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Review

ORGANOSILICON SYNTHESIS OF ISOCYANATES *

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Contents

I. Introduction

During the past decade there has appeared the new field of the application of organosilicon compounds as reagents in preparative organic chemistry.

At the present time we can confirm the existence of an organosilicon method for the synthesis of a number of classes of compounds which favourably complements other organometallic methods of synthesis based on compounds of such elements as magnesium, alkali metals, aluminium, boron, etc.

The application of organosilicon methods appeared to be exceptionally fruitful in the synthesis of organic isocyanates, and this has led to the elaboration of new routes to prepare them, including phosgene-free ones.

Below we describe the main results of our investigations in the area of the organosilicon synthesis of isocyanates, part of which has already been reported in review papers [1–9].

* The author dedicates this review to an outstanding scientist, Professor M. Kumada.

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II. Synthesis of alkyl and aryl isocyanates

2.1. Phosgenation of N-Silylamines

We have found that the method of synthesis of isocyanates by phosgenation of silyl-substituted amines [10–18] is of great advantage over the application of free amines in this reaction, e.g. the phosgenation of methylamine results in the formation of methylcarbamoyl chloride which decomposes to methyl isocyanate and hydrogen chloride only at ~ 100 °C:

$$MeNH_2 + COCl_2 \xrightarrow[-HCl]{} MeNHC(=O)Cl \overset{100\,^\circ C}{\rightleftharpoons} MeNCO + HCl$$

The latter reaction is reversible, therefore in order to isolate the methyl isocyanate the methylcarbamoyl chloride is usually dehydrochlorinated in the presence of HCl acceptors.

However, the substitution in methylamine and in other primary alkylamines of even one N–H hydrogen bond by a trimethylsilyl group enables one to obviate the difficulty of isolating the isocyanates in the reaction:

$$RNHSiMe_3 + COCl_2 \xrightarrow[-HCl]{} \left[RNCOCl \atop | \atop SiMe_3 \right] \xrightarrow{<0\,^\circ C} RNCO + Me_3SiCl \quad (90\text{–}99\%)$$

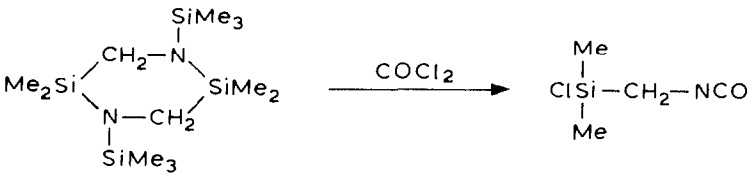
The high isocyanate yields obtained, even at low phosgenation temperatures (−60° to 0°), are accounted for firstly by the fact that the forming *N*-silylcarbaminoyl chlorides contain a σ,σ-conjugated Si–N–C–Cl bonding system, and therefore they can easily undergo an intramolecular β-elimination reaction [2], and secondly, the isocyanate and trimethylchlorosilane products do not react with each other.

The method of preparation of organic isocyanates by silylamine phosgenation has also been extended to *N,N*-disilylamines [10–14,18]:

$$RN(SiR'_3)_2 + COCl_2 \xrightarrow{\sim 0\,^\circ C} RNCO + 2\ R'_3SiCl$$

As in the case of *N*-monosilylamines the reaction proceeds under mild conditions, the isocynate yields nearing quantitative.

For example [14]:



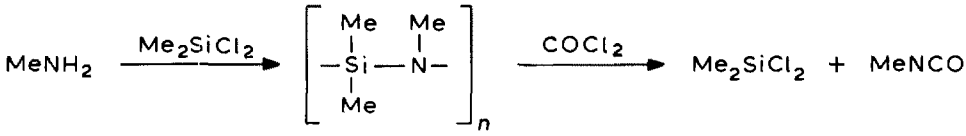
The phosgenation of *N,N'*-disilylated diamines resulted in the formation of diisocyanates of the aliphatic and aromatic series [16,17]:

$$Me_3SiNH\text{–}R\text{–}NHSiMe_3 + 2\ COCl_2 \xrightarrow[-2HCl]{} O{=}C{=}N\text{–}R\text{–}N{=}C{=}O + 2\ Me_3SiCl$$

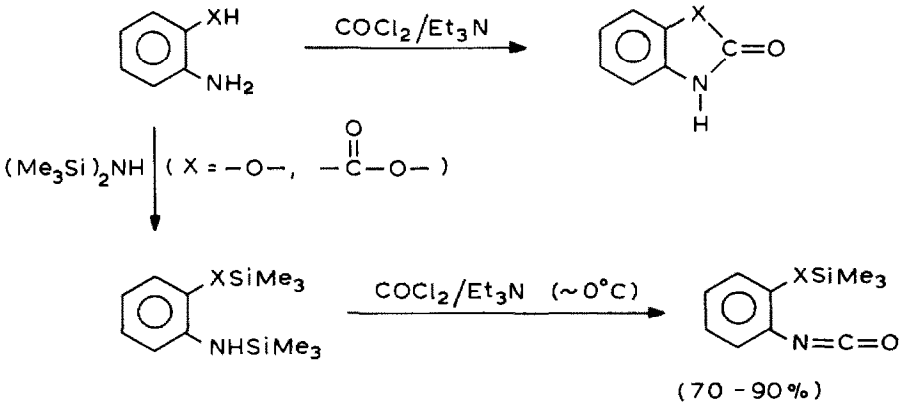
In the case of diamines not containing N–H bonds, i.e. tetrasilyl derivatives, phosgenation proceeds quantitatively [17].

