the products. This applies equally to the synthesis of a polyurethane based on diphenylsilanediol and dimethylsilylene di-isocyanate [132], since, in contrast to alcohols, silanols and silanediols are inert towards e.g. trimethylsilyl isocyanate [133]. The claimed formation [134] of polysilylurethanes containing $\gtrless$Si.NH.CO.OR′– by the reaction of $R_nSi(NCO)_{4-n}$ and $(RO)_nSi(NCO)_{4-n}$ ($n = 0–2$) with glycols $R'(OH)_2$ and a polyethylene glycol ether is just as improbable.

Reactions with amines. In early studies of the reaction of isocyanatosilanes with amines it was erroneously concluded that the isocyanato-group was eliminated [62,135,136]. By the use of ammonia and primary and secondary aliphatic and aromatic amines with a variety of isocyanatosilanes Goubeau and Heubach as well as other workers were able to show [38,65,84,133] that the amines add at the C=N bond to form N-silylureas:

$$Me_nSi(NCO)_{4-n} + R_mNH_{3-m} \rightarrow Me_nSi(NHCONH_{2-m}R_m)_{4-n}$$

The reactivity of amines towards silicon isocyanates fell in precisely the same sequence as their reactivity towards organic isocyanates [43]:

$$AlkNH_2 > Alk_2NH > ArNH_2 \gg ArNHR > Ar_2NH$$

Silicon tetraisocyanate was found to be more reactive than its alkyl and aryl derivatives [62,133]: with trimethylsilyl isocyanate, for example, addition was observed only with amines of basicity $pK > 10$ [137]. The steric factor plays an important part, besides the basicity of the amine: 2,6-dibromoaniline reacts slowly even with silicon tetraisocyanate [43].

Symmetrical di-isocyanatodisilanes form disilylureas in conformity with the general scheme [38]. Tertiary amines do not react with isocyanatosilanes [133]. Hydrazines and silylhydrazines give silylsemicarbazides with trimethylsilyl isocyanate; the isocyanatosilane acts more selectively in these reactions than do organic isocyanates [137]. Free hydrazine undergoes exchange with trimethylsilyl isocyanate, and adds at the isocyanato-group [84,137].

Other reactions. The isocyanato-group in triethylsilyl isocyanate does not react with methylmagnesium iodide, nor do those in the tetraisocyanate interact with dimethylmercury [19]. Triphenylsilyl isocyanate adds phenyl-lithium and phenylmagnesium bromide with difficulty at the carbonyl bond to form after hydrolysis triphenylsilanol and benzamide [46]. With bistrimethylsilylsodamide isocyanatosilanes are converted into disilylcarbodi-imides [138–141].

In the reaction of oxirans with isocyanatosilanes $R_nSi(NCO)_{4-n}$ ($n = 0–3$) the ring is opened [142–144]:

$$R_nSi(NCO)_{4-n} + CH_2{-}CH_2 \overset{O}{\diagup\diagdown} \xrightarrow[R_3N]{P \geqslant 1\ atm} R_n(OCN)_mSi(OCH_2CH_2NCO)_{4-m-n}$$

Use in the reaction of aldehydes [145] or of ketones containing an α-hydrogen atom [146] gives polymeric products of undetermined structure.

Sulphur tetrafluoride [147] and carbonyl fluoride [148] rupture the silicon–nitrogen bond in isocyanatosilanes:

$$Si(NCO)_4 + 4SF_4 \rightarrow SiF_4 + 4F_2S{=}N{-}C(O)F$$
$$Me_nSi(NCO)_{4-n} + (4-n)COF_2 \rightarrow (4-n)Me_nSiF_{4-n} + (4-n)FC(O)NCO$$

The reactions of isocyanatosilanes containing unsubstituted hydrogen are illustrated by the examples [29]

$$H_3SiNCO + NaOH \rightarrow NaOCN + H_2 + SiO_2$$
$$H_3SiNCO + H_2CO_3 \rightarrow H_2 + SiO_2 + CO_2 + HNCO$$
$$H_3SiNCO + MeOH \rightarrow SiH_4 + (MeO)_3SiH + (MeO)_4Si + MeOC(O)NH_2$$
$$H_3SiNCO + HCl \rightarrow H_3SiCl + {}^1/_3(HNCO)_3$$
$$H_3SiNCO + BF_3 \rightarrow H_3SiF + F_2BNCO \rightarrow BF_3 + [B(NCO)_3]_n$$

In this case addition products are not formed with diborane either at 20° or at −78°C, although the isocyanates are

decomposed in the presence of diborane at room temperature.

In conclusion, tri-isocyanatosilanes $XSi(NCO)_3$ (X = Cl, F, CH_3O, etc.) exhibit a strong tendency to disproportionate, which is greatly hindered by isolation of the compounds in pure form [10].

Isocyanatosilanes containing unsubstituted hydrogen can take part in hydrosilylation in conformity with the generally accepted scheme. They undergo neither di-, tri-, and poly-merisation nor decarboxylation when boiled for a long time with such catalysts as metal carbonyls, dimethyl tolyl phosphate, methylphosphafluorene oxide, and bis-*P*-methyl-*P*-phenyl-thiophosphoryl [94].

3. Prospects for the Application of Isocyanatosilanes

The great reactivity of isocyanatosilanes enables them to be used in the manufacture of various polymeric materials. Thus they have been proposed for the production of plastics [45], insulating materials, dielectrics [79], and pesticides [70,79], and as textile finishes [149], hydraulic fluids, components of self-setting compositions [150,151], and catalysts in the synthesis of polyurethanes, for the water-repellent treatment of glass, porcelain, and cloth, and for other purposes [33,44,57,68]. Polymers obtained by the reaction of dialkylsilylene di-isocyanates with amines or alcohols [134,142-144], aldehydes [145], and ketones [146] are suitable for the production of moulded articles and glass—plastic laminates, as additives to rigid foam plastics, and as adhesives for wood, metals, and other materials. Products of the interaction of silanediols† with isocyanatosilanes have been recommended for coating the internal surfaces of fuel tanks [132].

