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Phosgene in the Chemistry of Organosilicon Compounds

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A systematic account of data concerning the problems of the synthesis of a wide variety of organic and organosilicon derivatives of carbonic acid (chlorocarbonates, carbonates, isocyanates, carbodiimides, acylcarbomoyl chlorides, etc.) by the reaction of phosgene with *N*- and *O*-silyl-substituted amines, amides, diazoles, iminoesters, and ethers derived from alcohols, glycols, etc. is given for the first time.
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I. INTRODUCTION

Phosgene is known[1-8] to be very important for preparative and particularly applied organic chemistry. However, there have been only a few scattered studies on the use of phosgene in the chemistry of organosilicon compounds up to 1965. Systematic investigation of the interaction of phosgene with various classes of organosilicon compounds was begun in 1965;[9] more than a hundred publications have now appeared in this field. These studies showed that, as in organic chemistry, $COCl_2$ has led in the chemistry of organosilicon compounds to simple methods for the synthesis of previously unobtainable substances and even whole classes of compounds.

The most novel results have been obtained in the reactions with phosgene of compounds having silicon-containing functional groups, particularly *N*-silylsubstituted derivatives. For example, the use of amines, amides, etc. silylated at the nitrogen atom instead of the corresponding initial organic compounds leads not only to better quantitative results but frequently also better qualitative results. In particular, new preparative pathways leading to the synthesis of lower organic isocyanates, which are difficult to obtain, previously unknown acylcarbamoyl chlorides, and other compounds have been developed.

It must be emphasised that silylation of organic compounds with functional groups, i.e. the replacement by a silyl group (usually Me_3Si) of the mobile hydrogen atom in hydroxy-, amino-, mercapto-, and other groups, can be achieved very simply using readily available reagents[10,11].

II. REACTIONS OF PHOSGENE WITH ORGANOSILICON COMPOUNDS HAVING CARBON-CONTAINING FUNCTIONAL GROUPS

C-Silyl-substituted alcohols, phenols, amines, and mercaptans react, as expected, with carbonic acid chlorides (phosgene, chlorocarbonates) without any fundamental differences from the analogous organic compounds.

1. *C*-SILYL-SUBSTITUTED ALCOHOLS, PHENOLS, AND MERCAPTANS

When $COCl_2$ interacts with organosilicon alcohols, the corresponding chloroformates (chlorocarbonates) are formed in a high yield[9,12-15]:

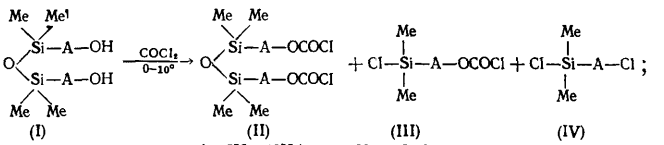
$$R_3Si(CH_2)_nOH \xrightarrow[-HCl]{COCl_2} R_3Si(CH_2)_nOCOCl\ ;\quad R=Alk,\ n=1,2,3.$$

In order to avoid the formation of the diesters of carbonic acids—the organosilicon carbonates $[R_3Si(CH_2)_nO]_2C{=}O$—in a side process, the reaction is carried out at temperatures not exceeding 0–5°C. The position of the hydroxy-group relative to the silicon atom does not influence significantly the yield and mode of reaction.

In contrast to alcohols, silylated mercaptans are more inert in the reaction with phosgene and require the presence of the HCl acceptor for the reaction to be completed[9,12,13,15]:

$$Me_3Si(CH_2)_3SH + COCl_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Me_3Si(CH_2)_3SCOCl\ .$$

The study of the interaction of organosilicon diols of the disiloxane series (I) with phosgene showed that the formation of the desired bischloroformates (II) is accompanied by the cleavage of the siloxane and ether linkages[9,14-20]:

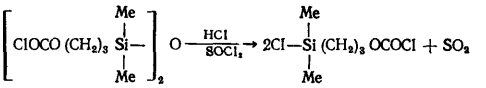


(I) (II) (III) (IV)

A=CH_2, $(CH_2)_3$, or $CH_2OCH_2CH_2$.

It was found that the fraction of side products depends on the type of diol employed[16,21], i.e. on the nature of A.