The only shortcoming in the use of *N,N*-disilylamines for isocyanate synthesis is the difficulty of substituting all the hydrogen atoms at nitrogen by TMS-groups, using the generally-accepted silylating techniques. However, in the case of silyl-substituents of smaller volume (e.g. HMe_2Si) this does not cause any problem [17,21].

Besides using the R_3Si group for the protection of amines, it is possible to employ $R_2Si=$ groups, as well as others, for the same purpose. For example [11]:



In phosogenating those compounds containing, in addition to NH_2 functions, other functional groups sensitive to the action of $COCl_2$ or HCl (amino alcohols, amino acids, etc.), as well as thermally weakly-stable compounds, the change from free amines to silyl-derivatives enables one to achieve not only quantitatively better, but also qualitatively superior results [15,19,20]. For example, although *o*-aminophenol and anthranilic acid, in the reaction with phosgene, form a benzoxazolone and the anhydride of isatic acid, respectively, in quantitative yield, phosgene treatment of their silyl derivatives results in formation of the corresponding isocyanates in good yield [19,20].



Also, it is possible to prepare isocyanates whose synthesis is difficult to perform without a preliminary silyl *N*-function protection. For example, phosgene treatment of *N*-TMS-novocaine produced the corresponding isocyanate (III) in an ~ 80% yield [20]:

$$p\text{-}Me_3SiNHC_6H_4COO(CH_2)_2NEt_2 + COCl_2 + Et_3N \xrightarrow{0 \text{ to } 20\,^\circ C}$$

$$p\text{-}O{=}C{=}NC_6H_4COO(CH_2)_2NEt_2$$

A number of carbon-functional isocyanates of elements of Group IV have been obtained in the same manner [11,14,22–25]:

$$\gtrless M(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} \gtrless M(CH_2)_3NCO$$

where M = Si, Ge, Sn,

as well as adamantyl isocyanate [26]

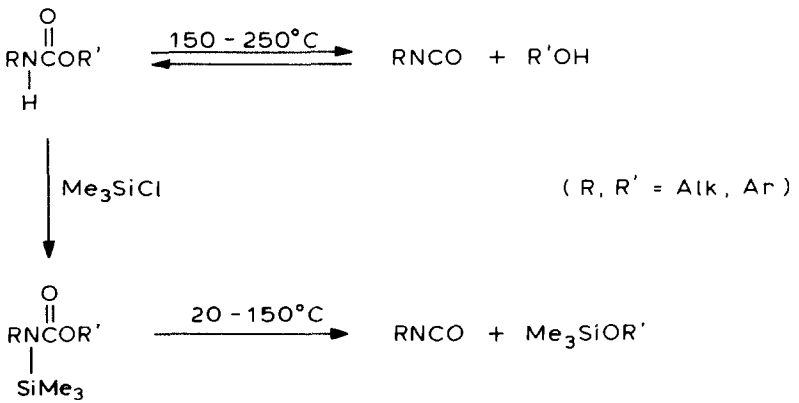
$$AdNHSiMe_3 \xrightarrow{COCl_2} AdNCO$$

Since this isocyanate synthesis method proved to be advantageous for preparative purposes, it has been used many times by investigators. For example, Rogozhin and coworkers considerably improved the ethyl ester yield of a range of isocyanatocarboxylic acids by using the silyl *N*-function protection in the amino acid series [9].

It should be pointed out that the chlorosilane corresponding to that used for the silyl protection of the original amines is almost completely regenerated by the phosgene treatment of silylamines.

2.2. Thermolysis of N-silylurethanes

As is known, isocyanates and alcohols are produced in the thermolysis of organic carbamates. However, this reaction is little use for preparative purposes as it is reversible. In contrast, *N*-silyl-substituted urethanes also undergo a non-reversible β-elimination to alkoxysilanes and isocyanates under considerably milder conditions, which allows the preparation of the latter in a practically quantitative yield [27]:



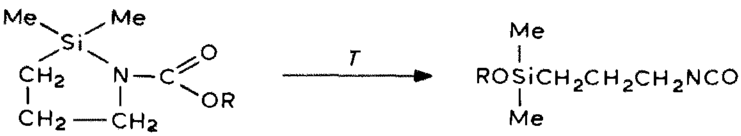
A study of the kinetics of the β-elimination in the *N*-silylcarbamate series, and the joint thermolysis of a mixture of *N*-silylurethanes, provide evidence in favour of the intramolecular character of the reaction, i.e. the β-elimination of *N*-silylurethanes proceeds through a four-membered transition complex [2,28–32].

The β-elimination reaction proceeds similarly in the case of other compounds containing the Si–N–C–O fragment. For example, the thermal decomposition of esters of silyl-carbazic- and -siloxycarbamic acids opens the way for the synthesis of the hypothetical amino- and oxy-isocyanates [33–35].