Compounds of type $(OCN)_nSi(OCH_2CH_2NCO)_{4-n}$ are capable of spontaneous polymerisation with the formation of resins or flexible films possessing good adhesion to glass [142-144]. Several materials based on isocyanatosilanes exhibit short-term fire-resistance and high thermal stability [68]. Modification with isocyanatosilanes sharply increases the adhesion of silicone rubbers to copper or brass [152]. Fillers treated with isocyanatosilanes improve the stability of polyurethane coatings for wood, metals, glass, concrete, and other materials [153].

A second promising usage of isocyanatosilanes is as ancillaries in organic synthesis. For example, the quantitative formation of silylureas by the reaction of isocyanatosilanes with amines and the ready hydrolysis of the products have been used to develop a general method for the preparation of ureas [43] which dispenses with the difficultly available alkyl isocyanates and alkyl(aryl, dialkyl, diaryl)carbamoyl chlorides.

III. "C-FUNCTIONAL" ORGANOSILICON ISOCYANATES

1. Methods of Preparation

(*a*) From derivatives of carboxylic acids

In contrast to isocyanatosilanes, carbofunctional organosilicon isocyanates (primarily compounds having isocyanato-alkyl and -aryl groups attached to the silicon atom) were little studied until quite recently. The first such compound was obtained in 1959 from *p*-trimethylsilylbenzoyl azide [154]:

$$p\text{-}Me_3SiC_6H_4COCl \xrightarrow{NaN_3} p\text{-}Me_3SiC_6H_4CON_3 \xrightarrow[-N_2]{t^\circ} p\text{-}Me_3SiC_6H_4NCO$$

Intermediate formation of isocyanates has been observed also in the decomposition of azides of silylated aliphatic acids [93,94].

The intermediate formation of 3-ethyldimethylsilylpropyl isocyanate has been noted during oxidation of the corresponding amide by lead tetra-acetate [93,94]:

$$RC(O)NH_2 \xrightarrow[HCON(CH_3)_2]{Pb(OAc)_4} [R{-}N{=}C{=}O] \xrightarrow{C_5H_5NH_2} RNHC(O)NHC_5H_5,$$

(R = Et—Si(Me)(Me)—$(CH_2)_3$—)

(*b*) Hydrosilylation of alkenyl isocyanates

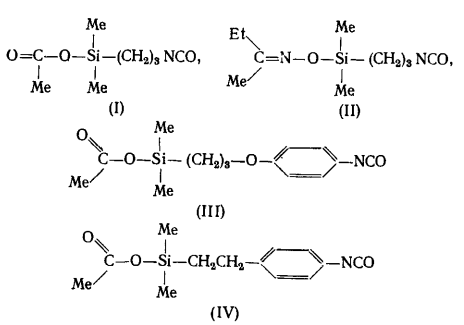
A convenient route for the preparation of monomeric, oligomeric, and polymeric organosilicon *C*-isocyanates consists in the catalytic addition of silanes containing unsubstituted hydrogen to unsaturated organic isocyanates. Monomers containing one, two, or three hydrolysable groups attached to the silicon atom can be obtained by this reaction [94,155-163].

Replacement of the chlorine atoms in trichlorosilane by alkyl groups leads to an appreciable decrease in the rate of addition to allyl isocyanate [94,156]:

$$MeCl_2SiH + CH_2{=}CHCH_2NCO \xrightarrow[3\ h]{H_2PtCl_6} Me{-}Si(Cl)(Cl){-}(CH_2)_3NCO \quad (80\%)$$

$$Me_2ClSiH + CH_2{=}CHCH_2NCO \xrightarrow[40\ h]{H_2PtCl_6} Cl{-}Si(Me)(Me){-}(CH_2)_3NCO \quad (40\%)$$

This reaction does not take place with methyldiethylsilane and triethylsilane. Several isocyanates, e.g. of the types



(I) (II) (III) (IV)

have been obtained by the addition of incompletely substituted silanes containing acyloxy- or hydroxyamino-groups to allyl, *p*-allyloxyphenyl, or *p*-vinylphenyl isocyanate in the presence of catalytic quantities of an ethylene–platinum complex [157]. Silicon-containing urethano-isocyanates have been prepared by the action of siloxanes and incompletely substituted silanes on urethano-isocyanates (products of the interaction of allyl and methylallyl alcohols with tolylene di-isocyanate) [158,159].

In contrast to silyl acetates, tetramethyldisiloxane does not add to allyl isocyanate [94,155]. However, a di-isocyanate could be obtained from another partly substituted silane, *p*-bisdimethylsilylbenzene [94,155], where addition takes place in steps.

†The products formed with alcohols and silanediols obviously do not possess a polysilylurethane structure (Subsection 2*b*), but comprise a mixture of polyoxasilaalkylenes or polysiloxanes with organic urethanes and polymeric forms of isocyanic acid.

The catalysts used have included, not only hexachloroplatinic acid and the ethylene–platinum complex, but also other platinum derivatives, palladium compounds, and certain catalysts of ionic and free-radical reactions [96,156–162].

In contrast to allyl isocyanate, isopropenyl isocyanate exhibits surprising inertness towards not only trialkylsilanes and tetramethyldisiloxane but also partly substituted alkoxy- and chloro-silanes [94].

The isocyanato-group, like the isoelectronic keten grouping [164,165], remains unchanged during hydrosilylation. Moreover, incompletely substituted silanes (especially those containing silicon–chlorine bonds) have a stabilising effect on the initial and the final isocyanates, diminishing their tendency to polymerise when heated.

Examination of the addition products of incompletely substituted silanes to allyl isocyanate by means of proton magnetic resonance spectroscopy has shown [94] that they all contain the isocyanato-group in the γ-position relative to the silicon atom.