Special experiments showed[9,14,16] that neither $COCl_2$ nor the bischloroformate (II) are involved directly in the cleavage of the siloxane linkage, while the monochloroformate (III) is formed as a result of the action of HCl, liberated during the reaction, on the disiloxane linkage. For example, the reaction



(IIa) (IIIa)

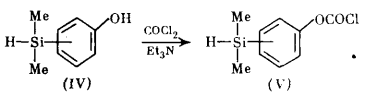
does not occur in the absence of HCl.[9] Like $SOCl_2$, phosgene is an insufficiently powerful reagent for the cleavage of the disoloxane group. For example, when $COCl_2$ is passed for a long time through boiling hexamethyldisiloxane, the rupture of disiloxane linkages does not occur[9,14]. It is also appropriate to mention here that the Si–H bond in hydrosilanes is likewise resistant to the action of $COCl_2$: $SiCl_4$ is formed on contact between $HSiCl_3$ and $COCl_2$ only under very severe conditions (~500°C).[9]

Organosilicon diols containing ether linkages react with $COCl_2$ via a still more complex mechanism[16,21]:

$$[HOCH_2CH_2OCH_2SiMe_2-]_2O \xrightarrow{COCl_2} \underset{65\%}{[ClOCOCH_2CH_2OCH_2SiMe_2-]_2O} + \underset{(17.0\%)}{ClOCOCH_2CH_2OCH_2SiMe_2Cl} + \underset{(2.0\%)}{[ClOCOCH_2SiMe_2-]_2O} + \underset{(1.8\%)}{[ClCH_2SiMe_2-]_2O} + \underset{(3.7\%)}{ClCH_2SiMe_2Cl} + \underset{(3.3\%)}{(ClOCOCH_2-)_2} + \underset{(1.6\%)}{ClCH_2CH_2Cl} .$$

In order to suppress side reactions, it is necessary to remove more completely the hydrogen chloride liberated: diols are treated with phosgene in the absence of solvents capable of retaining HCl, which is displaced by bubbling with dry nitrogen or bound by organic bases[14-16,18,19,22].

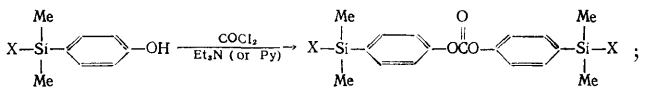
In contrast to aliphatic compounds, organosilicon phenols (IV) are inert in relation to $COCl_2$ at moderate temperatures. In order to avoid the thermal rearrangement of silylphenols to phenoxysilanes[23,24] as well as other side reactions, organosilylphenyl chloroformates (V) were therefore synthesised in the presence of organic bases as HCl acceptors[15-18,21,23,25,26], for example[16,23]:



(IV) (V)

o- and *p*-isomers

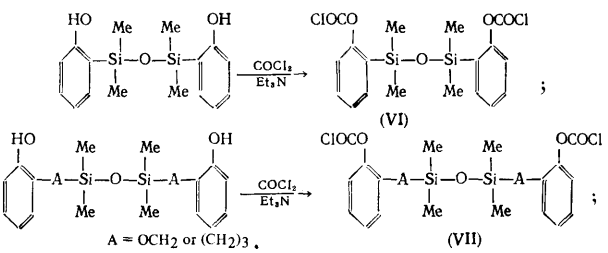
In the presence of an excess of phenol, the corresponding carbonates are formed in a single stage[16,23,26]:



X=H, Cl, or OAlk.

Analogous carbonates were obtained also by the esterification of chlorocarbonates of type (V) by the corresponding silylphenols[16,17,23].

The bischloroformates (VI) and (VII) have been synthesised from bisphenols of the disiloxane series[15-18,21,23,25,26]:



(VI)

A = OCH_2 or $(CH_2)_3$. (VII)

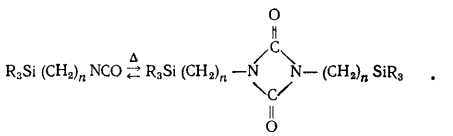
The above bischloroformates are thick transparent compounds soluble in the usual organic solvents. They always distil in an atomosphere of nitrogen without decomposition on heating to 300°C. This finding demonstrates yet again the stability of the Si–O–Si linkages in relation to the action of the chloroformate group even at elevated temperatures. The disiloxane fragment in the above compounds is resistant in the absence of HCl also to the action of $COCl_2$, COF_2, and $SOCl_2$.[16,21,27]