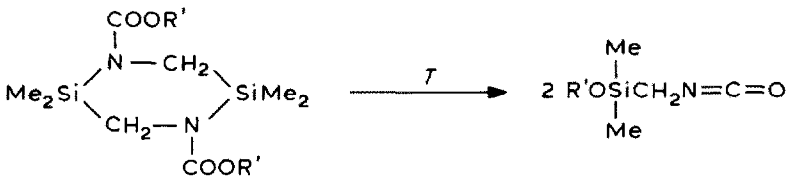
$$\underset{\substack{|\\ Me_3Si}}{Me_2NNCOOR'} \xrightarrow{T} [Me_2NNCO]$$

$$\underset{\substack{|\\ Me_3SiO-C=O}}{Me_3SiO-N-SiMe_3} \xrightarrow{T} [Me_3SiONCO] \qquad [35]$$

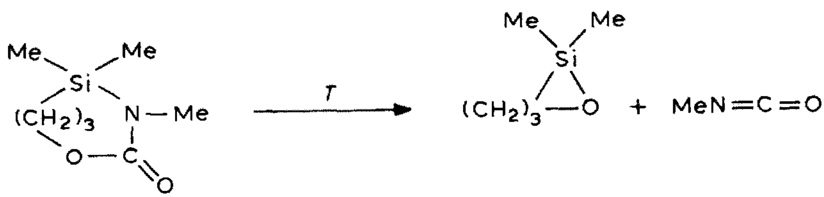
The thermolytic reaction of cyclic silylurethanes proceeds along different pathways, depending on the *exo-* or *endo*-arrangement of the Si–N–C–OR′ bond system. For example, in one case the β-elimination proceeds with ring opening [15,27],



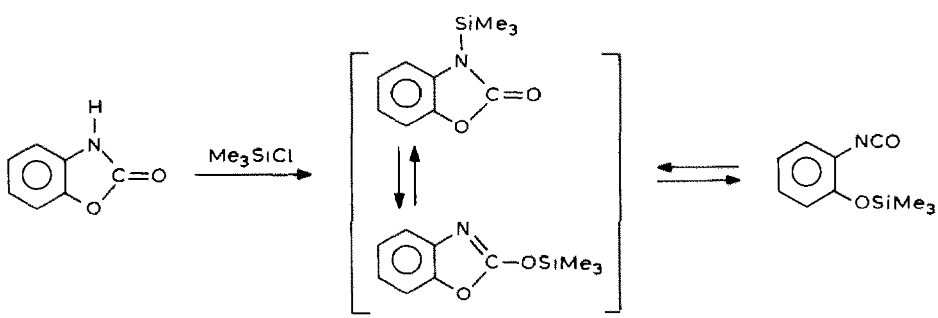
while in another case, the silylcyclourethane decomposes to two isocyanate molecules [28,29,32],

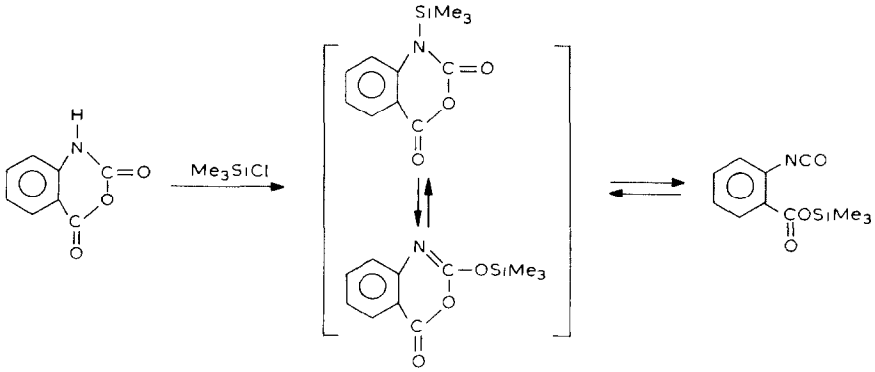


and in a third case, the reaction proceeds with ring contraction [27]:



Interesting ring-chain rearrangements also take place in the cases of *N*-silyl-substituted benzoxazolone and the anhydride of isatic acid:





Recently, we showed that from the preparative aspect a more favourable synthesis variant than the thermolyses of the *N*-TMS-carbamates is the direct reaction of *N*-alkyl- and -aryl-carbamates with polychlorosilanes in the absence of HCl acceptors, see Table 1 [36].

$$RNHCOOR' + R''SiCl_3 \xrightarrow[-HCl]{50\text{–}220\,^\circ C} \left[\begin{array}{l} RNCOOR' \\ | \\ R''SiCl_2 \end{array}\right] \rightarrow RNCO + R'OSiCl_2\text{–}R'', \quad (77\text{–}99\%)$$

The intermediately-forming *N*-chlorosilylurethanes are less stable thermally than the *N*-trimethylsilylurethanes and decompose with elimination of isocyanate at the moment of their formation. For example, the thermolysis temperature is 100 °C for $Me_3SiN(Ph)COOMe$, − 20 °C for $ClMe_2SiN(Ph)COOMe$ and considerably below 20 °C for $Cl_2MeSiN(Ph)COOMe$.

Taking into account the availability of organic urethanes, e.g. phenylurethane (PhNHCOOMe), the last method of synthesis of phenyl isocyanate is one of the most convenient methods for preparative purposes.