(c) Reaction of silylated amines with carbonyl chloride

Another convenient method for obtaining organosilicon *C*-isocyanates is the action of carbonyl chloride on the corresponding primary amines. Aliphatic isocyanates were first obtained in this way [93,163,166]:

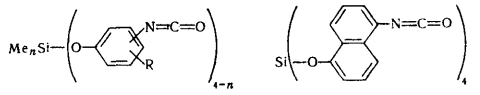
$$2R_3Si(CH_2)_nNH_2 + COCl_2 \xrightarrow{20^\circ C} R_3Si(CH_2)_nNHCOCl + R_3Si(CH_2)_nNH_2 \cdot HCl$$
$$R_3Si(CH_2)_nNHCOCl \xrightarrow{110-150^\circ C} R_3Si(CH_2)_nNCO + HCl$$
$$R_3Si(CH_2)_nNH_2 \cdot HCl + COCl_2 \xrightarrow{110-150^\circ C} R_3Si(CH_2)_nNCO + 3HCl$$
$$2R_3Si(CH_2)_nNH_2 + 2COCl_2 \rightarrow 2R_3Si(CH_2)_nNCO + 4HCl$$
(R=Alk, Ar; $n = 1; 3$)

Dimeric compounds having a dioxouretidine structure are formed by a side-reaction [166]. 3-Trimethylsilylpropyl isocyanate isolated in pure form was completely stable, and did not dimerise either on storage or when distilled.

With amines containing alkoxy- or siloxy-groups attached to silicon, carbonyl chloride may act also on the silicon–oxygen bonds [94,163,167–169]:

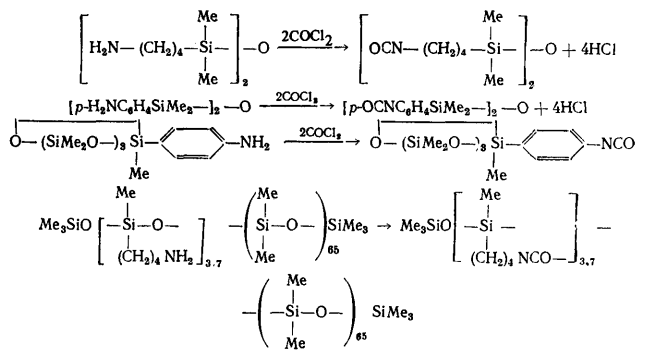
$$(EtO)_3Si(CH_2)_3NH_2 \xrightarrow[110-120^\circ C]{COCl_2} Cl_n(EtO)_{3-n}Si(CH_2)_3NCO + EtOC(O)Cl + HCl$$
$$NH_2(CH_2)_3\underset{\underset{Me\ Me}{|\ \ |}}{SiOSi}(CH_2)_3NH_2 \xrightarrow[-4HCl]{COCl_2} 2Cl\underset{\underset{Me}{|}}{Si}(CH_2)_3NCO + CO_2$$
$$NH_2(CH_2)_4\underset{\underset{Me\ Me}{|\ \ |}}{SiOSi}(CH_2)_4NH_2 \xrightarrow{COCl_2} Cl\underset{\underset{Me}{|}}{Si}(CH_2)_4NCO + OCN(CH_2)_4\underset{\underset{Me\ Me}{|\ \ |}}{SiOSi}(CH_2)_4NCO$$

Silyl ethers of amino-alcohols of type $R_2Si(OCH_2CH_2NH_2)_2$ are completely cleaved at the silicon–oxygen bond on reaction with carbonyl chloride, but the final products were not identified [168]. Nevertheless, the analogous aminophenol and aminonaphthol derivatives, whether as the free bases or as the hydrochlorides, form the corresponding isocyanates [168,170]:



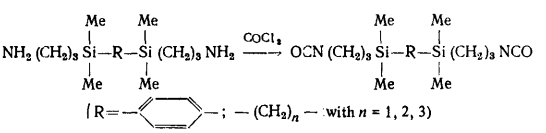
($n = 1-3$; R = H, Me)

Organic mono- and di-isocyanates containing silicon have been obtained by treating aminoalkyl and aminoaryl derivatives of di-, tetra-, and oligo-siloxanes with carbonyl chloride in toluene [169]:



A striking feature of this work is that the siloxane bonds remain unchanged under the severe conditions of treatment with carbonyl chloride and hydrogen chloride.

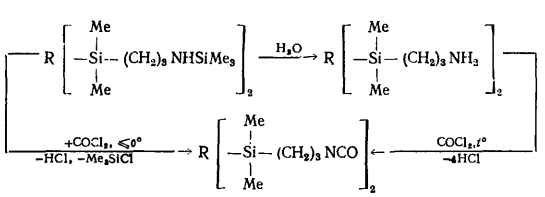
A new type of difunctional organosilicon monomers was obtained by the action of carbonyl chloride on diamines containing alkylene or phenylene bridges between the silicon atoms [94,171]:



Whether in a diamine with an arylene bridge or in 3-phenyldimethylsilylpropylamine the Si–Ar bond is stable towards the chlorinating action of carbonyl chloride, hydrogen chloride, and the chloroformamido-group [94,171].