2. *C*-SILYLALKYL(ARYL) AMINES

The reaction of aminoalkylsilanes with phosgene, like the reactions of the *C*-silyl-substituted alcohols, phenols, and mercaptans discussed above, do not show fundamental differences from the reactions of the corresponding purely organic compounds[9,12-15,28]:

$$2R_3Si(CH_2)_nNH_2 + 2COCl_2 \rightarrow 2R_3Si(CH_2)_nNCO + 4HCl ;$$
R = Alk or Ar; $n = 1, 3$.

The dimeric compounds (VIII) [9,12] (analogous to the dimers of organosilicon ketens[29]) are formed as side products, which tentatively have the uretidinedione structure and which are in equilibrium with the monomeric form when heated†:

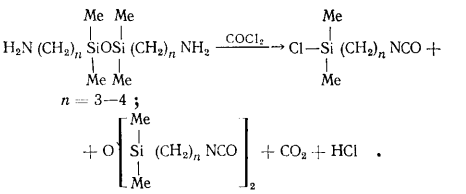


(VIII)

Nevertheless the monomeric isocyanatoalkylsilanes isolated in a pure form are entirely stable. For example, $Me_3Si(CH_2)_3NCO$ does not dimerise on storage or during distillation[9].

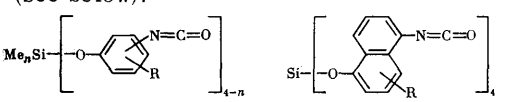
When $COCl_2$ interacts with amines containing alkoxygroups at the silicon atom or siloxane units, the reaction can involve Si–O bonds[9,13,14,31-33]:

$$(EtO)_3Si(CH_2)_3NH_2 \xrightarrow[110-120°]{COCl_2} Cl_n(EtO)_{3-n}Si(CH_2)_3NCO + EtOCOCl + HCl ;$$



$n = 3-4$;

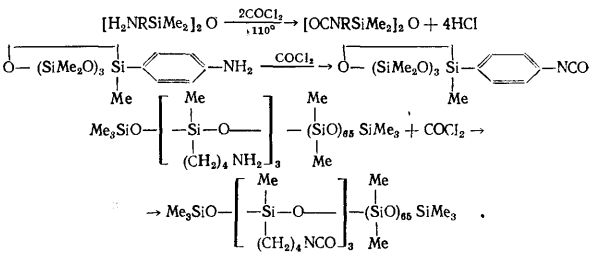
Silyl ethers of aminoalcohols of the type $R_2Si(OCH_2CH_2.NH_2)_2$ are fully cleaved by phosgene at Si–O bonds[32], but the final products have not been identified. At the same time the analogous aminophenol and aminonaphthol derivatives, both in the form of free bases and as the hydrochlorides, form the corresponding isocyanates (IX) and (X) [32,34] (see below):



(IX) (X)

$n = 1-3$; R = H, or Me.

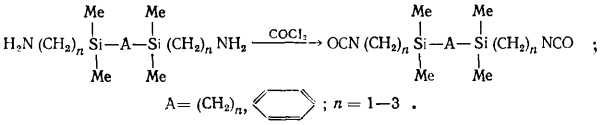
Examples of the synthesis of organosilicon mono- and di-isocyanates by treating with aminoalkylphosgene and aminophenyl derivatives of di-, tetra-, and oligo-siloxanes are known[33,35-37]:



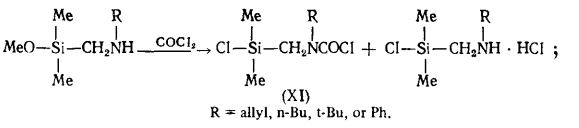
† The formation of the dimers (VIII) was also noted in the reaction of halogenoalkylsilanes with KOCN in dimethylformamide[30].

The retention of siloxane linkages on treatment with phosgene and HCl under severe conditions is doubtful, because it conflicts with the above findings, showing the undoubted cleavage of these bonds[9,14,15].