TABLE 1

PREPARATION OF ISOCYANATES BY INTERACTION OF THE CARBAMATES RNHCOOR' WITH CHLOROSILANES

Carbamate		Chlorosilane	Isocyanate yield (%)
R	R'		
Me	Et	$PhSiCl_3$	77
Et	Me	$PhSiCl_3$	87
All	Me	$PhSiCl_3$	77
All	Me	$Cl_2CHSiCl_3$	81
n-Bu	Et	Ph_2SiCl_2	85
n-Bu	Et	$PhSiCl_3$	89
i-C_6H_{13}	Me	$PhSiCl_3$	84
cyclo-C_6H_{11}	Me	$PhSiCl_3$	80
cyclo-C_6H_{11}	Me	$SiCl_4$	98
Ph	Me	$PhSiCl_3$	85
Ph	Et	Ph_2SiCl_2	69
Ph	Et	$PhSiCl_3$	99

2.3. Thermolysis of O-silylurethanes

O-trimethylsilyl esters of carbamic acids (*O*-silylurethanes) form rather readily according to the following reaction [5,37]:

$$RNHSiMe_3 + CO_2 \rightarrow RNHCOOSiMe_3$$

We observed [38,39] that these *O*-silylurethanes, upon heating, decompose to the corresponding isocyanate and trimethylsilanol:

$$Me_3SiO\overset{\overset{O}{\|}}{C}NHR \xrightarrow{100\,^\circ C} Me_3SiOH + RNCO$$

However, due to dehydration of Me_3SiOH, a large part of the isocyanate is hydrolyzed by the released water and the main reaction products of the β-elimination of urethane may be hexamethyldisiloxane and the *sym*-dialkylurea.

Generally, if the thermolysis of urethane is carried out in the presence of polychlorosilanes (e.g. $PhSiCl_3$), the organic isocyanate can appear in high yield [37–40]. The role of the polychlorosilane in the reaction amounts, not so much to the binding of the water being released, but to the formation of *O*-chlorosilylurethanes as a result of the resilylation reaction. The chlorosilylurethanes are thermally more unstable than the *O*-TMS-derivatives: their decomposition occurs already in the process of their formation at temperature $< 20\,^\circ C$:

$$RNHSiMe_3 + CO_2 \xrightarrow{20\,^\circ C} RNHCOOSiMe_3 \xrightarrow[-Me_3SiCl]{+PhSiCl_3}$$

$$RNHCOOSiCl_2Ph \xrightarrow{20\,^\circ C} RNCO + [HOSiCl_2Ph]$$

Later, other modifications to this method of synthesis of isocyanates were suggested, involving the combining of the silylation and amine carboxylation processes [41]. This variant laid the basis for the phosgene-free industrial production of methyl isocyanate:

$$MeNH_2 + (Me_3Si)_2NH \xrightarrow[-NH_3]{CO_2} MeNHCOOSiMe_3 \xrightarrow[-Me_3SiCl]{+PhSiCl_3}$$

$$[MeNHCOOSiCl_2Ph] \xrightarrow{T} MeNCO + [HOSiCl_2Ph]$$

Recently, it was found [42] that the process could be facilitated by direct synthesis of *O*-chlorosilylurethanes by by-passing the production of *O*-TMS-urethanes. This is achieved through the reaction of chlorosilanes with the ammonium salts of *N*-alkylcarbamic acids:

$$[RNHCOO]^-[RNH_3]^+ + PhSiCl_3 \xrightarrow[-RH_2N\cdot HCl]{} [RNHCOOSiPhCl_2] \xrightarrow{T}$$

$$RNCO + [HOSiCl_2Ph]$$

Carbamic acid salts are readily formed from CO_2 and the corresponding amines (or their mixture with a tertiary amine): *O*-silylurethanes can be obtained by interacting CO_2, not only with the primary amines [38–45], but also with ammonium salts (hydrochloride, sulfates, carbamates) [43,46–48] in the presence of a silylating agent, e.g. hexamethyldisilazane. Such a process for preparing *O*-silylurethanes are also

TABLE 2

PREPARATION OF THE ISOCYANATES RNCO BY INTERACTING THE UREAS RNHC(O)NHR' WITH CHLOROSILANE

Urea		Chlorosilane	Isocyante yield (%)
R	R'		
Me	Me	$PhSiCl_3$	95
Me	Me	$(Cl_3Si)_2O$	68
Me	Me	$Cl_3SiCHCl_2$	51
Me	n-Bu	$PhSiCl_2$	64
Et	Ph	$PhSiCl_3$	73
t-Bu	t-Bu	$PhSiCl_3$	97
cyclo-C_6H_{11}	cyclo-C_6H_{11}	$PhSiCl_3$	97
cyclo-C_6H_{11}	cyclo-C_6H_{11}	$Cl_3SiCHCl_2$	87
Ph	Ph	$PhSiCl_3$	79

suitable for low-basicity amines, particularly aniline [41,47] and amino acids [49]. Diisocyanates can also be prepared from *O*-silylurethanes; however the latter are readily prepared only by the siloxycarbonylation process [47,50,51].

$$NH_2RNH_2 \xrightarrow{R_2NCOOSiMe_3} R_2NH + (Me_3SiOOCNH)_2R \xrightarrow{PhSiCl_3} OCNRNCO$$

Finally, another way of preparing *O*-silylurethanes was recently found [52]:

$$RNH_2 + Me_3SiNHCOOSiMe_3 \rightarrow RHNCOOSiMe_3$$

2.4. Interaction of sym-diorganylurea with chlorosilanes

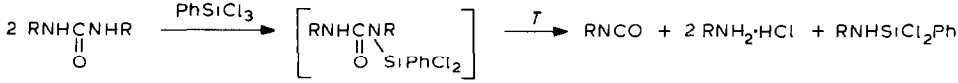
As is known, *sym*-diorganylureas dissociate by thermolysis to amine and isocyanate; however, the separation of the latter is complicated by the reversibility of the reaction:

$$RNHC(O)NHR \overset{200\,^\circ C}{\rightleftharpoons} RNCO + RNH_2$$

However, we found [53,54] (see Table 2) that aliphatic and aromatic isocyanates were formed in high yield when these ureas were heated with high boiling (> 100 °C) chlorosilanes (see Table 2).