(d) Action of carbonyl chloride on *N*-silylamines

It was discovered in 1969 that organosilicon di-isocyanates of the above type can be obtained in high yields and under milder conditions by the action of carbonyl chloride on the *N*-trimethylsilyl derivatives of the amines [94,172–176]:



Monoisocyanates have been obtained similarly [94,174–176]:

$$MeEt_2SiH + CH_2{=}CHCH_2NHSiMe_3 \rightarrow MeEt_2Si(CH_2)_3NHSiMe_3$$
$$MeEt_2Si(CH_2)_3NHSiMe_3 \xrightarrow[\leqslant 0^\circ]{COCl_2} MeEt_2Si(CH_2)_3NCO + Me_3SiCl$$

These observations provided an extraordinarily simple method for preparing 3-dimethylchlorosilylpropyl isocyanate [173,177]:

$$Me_2SiHCl + CH_2{=}CHCH_2NH_2 \rightarrow CH_2{=}CHCH_2NHSiMe_2H \xrightarrow{H_2PtCl_6} \rightarrow \left[-CH_2CH_2CH_2NH\underset{\underset{Me}{|}}{Si}-\right]_x \xrightarrow[-xHCl]{xCOCl_2} xClMe_2Si(CH_2)_3NCO$$

It was subsequently established[173-176] that the reaction of carbonyl chloride with *N*-silylated primary amines is general in character, and can be used to obtain not only organosilicon but any other isocyanates containing groups sensitive to heating and to the action of hydrogen chloride, carbonyl chloride, and the chloroformamido-grouping. For example, saturating the reaction mass with carbonyl chloride at a low temperature removes hydrogen chloride rapidly, which has enabled the previously difficultly accessible disiloxane di-isocyanates to be obtained:

$$[Me_3SiNH(CH_2)_3-SiMe_2-]_2-O \xrightarrow[-2HCl]{2COCl_2} OCN(CH_2)_3-\underset{Me}{\overset{Me}{SiO}}\underset{Me}{\overset{Me}{Si}}-(CH_2)_3NCO + 2Me_3SiCl$$

N-Silylated amines react with carbonyl chloride under very mild conditions (−60° to 0°C). The yields of isocyanates reach 90–99%.

The pattern observed might have been quite different if the reaction had involved initial cleavage of the silicon–nitrogen bond in the silylamine. In fact the intermediate carbamoyl chlorides are quite stable under the reaction conditions, and decompose into hydrogen chloride and the isocyanate only when heated to ~100°C and above:

$$R-\underset{H}{N}-SiMe_3 \xrightarrow[-Me_3SiCl]{COCl_2} R-\underset{H}{N}-\underset{Cl}{C}=O \underset{\leftarrow}{\overset{\sim 100^\circ}{\rightarrow}} RNCO + HCl$$

To explain the formation of hydrogen chloride with such a reaction scheme it was necessary to assume that trimethylsilyl chloride already reacts with the carbamoyl chloride under the mild conditions, yielding ultimately the isocyanate:

$$R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-Cl + Me_3SiCl \xrightarrow{-HCl} R-\underset{SiMe_3}{N}-\overset{O}{\overset{\|}{C}}-Cl \rightarrow RNCO + Me_3SiCl$$

Actually it was found, however, that little or no substitution at the nitrogen–hydrogen bond with evolution of gaseous hydrogen chloride takes place even when trimethylsilyl chloride, triethylsilyl chloride, silicon tetrachloride, etc. are heated with methylcarbamoyl chloride at 90°C for a long time. It was thus established that carbonyl chloride attacks $RNHSiR'_3$ by rupturing the N–H bond, not the Si–N bond, and by forming *N*-trialkylsilylcarbamoyl chlorides as intermediate products:

$$R-\underset{H}{N}-SiMe_3 \xrightarrow[-HCl]{COCl_2} R-\underset{SiMe_3}{N}-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{-Me_3SiCl} R-N=C=O$$

The high yields of isocyanates at low temperatures of treatment with carbonyl chloride are explained by the thermal instability of the silylated carbamoyl chlorides due to the σσ-conjugated bond system Si–N–C–Cl for even below room temperature they undergo β-elimination with separation of isocyanate and trialkylchlorosilane molecules. A similar tendency to β-elimination is exhibited[178] by the well studied systems of the type Si–C–C–Y (where Y = Hal, OH, etc.).

The ease of thermal cleavage of *N*-silylcarbamoyl chlorides is especially marked in comparison with related compounds containing an analogous Si–N–C–X bond system but with different X substituents (X = OR, where R = Alk, Ar). In the case of *N*-silylurethanes, for example, containing the $\gtrdot$Si–NR′–CO–OR fragment, the tendency to β-elimination becomes much stronger on passing from alkoxy- to aryloxy-derivatives[94,179]. Replacement of OR by the more electronegative Cl intensifies σσ-conjugation still more, and enhances the thermal instability of *N*-silylcarbamoyl chlorides in comparison with *N*-silylurethanes. Furthermore, since chlorosilanes do not react with isocyanates, breakdown of the *N*-silylcarbamoyl chlorides is an irreversible stage, which is another important reason for the high yield of isocyanates at low temperatures of treatment with carbonyl chloride.

The method of preparing organic and organosilicon isocyanates by treating silylamines with carbonyl chloride was extended to *NN*-disilylamines of type $R.N(SiR'_3)_2$. The silicon–nitrogen bonds in these compounds are easily broken even at temperatures below 0°C with formation of an isocyanate and a chlorosilane[94,173-176]:

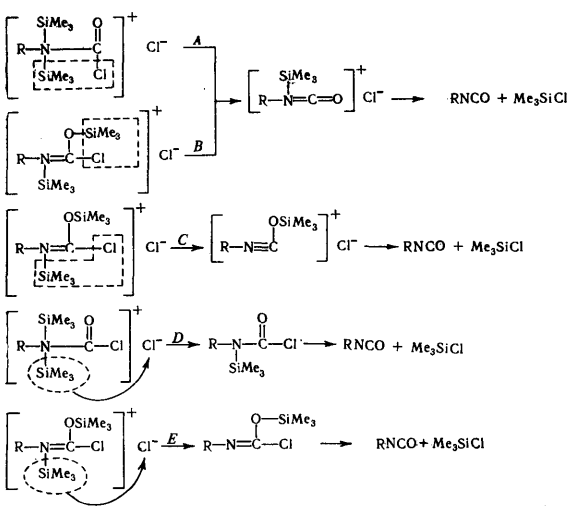
$$RN(SiR'_3)_2 + COCl_2 \rightarrow RNCO + 2R'_3SiCl$$

In this case the yield of saturated and unsaturated aliphatic, aliphatic–aromatic, and purely aromatic isocyanates, including those containing organosilyl substituents, approaches theoretical.