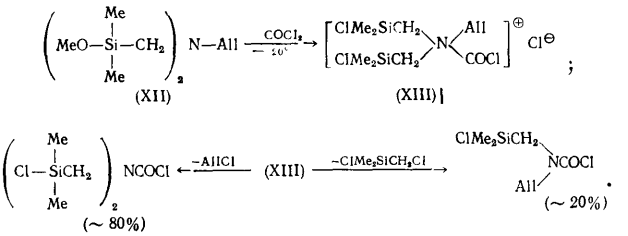
Organosilicon bifunctional monomers of another type were obtained when diamines with alkylene or phenylene bridges between silicon atoms were treated with phosgene[9,28]:



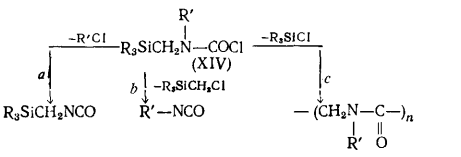
Secondary aminoalkylsilanes react with phosgene to form the corresponding organosilicon carbamoyl chlorides (XI). As for primary amines, when -Si-OAlk groups are present, they are converted into Si-Cl groups[38]:



At 20°C the tertiary organosilicon amine (XII) forms with phosgene an intermediate complex (XIII), which on heating splits off one of the substituents in the form of RCl:



It has been established that the pyrolysis of asymmetrically substituted organosilicon carbamoyl chlorides (XIV) leads to organic and organosilicon isocyanates‡. The mode of decomposition under these conditions depends on the nature of the substituents at the nitrogen and silicon atoms (see Table)[38,39]:



Silyl group	Group R′	Mode of decomposition
$ClMe_2Si$	$ClMe_2Si$	$a > c$
$ClMe_2Si$	All	$b > a + c$
Me_3Si	All	$c > a$

‡ It is known[40] that disubstituted organic carbamoyl chlorides of the type $Me_3CN(R)COCl$ (R = $PhCH_2$, allyl, or t-Bu) decompose to RNCO and Me_3CCl at 200°C.

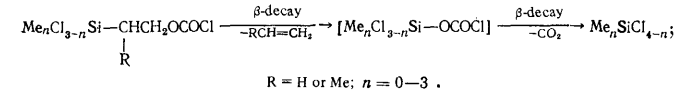
III. REACTIONS WITH COMPOUNDS HAVING SILICON-CONTAINING FUNCTIONAL GROUPS

1. COMPOUNDS CONTAINING THE SILOXANE LINKAGE

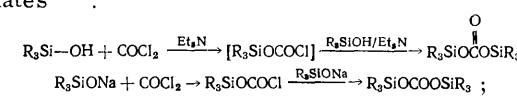
When phosgene interacts with organosilicon compounds containing the siloxane linkage (Si-O), the latter is frequently cleaved, not so much directly by phosgene as by reaction products such as HCl, carbamoyl chlorides, etc. The particular mode of the reaction involving the cleavage of the siloxane linkage is determined mainly by the nature of the atom or group X at the siloxane linkage Si-O-X.

(a) Silanols

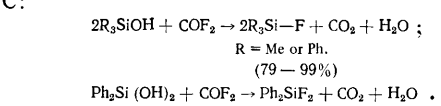
The silyl esters of chlorocarbonic acid—organosilyl chlorocarbonates (organosilyl chloroformates)—of the type $R_3SiOCOCl$, which should be formed from silanols and phosgene, are at present unknown. Such compounds are only mentioned as possible unstable intermediates[9,41,42]:



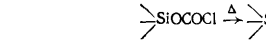
They are probably formed also in the synthesis of disilyl carbonates[16,17]:

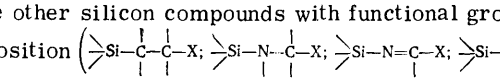


In the absence of an HF acceptor, difluorophosgene acts on silanols and silanediols as a fluorinating agent at 0°-20°C:[27]



The instability of the silyl esters of chlorocarbonic acids can be explained by their extremely high tendency towards β-elimination:



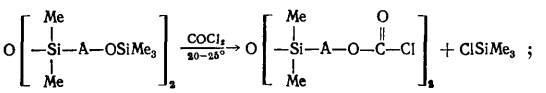
i.e. like other silicon compounds with functional groups in the β-position (), compounds of this class exhibit a distinct 1 - 4 interaction between the silicon and halogen atom (σ,σ-conjugation[43-47]). The rate of β-decomposition increases with increasing electronegativity of the group X: Cl ≫ OR > $OSiR_3$ > NR_2.[48-52]

(b) The Silyl Ethers Derived from Alcohols, Glycols, and Phenols and Silylcarboxylate Esters

Treatment of silyl ethers derived from alcohols and phenols with phosgene is in many cases preparatively preferable to the direct reaction of $COCl_2$ with the corresponding alcohols, diols, phenols, and dihydric phenols.