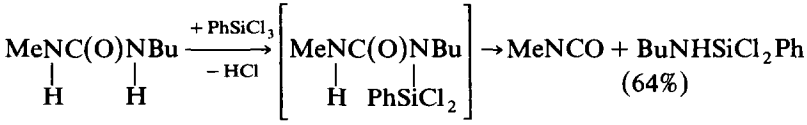
$$MeNHC(O)NHMe + PhSiCl_3 \xrightarrow{160\text{–}190\,^\circ C} MeNCO + MeNHSiCl_2Ph$$

The separation of HCl in the first step of the reaction, as well as the significantly lower temperature of dissociation to isocyanates than upon heating the same ureas in the absence of chlorosilanes, indicates that there silylation of the ureas by chlorsilane takes place first, followed by β-elimination of the thermally unstable chlorosilyl-derivatives [54]:

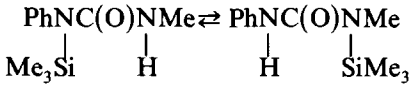


An increase in the reactivity of the chlorosilane ($PhSiCl_3 < Cl_2CHSiCl_3 < Cl_3SiOSiCl_3$), leads to a decrease in the starting temperature of the reactions and to a rise in the reaction rate.

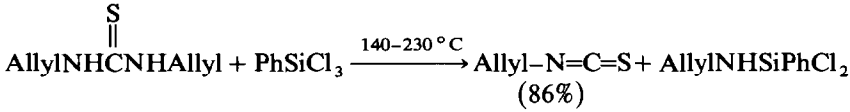
In the case of ureas with different substituents at the *N* and *N'* atoms, the silylation proceeds predominantly at the more nucleophilic of them [54]. For example:



However, the composition of the reaction products may be affected by the silyl proton exchange between the *N* and *N'* atoms [4, 54]:



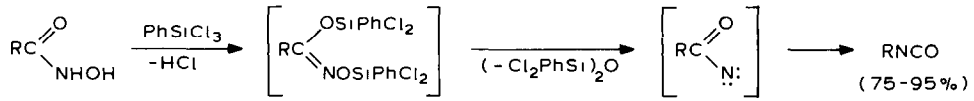
N,N'-Diorganylthioureas interact with chlorosilanes in the same manner [54]:



To conclude, we wish to note that the availability of the initial reagents, the simplicity of the instrumentation of the process, and the high yields of isocyanates, allow us to regard this organosilicon method of synthesis of isocyanates as one of the most suitable one.

2.5. Thermolysis of silylhydroxamic acids

Bis-TMS-derivatives of hydroxamic acids, when heated (~ 150 °C), are converted into isocyanates by the Lossen rearrangement [3]. However, we have found [55] that a more convenient method from the preparative view which does not require the special synthesis of bis-TMS-hydroxamic acids, is by heating (~ 100 °C) the hydroxamic acids or their salts in the presence of a polychlorosilane. Obviously, as in the case of other compounds with amido-functions (urethanes, ureas) considered above, the reaction scheme includes the intermediate formation of thermally partially-stable chlorosilyl-derivatives which then undergo rapid dissociation to nitrenes, which isomerize to isocyanates:



Such a modification to the Lossen rearrangement, using the organosilicon compounds, is distinguished favourably from the classical variant by a practically-complete absence of side-reactions, which allows the preparation of isocyanates in yields close to quantitative.

An attempt to combine in one process the preparation of hydroxomic acids, their silylation and their subsequent thermolysis to isocyanate, gave good results only in

the aromatic series [55]:

$$(PhCO)_2O + HONH_2 \cdot HCl \xrightarrow{PhSiCl_3} PhNCO + PhCO_2SiPhCl_2 + HCl + (PhCl_2Si)_2O$$

III. Synthesis of acyl isocyanates

3.1. Acylation of isocyanatosilanes

Isocyanatosilanes (>SiN=C=O) have attracted our attention as they are available, extremely stable and highly soluble (in organic compounds) potential sources of the isocyanate group in organic synthesis [3].

Me_3SiNCO and other isocyanatosilanes, in the presence of catalytic amounts of halides of the elements of Groups II–VIII of the Periodic System, were found readily to enter the exchange reaction with halogenoanhydrides of carbonic, sulfonic and carboxylic acids, to form acyl isocyanates in high yield (Table 3) [56–58]:

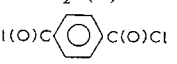
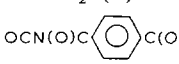
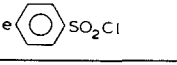
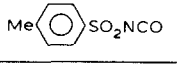
$$R{-}X{-}Y + Me_3SiN{=}C{=}O \xrightarrow[-Me_3SiY]{\text{catalyst, } 90\text{–}150\,^\circ C} R{-}X{-}N{=}C{=}O$$

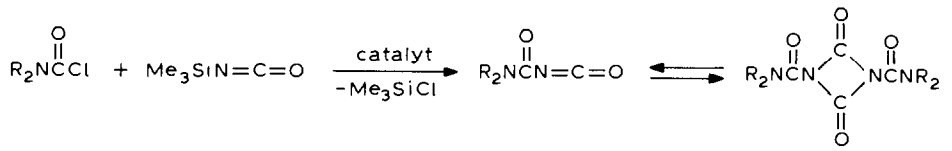
$$X = -\overset{O}{\overset{\|}{C}}-,\quad -O\overset{O}{\overset{\|}{C}}-,\quad -\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-;\qquad Y = Cl, Br$$

The same reaction with dialkylcarbamoyl chlorides [59] results in dialkylcarbamoyl isocyanates in a much higher yield (1–1.5 times) than obtained in the known method of their synthesis by the interaction of *N,N*-dialkylurea with oxalyl chloride.