The mechanism of the reaction of silylamines with carbonyl chloride probably involves initial formation of an adduct resembling the complexes of tertiary organic amines with carbonyl chloride[180] and having the structure of an imidate with two equivalent and equally polarised silicon–nitrogen bonds. In considering the mechanism of the breakdown of such a salt we must take into account its possible existence in the tautomeric *O*-form (by analogy with *NN*-bistrimethylsilylamides of carboxylic acids[81])

$$\left[\begin{array}{l} Me_3Si \\ R-N \\ Me_3Si \end{array}\!\!-\!\!\overset{O}{\underset{Cl}{C}}\right]^+ Cl^- \rightleftharpoons \left[R-N=\overset{OSiMe_3}{C}-Cl\right]^+ Cl^-$$

and also the possibility that the first stage of breakdown may involve a chlorine atom either in the inner sphere of the molecule (reactions *A*–*C*) or in the outer sphere (reactions *D* and *E*):



At present it is difficult to say what is the true course of the reaction. In view of the greater tendency of the Si–N–C–X bond system than of Si–N=C–X to undergo β-elimination, however, mechanism *C* can be regarded as the least probable. The other four paths are equally probable, although ionic chlorine is probably more active.

Small quantities of carbamoyl chlorides and amine hydrochlorides are formed as side-products in the reaction of *N*-monosilylamines with carbonyl chloride. Formation of the carbamoyl chlorides is due either to some reaction at the silicon–nitrogen bond or to the addition of incompletely removed hydrogen chloride to the isocyanate. Amine hydrochlorides result from cleavage of the initial silylamine or the silylated carbamoyl chloride by hydrogen

chloride. The formation of secondary products can be reduced to a minimum by conducting the reactions in solvents which only weakly retain hydrogen chloride or in the absence of a solvent, by adding the silylamine to the carbonyl chloride, and by keeping the temperature conditions as mild as possible. The action of carbonyl chloride on disilylated organic and organosilicon amines is unambiguous.

The amino-group can be protected not only with trialkylsilyl groups R_3Si- but also with other groups such as $R_2Si=$, $RSi\equiv$, and $=S=$, as well as incompletely substituted silyl groups.

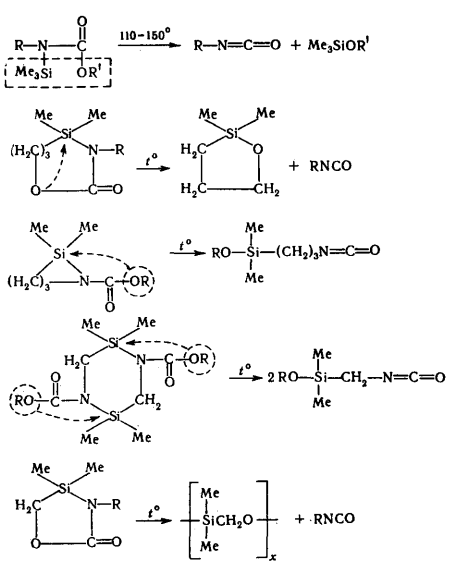
Thus the method of treating *N*-mono- and *NN*-di-silylamines not only simplifies the preparation of organosilicon isocyanates but also enables compounds to be obtained whose preparation is difficult or impossible without silyl protection. For example, it has recently been shown that this method is extremely convenient for preparing esters of *N*-carbonyl-α-amino-acids [181]. Since the production of silylamines is a simple operation, and the silicon-containing fragment is completely regenerated during treatment with carbonyl chloride, this method of obtaining isocyanates shows great industrial promise.

(*e*) Pyrolysis of esters of silicon-containing carbamic acids

The characteristic thermal decomposition of carbamic esters to isocyanates has proved entirely suitable for the preparation of organosilicon isocyanates, including those with alkoxy-groups attached to the silicon atom. The reaction is reversible, and the alcohol must be removed from the reaction mixture for complete conversion of the urethane into the isocyanate [94,182]:

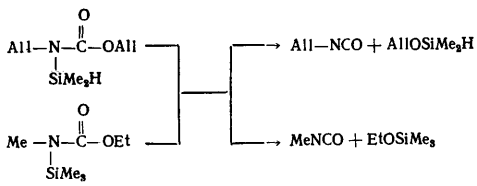
$$R_n(R'O)_{3-n}Si(CH_2)_mNHC(O)OR'' \xrightarrow{t^\circ} R_n(R'O)_{3-n}Si(CH_2)_mNCO + R''OH$$

N-Silylated urethanes show a greater tendency than the unsubstituted compounds to decompose. This is probably due to the irreversibility of cleavage of the σσ-conjugated bond system $\geqslant$Si–N–C–OR. This is a general reaction [94,179,183–189] and can be successfully used for the preparation of various organic and organosilicon isocyanates: e.g.



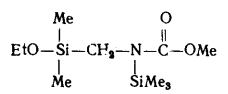
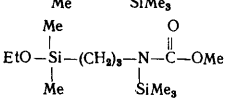
where R is an organic or organosilicon group.

When two urethanes having different *N*-silyl substituents and different alkoxy-groups undergo pyrolysis together, no alkoxysilanes of mixed structure are present among the decomposition products [190]:



This shows that no exchange of silyl groups between the urethanes occurs before the β-decomposition, which takes place by an intramolecular mechanism.

Proportions of products of trans-silylation and of β-decomposition from *N*-silyl-*N*-silylalkylurethanes.

N-Silyl-*N*-silylalkylurethane	Alkoxysilane (%) formed by	
	trans-silylation	β-elimination
	Me_3SiOEt 30	Me_3SiOMe 70
	Me_3SiOEt 87	Me_3SiOMe 13

The composition of the pyrolysis products from specially prepared compounds indicates that the β-elimination of *N*-silylurethanes containing also an *N*-alkoxysilylalkyl group is preceded by trans-silylation [191] (see Table). In contrast to the intramolecular process of β-elimination, trans-silylation can probably occur by both intramolecular and intermolecular mechanisms. The latter mechanism probably predominates in the first example, in view of the difficulty of formation of an azasilacyclobutane derivative, and intramolecular trans-silylation in the second example. The complicating effect of trans-silylation should be taken into account when examining kinetic data on the β-elimination of *N*-alkoxysilylalkyl-*N*-silylcarbamic esters [94,188,192,193].