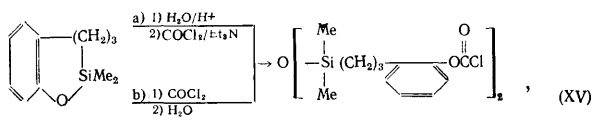
Firstly, at the end of the reaction, the reaction mixture does not contain the corrosive HCl; instead the product is chlorotriphenylsilane, which is readily

removed and which does not cleave the Si–Ar, C–O–C, Si–O–Si, and Si–O–C linkages[15–17,22,23,25,53–56], for example:



A = CH_2, $CH_2OCH_2CH_2$, or $CH_2CH_2CH_2$.

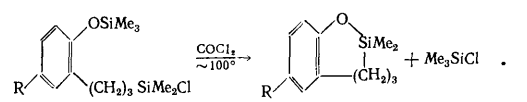
Secondly, the formation of both carbonates and chloroalkylsilanes under the influence of tertiary amines, usually employed as HCl acceptors, is fully ruled out. For example, of the following two mechanisms of the synthesis of compound (XV) (pathways *a* and *b*)



(XV)

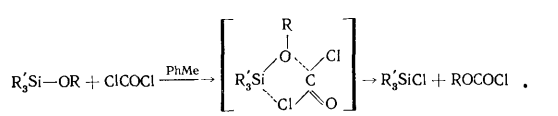
the latter is preferable, since it rules out contact between the chlorocarbonate formed and Et_3N.

Sometimes an attempt to treat substituted silylated phenols with phosgene does not lead to the required chloroformate, because the *trans*-silylation reaction is faster than the insertion of the $COCl_2$ in the Si–O bond, and the resulting heterocycles react with phosgene at much higher temperatures[16]:



As was to be expected, the reactivities of alkoxysilanes and acyloxysilanes in the reaction with $COCl_2$ proved to be different and were found to be determined by the nature of the groups incorporated in the organic and organosilicon parts of the molecule[16,55].

Reactions involving the nucleophilic substitution of the group RO in the silanes R'_3SiOR in a non-polar solvent evidently proceed via a mechanism with formation of a four-membered transition complex[40]:



Difluorophosgene reacts with alkoxysilanes like phosgene[27]. In the presence of a deficiency of COF_2 the yield of EtOCOF in the reaction with $Me_2Si(OEt)_2$ falls to 56%, since part of it is consumed in the formation of diethyl carbonate:

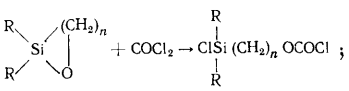
$$Me_2Si(OEt)_2 + 2EtOCOF \rightarrow Me_2SiF_2 + (EtO)_2CO .$$

Difluorophosgene does not cleave the siloxane linkage in $PhOSiMe_3$ and hexamethyldisiloxane at 20°C.

Compared with $COCl_2$ and ROCOF, aliphatic and aromatic chlorocarbonates are less reactive in relation to silyl ethers derived from alcohols and phenols. The reaction proceeds at an appreciable rate only at 120–220°C even with alkoxytrimethylsilanes which are most readily cleaved by phosgene[16,17,55,56]. As in the case of $COCl_2$, the Si–OCAr bond proved to be less reactive than Si–OCAlk.

(c) Silaoxacycloalkanes and Their Polymerisation Products

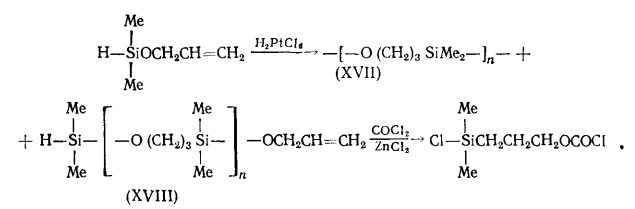
Silaoxacycloalkanes, which are cyclic silyl ethers derived from alcohols, react with phosgene, undergoing ring cleavage at the Si–O bond and giving rise to chloroformates[9,16,17,22,25,53–58]:



(XVI) R = Alk or AlkO; $n \geqslant 3$.