TABLE 3

SYNTHESIS OF ACYL AND SULFONYL ISOCYANATES OBTAINED WITH Me_3SiNCO

Initial reagent	Product	Yield (%)
MeC(O)Cl	MeC(O)NCO	76
$Me_2CHCH_2C(O)Cl$	$Me_2CHCH_2C(O)NCO$	87
MeCHClC(O)Cl	MeCHClC(O)NCO	64
$Me_2CHCHClC(O)Cl$	$Me_2CHCHClC(O)NCO$	63
PhC(O)Cl	PhC(O)NCO	68
$PhCH_2C(O)Cl$	$PhCH_2C(O)NCO$	79
$PhOCH_2C(O)Cl$	$PhOCH_2C(O)NCO$	98
		78
MeOC(O)Cl	MeOC(O)NCO	32
$ClMe_2Si(CH_2)_3C(O)Cl$	$ClMe_2Si(CH_2)_3C(O)NCO$	76
$ClMe_2Si(CH_2)_3C(O)Cl$	$(OCN)Me_2Si(CH_2)_3C(O)NCO$	75
$ClMe_2Si(CH_2)_{10}C(O)Cl$	$ClMe_2Si(CH_2)_{10}C(O)NCO$	41
$ClMe_2Si(CH_2)_{10}C(O)Cl$	$(OCN)Me_2Si(CH_2)_{10}C(O)NCO$	76
$(MeC(O))_2O$	MeC(O)NCO	91
$(EtC(O))_2O$	EtC(O)NCO	89
$(PhC(O))_2O$	PhC(O)NCO	86
$PhSO_2Cl$	$PhSO_2NCO$	80
		90

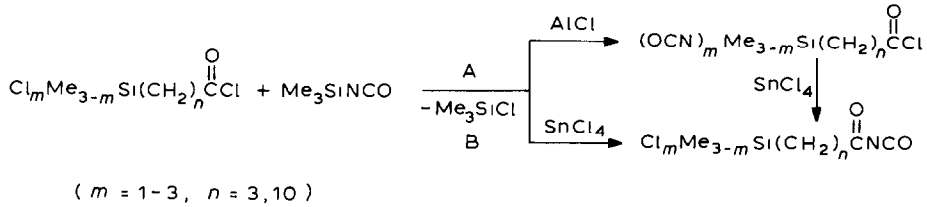


In the ease of acylation of Me_3SiNCO, the chlorides of acids have a reactivity distribution as in the following series:

$RSO_2Cl > RC(O)Cl > R_2NC(O)Cl > ROC(O)Cl.$

From among the catalysts under investigation ($ZnCl_2$, BCl_3, BF_3, OEt_2, $AlCl_3$, Et_2SnCl_2, Bu_2SnCl_2, $SnCl_4$, $GeCl_4$, $TiCl_4$, $FeCl_2$) the most catalytically-active one was tin tetrachloride.

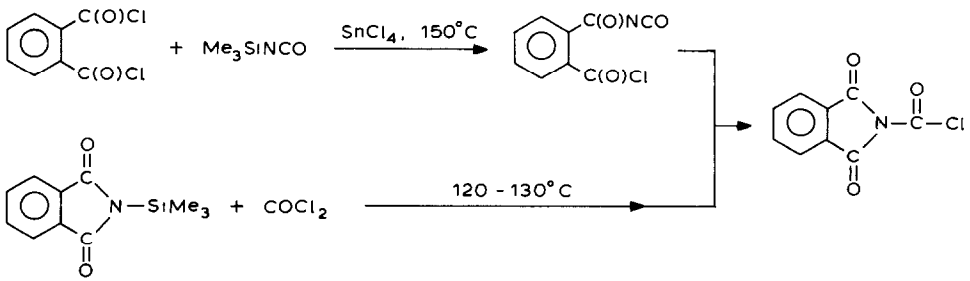
The exchange reaction of Me_3SiNCO with chlorides of silylcarboxylic acids give the first representatives of organosilicon-substituted acyl isocyanates [58]. In the presence of a Si–Cl bond in the initial chlorides, the exchange in the Si–Cl bond (Route A) as well as in the C–Cl bond (Route B) may take place, depending on the catalyst involved:



(m = 1-3, n = 3,10)

With an excess of Me_3SiNCO the substitution takes place at both Si–Cl and C–Cl bonds.

The reaction of Me_3SiNCO with phthaloyl chloride proceeds anomalously: due to the high rate of phthalimide cyclization in the exchange reaction only one chlorine atom participates and the derived product is *N*-chlorocarbonylphthalimide, whose structure is supported by the independent synthesis:



Under severe conditions (autoclave, ~ 120 °C) the chlorides of carboxylic and silylcarboxylic acids are also capable of reacting with isocyanatosilanes without a catalyst. However, in this case a total decarboxylation of the forming isocyanatosilane takes place to given the nitrile [56,58]:

$$RC(O)Cl + Me_3SiNCO \xrightarrow[-Me_3SiCl,\ -CO_2]{200\,^\circ C} RC{\equiv}N$$

In a number of cases this reaction may serve as a suitable preparative method for organic and organosilicon nitriles.