(*f*) Reaction of silylalkyl halides with metal cyanates

The first attempts to obtain isocyanates by exchange between silylmethyl halides and metal cyanates were unsuccessful [195–197]. Silylalkyl isocyanates have recently been obtained (though in moderate yield) [198–202] by the use of dimethylformamide as solvent:

$$R_3Si(CH_2)_nCl + MOCN \xrightarrow[H.CON(CH_3)_2]{140-150^\circ C} R_3Si(CH_2)_nNCO + MCl\ .$$

($n = 1.3$; M=K, Na)

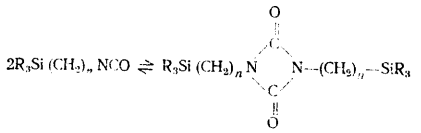
The effects of temperature, nature of solvent, and reactant and catalyst concentrations on the rate and the direction of the exchange between trialkylsilylalkyl chlorides and potassium cyanate have been examined [182,203–206]. This indicated that the optimum conditions for the preparation of silylalkyl isocyanates in dimethylformamide involve equimolecular proportions of 0.6 M silylalkyl

chloride and potassium cyanate with 5% (on weight of salt) of tetra-alkylammonium iodide as catalyst at 150°C for 20 min, when the yield of isocyanate reaches 60–70%.

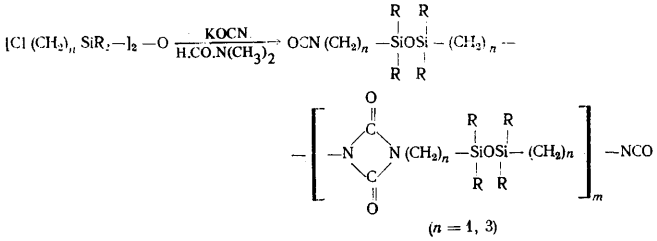
When the time of contact between the reactants is increased to 2–3 h, only dimeric products are formed [94,203-206]. The alkali-metal (sodium or potassium) cyanates used catalyse the dimerisation. Pyridine, triethylamine, and phenyldiethylphosphine also catalyse this reaction. Salts such as potassium, sodium, and tetra-alkylammonium chlorides and tetra-alkylammonium iodides present in the reaction mixture have no catalytic effect.

Replacement of potassium cyanate by the sodium salt has no significant effect on the yield of silylalkyl isocyanate although the duration of the preparation is increased [205]. Silylalkyl isocyanates are not formed in the absence of a solvent, in such solvents as benzene, acetone, and acetonitrile (probably because of the sparing solubility of potassium cyanate), nor in the presence of excess of the initial silylalkyl halide. 3-Chloropropylsilanes are rather less reactive than the chloromethyl derivatives in the exchanges, which is explained by the possible participation of *d*-orbitals of the silicon atom in formation of the intermediate complex in the case of α-derivatives [203].

A dioxouretidine structure was assigned to the dimeric form of the silylalkyl isocyanates, at first conjecturally [166] and then on the basis of infrared spectra [204]. Dimeric and monomeric forms are present in equilibrium [94,204]:



Bishalogenoalkyldisiloxane derivatives form with potassium cyanate in dimethylformamide mainly oligomeric and polymeric products having terminal isocyanato-groups (together with small quantities of the monomeric di-isocyanates) [182,202-205,207]:



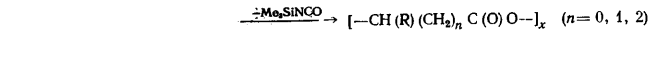
($n = 1, 3$)

When the initial mixture of reactants is heated for 20–30 min, di-isocyanates cannot be isolated at all, since only polymeric products are formed.

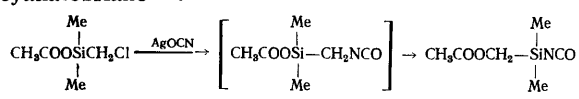
(*g*) Other reactions

A number of other chemical reactions of organosilicon compounds have been described, in which isocyanates are quite often formed only as intermediate products. These reactions can be briefly illustrated by the following schemes.

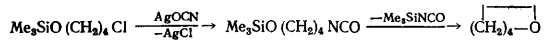
1. Decomposition of products of the reaction of trimethylsilyl α-, β-, and γ-bromo-carboxylates with silver cyanate [208]:



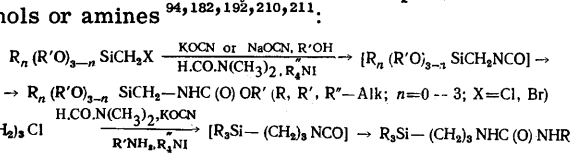
2. Isomerisation of an isocyanatomethylsilane into an isocyanatosilane [208]:



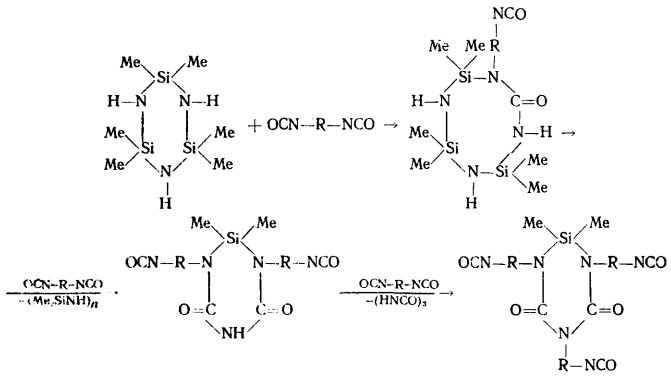
3. δ-Elimination from 4-siloxybutyl isocyanates [208] (in contrast to the stable tetrakisisocyanatomethoxysilane [209]):