The reactivity falls in the series of silaoxacycloalkanes with increasing ring size[9,16,54,55]. For example, whereas silaoxacyclopentanes (XVI, $n = 3$) interact vigorously with $COCl_2$ even in the cold, the reaction of silaoxacyclohexanes (XVI, $n = 4$) with phosgene is slow even at a higher temperature (20–50°C). The reaction is sharply accelerated with increase of temperature to 100–150°C and is catalysed by Lewis acids ($ZnCl_2$, $AlCl_3$, etc.). In view of the relatively ready availability of silaoxacycloalkanes, the above reaction constitutes one of the most convenient methods for the synthesis of organosilicon monochlorocarbonates, whose yield reaches 80%.

The products of the polymerisation of silaoxacycloalkanes as well as macrocyclic silaoxacycloalkanes proved to be more passive in relation to $COCl_2$.[9,16,22,25] In particular, the study of the oligomeric product having the general formula $-[-O(CH_2)_3SiMe_2-]_n-$ and consisting of a mixture of macrocyclic silaoxa-alkanes (XVII, $n = 7–9$) and linear silaoxa-alkanes (XVIII, $n = 7–9$), showed that the reaction with phosgene does not occur even at comparatively high temperatures and the corresponding chlorocarbonate can be obtained in a yield of ~17% only in the presence of catalytic amounts of $ZnCl_2$:[9,22,54]

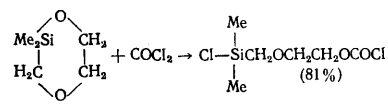


(XVII) (XVIII)

Incidentally, the yield of chlorocarbonate can be raised to 60% by treating with phosgene (in the absence of a catalyst) the products of the thermal depolymerisation of a mixture of (XVII) and (XVIII), obtain by distillation at 280° and 350°C with subsequent rapid cooling of the condensate by a mixture of dry ice and acetone[9,22,54].

Overall, the reactivity of silaoxacycloalkanes and their condensation (dimerisation, trimerisation, etc.) products with respect to $COCl_2$ is found to be inversely related to their resistance to polymerisation.

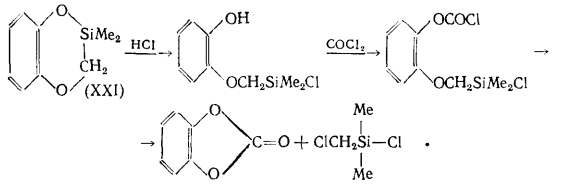
Apart from ring strain in silacycloalkanes, the rate at which their rings are opened by phosgene is influenced also by other factors. For example, the siladioxan (XIX) reacts vigorously with $COCl_2$ and gives high yields of the chlorocarbonate (XX):[16]



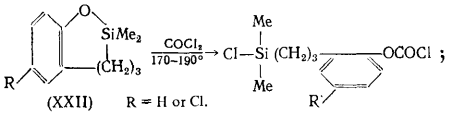
(XIX) (XX) (81%)

On passing from silaoxacycloalkanes to benzosilaoxacycloalkanes, the reactivity falls sharply: the heterocycle (XXI) proved to be inert in relation to $COCl_2$ on heating to

120–140°C and the ring is open and undergoes a rearrangement only when $COCl_2$ and gaseous HCl are passed jointly through heated (XXI):[16,24]



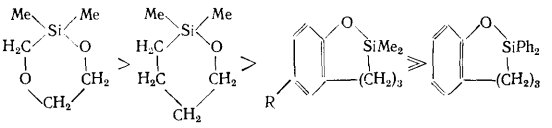
The cleavage of the $Si-OC_{Ar}$ bond in other benzosilaoxacycloalkanes by phosgene also takes place under severe conditions at 170–190°C,[16,54] for example:



(XXII) R = H or Cl.