In comparison with chlorides of acids, carboxylic acid anhydrides react with isocyanatosilanes with great ease [58]; the acyl isocyanate yield reaching 97%:

$$\left(R{-}\overset{\overset{O}{\|}}{C}{-}\right)_2 O + Me_3SiNCO \xrightarrow[-20\,^\circ C]{SnCl_4} RC(O)NCO + RC(O)OSiMe_3$$

At temperatures higher than 100 °C, decarboxylation leads to the formation not of acyl isocyanates but of the corresponding nitriles.

Thus, isocyanatosilanes may be regarded as promising organo-element reagents, opening a simpler and more convenient way for preparing a great variety of isocyanates, as contrasted with other known methods. As far as the synthesis of isocyanatosilanes themselves is concerned [3], we have recently designed a number of new simple methods of preparing them [60–62]; the one especially suitable for preparative purposes is the reaction of urea with hexaalkyldisilazanes:

$$2H_2N\overset{\overset{O}{\|}}{C}NH_2 + (R_3Si)_2NH \xrightarrow[-NH_3]{100\text{–}130\,^\circ C,\ \text{catalyst}} \underset{(90\text{–}100\%)}{2R_3SiNCO}$$

3.2. Acylation of N,O-bis-TMS-carbamate

Acyl isocyanates in satisfactory yields are formed as a result of the acylation of *N,O*-bis-TMS-carbamate with chlorides of acids, and subsequent treatment of the reaction mass with silicon tetrachloride or with phenyltrichlorosilane [63]:

$$RC(O)Cl + Me_3SiNHCOOSiMe_3 \xrightarrow[-Me_3SiCl]{20\text{–}60\,^\circ C} RC(O)NHCOOSiMe_3 \xrightarrow[-Me_3SiCl]{PhSiCl_3}$$

$$RC(O)NHCOOSiCl_2Ph \xrightarrow{0\,^\circ C} RC(O)NCO + [HOSiCl_2Ph]$$

The *N,O*-bis-TMS-carbamate used as the starting material, may be prepared by silylation of ammonium carbamate which, in turn, is quite easily derived from carbon dioxide and ammonia [52,64]:

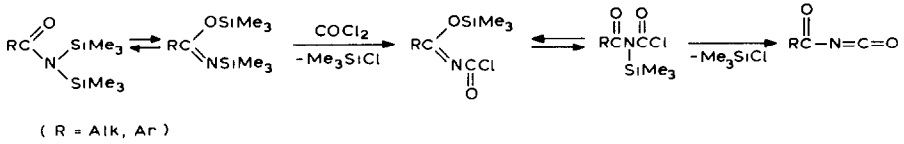
$$CO_2 + NH_3 \rightarrow H_2NCOONH_4 \xrightarrow{(Me_3Si)_2HN} Me_3SiNHCOOSiMe_3\ (\sim 80\%)$$

3.3. Interaction of bis-TMS-amides of carboxylic acids with phosgene

The reaction of amines with phosgene, widely used for preparing alkyl and aryl isocyanates is unsuitable for the synthesis of acyl isocyanates from the amides of acids. Therefore, in spite of the non-rationality of such an exchange, the treatment of amides to prepare acyl isocyanates is carried out not with phosgene, but with oxalyl chloride (Speziale-Smith method).

We found [65] that the bis(trimethylsilyl)amides of carboxylic acids, as distinct from non-silylated initial amides, react, as a rule, considerably easier with phosgene

in this case not nitriles, but the corresponding acyl isocyanates are formed. Despite their tendency to di- and tri-merization [66] under the conditions of this reaction, the acyl isocyanates may be obtained in a monomeric form (the overall yield of products approaches quantitative, if we take into account their partial di- and trimerization):

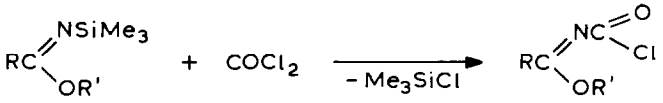


(R = Alk, Ar)

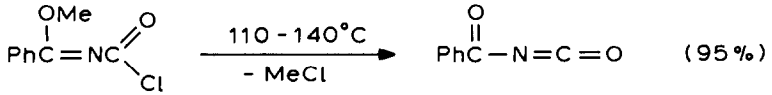
The reaction under consideration, because of the availability of bis(trimethylsilane)amides of carboxylic acids, opens up a new comprehensive pathway for the production of acyl isocyanates, including the lower members of the aliphatic series which are formed via the Speziale-Smith method in extremely low yield. In particular, acetyl isocyanate were prepared in this way: earlier attempts to obtain this compound on the basis of the amide ended in failure, and to synthesize it, it was necessary to carry out an acetyl chloride reaction with cyanic acid or its salts.

3.4. Phosgenation of N-silylimino esters

The interaction of phosgene with *N*-TMS-imino esters [67], as distinct from similar reactions with non-silylated imino esters proceeds under considerably milder conditions and leads to the formation of *N*-chlorocarbomylimino esters in better yields:



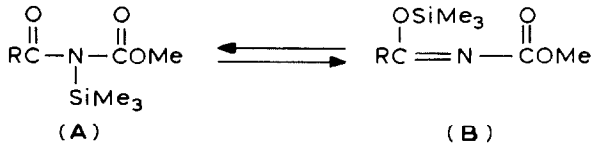
The latter, heated, is converted into the acyl isocyanate, for example [67]:



The preparative importance of this method is determined by the availability of the initial imino esters.