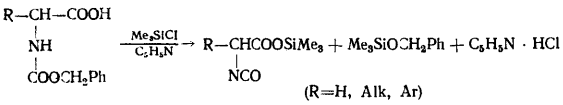
4. Formation of urethanes and ureas when silylalkyl halides react with metal cyanates in the presence of alcohols or amines [94,182,192,210,211]:



5. Interaction of hexamethylcyclosilazanes with excess of a di-isocyanate [212]:

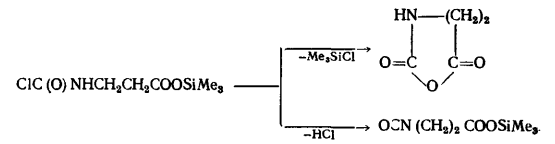


6. Decomposition of derivatives of organic amino-acids with strong silyl protection [185,186]:

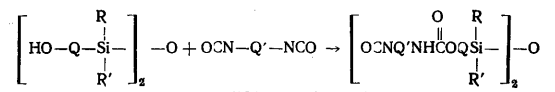


(R=H, Alk, Ar)

7. Interaction of bistrimethylsilyl α-azaglutarates with thionyl chloride, carbonyl chloride, or a phosphorus trihalide [213]. Isocyanates are formed as side-products in this reaction, which yields predominantly amino-acid anhydrides:

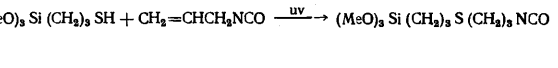


8. Addition of silicon-containing organic diols to di-isocyanates [214]:

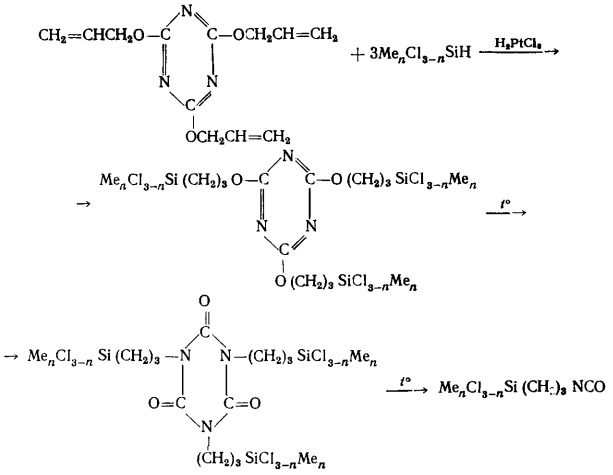


(R=Me, R'=Ph; Q=$-(CH_2)_4-$, Q'=$-(CH_2)_6-$, $-MeC_6H_3-$)

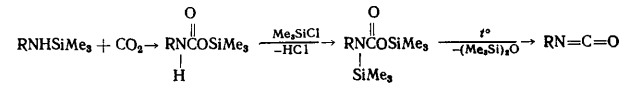
9. Addition of silylalkanethiols at the double bond of allyl isocyanate [162]:



10. Pyrolysis of products of the hydrosilylation of triallyl cyanurate [94]:



11. An interesting method for obtaining organic and organosilicon isocyanates avoids the use of carbonyl chloride [215]:



(*h*) Oligomeric and polymeric silylalkyl and silylaryl isocyanates

A great deal of information has been published on oligomeric and polymeric organosilicon *C*-isocyanates, chiefly in the patent literature. These compounds can be formed in principle by the following processes—(i) hydrosilylation of alkenyl isocyanates with oligo(or poly)siloxanes having terminal Si–H bonds [159], (ii) chain termination in polysiloxanes by ω-isocyanatoalkylsilanes [216], (iii) treatment of siloxanes having terminal hydroxyalkyl and other groups with excess of an organic di-isocyanate [217–221], (iv) reaction of excess of an organic di-isocyanate with hydroxyl containing unsaturated compounds followed by addition of incompletely substituted silanes at ethylemic bonds [158,159], (v) action of excess of an organic di-isocyanate on silocanes having terminal aminoalkyl groups [218], (vi) condensation of organosilicon alcohols with organic or organosilicon di- or tri-isocyanates [167,214,217,220], (vii) pyrolysis of adducts of oligosiloxanes (having terminal aminoalkyl groups) with phenyl chloroformate [159], (viii) interaction of excess of an organosilicon di-isocyanate with silazanes and cyclosilazanes [212,222], (ix) stepwise action of carbonyl chloride on oligosiloxanes containing terminal amino-groups [169,223–225], and (x) synthesis of polyisocyanates from 1,3-bis-ω-chloroalkyldialkyldisiloxanes and alkali-metal cyanates [206].

2. Physical Properties

Monomeric and oligomeric organosilicon *C*-isocyanates are colourless or slightly yellowish liquids, indefinitely stable in the absence of moisture but easily hydrolysed in moist air [94,159,170,207]. When heated to 150–200°C, monomeric di-isocyanates form oligomeric products having terminal isocyanato-groups [207].

The infrared spectra of monoisocyanates [94,162,185,186,204,214,226] contain an intense absorption band due to the isocyanato-group in the range 2267–2243 cm^{-1}. A similarly intense bond has been observed with di-isocyanates (2270–2243 cm^{-1}).

The nuclear magnetic resonance spectra of several mono- and di-isocyanates have been discussed in Ref. 94.

3. Chemical Properties

Like their carbon analogues, silicon-containing isocyanates react vigorously with ammonia and with primary and secondary amines to form silicon-containing ureas [94,154,163,203,227], and with hydrazides and amides of carboxylic acids to give the corresponding semicarbazides [203,226] and acylureas [203]. Urethanes and symmetrical ureas respectively are obtained with alcohols and with water [94,154,203,228].

Silicon-containing di-isocyanates on treatment with ammonia and with primary and secondary amines can be converted into the corresponding bisureas, and by the action of *NN'*-dialkylhydrazines into the bis-semicarbazides [94,173,207,229–234]. Reaction of the di-isocyanates with organic diamines or hydrazines yields polysilylalkylureas or polysilylalkylsemicarbazides [235–237].

Various reagents containing a mobile hydrogen atom form the sequence

amines > hydrazides ≫ water > alcohol > amides

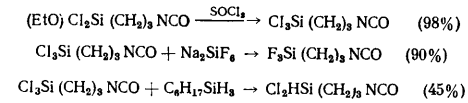
according to their reactivity towards 3-triethylsilylpropyl isocyanate [226]. The reactivity of an isocyanate of type $R_3Si.[CH_2]nNCO$ with $n = 3$ exceeds that of the compound having $n = 1$ about twentyfold [226].

Heating converts silicon-containing aromatic isocyanates into carbodi-imides:

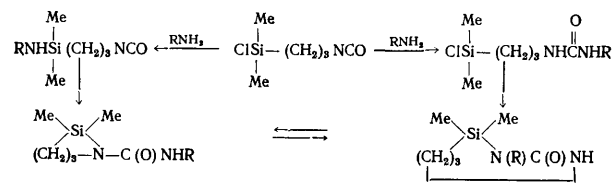


This reaction is catalysed by phosphorus compounds such as phosphafluorene. The aliphatic isocyanates do not undergo this reaction. In the presence of amines, amides, sodium benzoate, and other basic catalysts they form isocyanurates [238,239].

Several reactions of silylalkyl isocyanates have been described that do not involve the isocyanato-group [169,240]:



Chloro- and alkoxy-silylalkyl isocyanates exhibit dual reactivity. With water, for example, they give siloxane di-isocyanates [94,177], but with more active reagents (amines) with functional groups are involved [241]:



The isocyanato-group is also extraordinarily reactive in oligomeric compounds of silicon, and reacts with all types of reagents containing active hydrogen atoms [159].

4. Prospects for the Application of Silicon-containing C-Isocyanates

The enhanced interest taken in silylalkyl isocyanates is due primarily to the possibility of obtaining from them cold-self-vulcanising polysiloxane rubbers and polyurethanes with improved resistance to heat, moisture, and frost[159,218,221]. Cold vulcanisation takes place under normal conditions; the only byproduct is carbon dioxide, which readily diffuses through the vulcanised product. These rubbers contain carbamide cross-links, and surpass in mechanical strength and resistance to oils and benzene their alkoxylated and acyloxylated organosilicon analogues. They differ advantageously from ordinary polyurethane rubbers in high moisture resistance and in low-temperature elasticity[135,136,142,159,218,219].

Polymeric materials based on silicon-containing organic isocyanates can be used for the manufacture of various articles by moulding and casting, as insulating materials, for coating electrical goods, and for other purposes. The ability to set at low temperatures enables them to be employed e.g. for treating sensitive materials such as leather, paper, and cloth, in the printing industry, as sealants, etc.[159,169,218]

Silicon-containing organic di-isocyanates have been proposed for the production of polyurethane, polyurea, polyamide, etc. materials[159,207,218,220,221] and also for the synthesis of polysiloxane polymers containing free isocyanato-groups. The latter have been used to obtain plastics, rubbers, resins, liquids, and films[159,170,218,242]. Information has been published on the use of silanes and siloxanes with isocyanato-groups in the radical as hydraulic fluids, rubbers, elastomers, and adhesives[169,243] and for conferring wear resistance on polyamide and polyester fibres, and water resistance and adhesion on coatings[244].

Silicon-containing organic polyisocyanates improve the adhesion to substrates of hardenable compositions such as as silicones, polyacrylates, polyurethanes, and polysulphides[167,245,246]. Silanes and siloxanes modified with isocyanate fragments can be employed to obtain film coatings[156,162,202,246], rubbers, and resins[246], for impregnating various materials in order to confer water-repellent properties[158,182,224,247], as glues[248], surface-active agents[248], foam stabilisers in the production of polyurethane foams[223,249], for cementing glass[162,174], and for other purposes[159,160,167,212,216,242,243,249-253].

Research is probably widely developed on the application of organosilicon compounds mixed with organic isocyanates (with the components chemically uncombined in the initial mixtures). Combinations of organopolysiloxanes with organic di-isocyanates have already been suggested as coatings for electrical goods, distinguished by high heat resistance, elasticity, good adhesion to metals, and improved insulating properties compared with the usual polysiloxane varnishes[254].

Combining polysiloxanes with a mixture of polyesters and di-isocyanates yields compositions which foam at relatively low temperatures without the use of blowing agents[255] and are stable when heated to 200–250°C.

Rubberlike polymers based on silanediols and organic polyesters with terminal isocyanato-groups are elastic, durable, and heat-resistant[256].

Treating fillers for silicone rubber with organic polyisocyanates tends to reinforce them[257,258], and the application of mixtures of organosiloxanes or hydrolysable organosilanes with organic isocyanates to natural or synthetic materials confers hydrophobic properties on them[259].

Organic and organosilicon compounds mixed with isocyanates either individually or as components of more complicated compositions have been proposed for the preparation of water-repellent lubricating greases[260,261], elastic fibres[262], and adhesives[263], as well as for many other purposes[264-268].

Organic isocyanates have been patented as quick-setting agents for liquid organosilicon oligomers, polymers, and copolymers[269,270]. Compositions based on silicones containing isocyanato-groups and purely organic di- and polyfunctional compounds will apparently be identical in properties with materials based on organic di- and polyisocyanates and carbofunctional polysiloxanes. Since polymers of the latter type are unrelated to the topic of the present Review, we will merely list references to this work[271-293]. Investigations have been made also on polymeric materials based on organic isocyanates in which the organosilicon component has a subordinate role (surface-active agents, fillers, pore-regulators, stabilisers, catalysts, adhesion additives, etc.[294-304]).

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