3.5. Thermolysis of N-acyl-N-silylurethanes

The method of synthesis of alkyl and aryl isocyanates by thermolysis of *N*-silylurethanes was also extended to acylurethanes [68]. However, in the case of the *N*-TMS-derivatives the corresponding urethane may be found in the state of tautomeric equilibrium with TMS-imino esters; the prevailing form being **A** for R = Me and **B** for R = Ph [68].

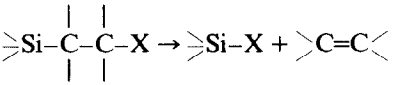


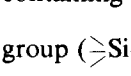
(A) (B)

The thermolytic results fit in rather well with these forms: with R = Me, the thermal decomposition proceeds via the formation of acetyl isocyanate (polymerizing under the reaction conditions), whereas with R = Ph, benzonitrile is obtained in a 92% yield [68].

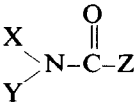
IV. Regularities of β-elimination reactions leading to isocyanate production

The typical feature of β-carbon-functional organosilicon compounds containing the Si–C–C–X fragment is their tendency towards an easy β-elimination (β-decomposition) reaction course under the action of different reagents or of heat.



Earlier we found [1,2] that organosilicon compounds of a similar structure but containing a nitrogen–carbon bridge between the silicon atom and the function group (), also show a pronounced tendency towards the β-elimination reaction, and in the case of *N*- and *O*-silyl-substituted urethanes and *N*-silylureas this leads to the formation of isocyanates.

With respect to the three above-mentioned compounds there exist certain general regularities of the β-elimination reaction course. For example, in the presence of an N–H bond, this reaction, irrespective of the nature of the remaining X, Y and Z substituents, proceeds exclusively in the H–N–C–Z bond system; otherwise the Si–N–C–Z bond system is involved. In both cases the multiplicity of the N–C bond rises and HZ or SiZ are eliminated, respectively.



Z = N<, OR, OSi<
X, Y = H, R, Si

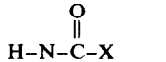
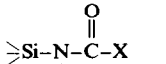
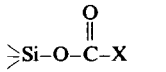
Only when X and Y = R and Z = OSi, does elimination of CO_2 takes place, in the Si–O–C–N bond system.

Thus, the β-elimination reaction in the above-indicated compounds proceeds through one of the three systems (1, 2, 3) of the 1,4-conjugated bonds reported in Table 4, and distributed in the order of reduction of the degree of conjugation and in this way to the β-elimination reaction.

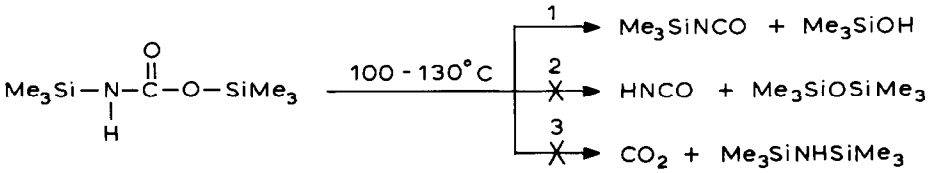
The decomposition direction is independent of the nature of the organic and silyl substituents.

If there are several types of conjugated bond systems in the molecule (1 + 2, 1 + 2 + 3, etc.), β-elimination proceeds predominantly in the bond system with a

TABLE 4

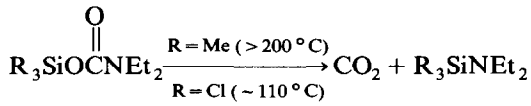
1,4-Conjugated bond	System type	X	Elimination direction
	(1)	OSi≤, NRSi≤	H–X + –N=C=O
	(2)	NRSi≤, NRR′ OSi≤, OR	≥Si–X + –N=C=O
	(3)	NRR′	≥Si–X + CO_2

greater degree of conjugation; for example:



In the cases with a similar X group, the thermal stability of the compounds with a 1,4-conjugated bond systems rises in the range $1 < 2 < 3$.

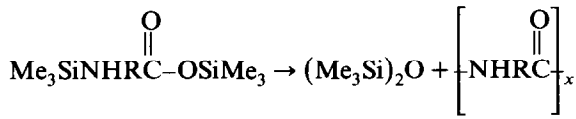
For compounds containing a Si–E–C–X bond system (E = N or O) the case of the β-elimination reaction increases with the transition from Me_3Si to Cl_3Si-derivatives, for example:



as distinct from compounds containing a Si–C–C–X bond system, for which, as is known, the inverse relationship is observed.

Thus, if the moving force in the β-elimination reaction course is a 1–4 interaction (σ,σ-conjugated) of atoms, then in the case of silylhydroxamic acids, the elimination of disiloxane proceeds from positions 1 and 5. This is probably one more example of a general dedisiloxanation [69–71]. This reaction, postulated by us recently [71], proceeds between the silylamine and silicone groups, irrespective of their position in one or in different molecules.

For example:



Conclusion

Use of organosilicon compounds as auxliliary substances, which regenerate readily, results in a number of advantages in isocyanate synthesis and facilitates their preparation by phosgene-free methods.

Acknowledgement

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