The replacement of methyl groups in the heterocycle (XXII) by phenyl groups makes the molecule completely inert to the action of $HCl/COCl_2$ mixture even when it remains in contact with the reagents at 200°C.

The decrease of the reactivity of silaoxacycloalkanes in the series of compounds



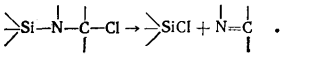
like that in the series of linear silyl ethers, is caused by the weakening of the nucleophilic properties of the O atom in the siloxane bond.

A number of procedures have been proposed for the activation of the reaction of phosgene with compounds containing the $Si-O-C_{Ar}$ linkage. One can use Lewis acids as reaction catalysts[9,16,54], which, however, have also a side effect—the initiated decomposition of the required chlorocarbonates to alkyl(aryl) halides. Another group of initiators was therefore put forward[9,16–53]—inorganic acids or hydroxylated organic compounds. The possibility of initiating the reaction by tertiary amines (pyridine, dimethylaniline, etc.), which are capable of ionising the $COCl_2$ molecule, merits attention.

Thus the reaction of $COCl_2$ with silyl ethers—intermediates in the synthesis of glycols and dihydric phenols of the siloxane series—is of preparative value in relation to alcohol derivatives, but is of limited importance in the case of compounds with an $Si-O-C_{Ar}$ linkage.

2. COMPOUNDS CONTAINING THE Si–N BOND

When the N–H bond in a wide variety of nitrogen-containing compounds is replaced by the N–Si bond their reaction with phosgene frequently follows another pathway. This can sometimes be accounted for by the absence of side and reversible reactions ($ClSiMe_3$ is formed instead of HCl), but the main explanation involves the formation of extremely unstable intermediates containing the σ,σ-conjugated bond system and responsible for the occurence of the irreversible β-elimination reaction



(a) Silazanes, Silylhydrazines, Cyanosilanes, and Isocyanatosilanes

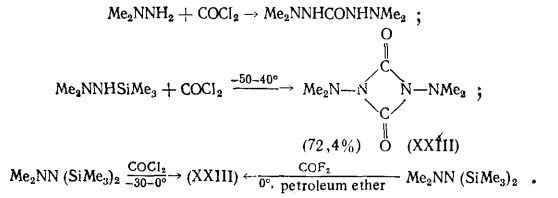
When $COCl_2$ interacts with hexamethyldisilazane, a complex mixture of products is formed[59–61]:

$$4\,(Me_3Si)_2NH + 3COCl_2 \rightarrow 5Me_3SiCl + 3Me_3SiNCO + NH_4Cl\ .$$

Sodium bis(trimethylsilyl) amide reacts with $COCl_2$ to give a 60% of *N,N'*-bis(trimethylsilyl)carbodi-imide[60,61]:

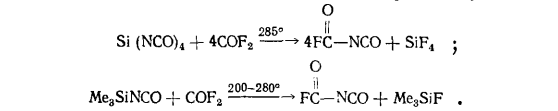
$$2\,(Me_3Si)_2NNa + COCl_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2O + 2NaCl\ .$$

By protecting Me_2NNH_2 with a silyl group before its reaction with COF_2 and $COCl_2$, it was possible to obtain the dimethylaminoisocyanate dimer[62,63] instead of the corresponding urea[64], formed from dimethylhydrazine itself§:

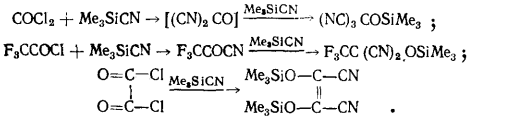


The yield of uretidinedione (XXIII) from $Me_2NN(SiMe_3)_2$ and $COCl_2$ is nearly quantitative (96.5%)[63], whereas in the reaction with COF_2 it is smaller approximately by a factor of two (46.0%)[62].

When isocyanatosilanes—$Si(NCO)_4$ or Me_3SiNCO—interact with COF_2 in an autoclave, the NCO group is substituted with formation of fluorocarbonyl isocyanates[65]:



Like trifluoroacetyl chloride and oxalyl chloride, phosgene interacts with Me_3SiCN to form the corresponding cyano-derivatives of carbonyl compounds[66]. However, dicyanocarbonyl is extremely reactive, combining with a Me_3SiCN molecule via the carbonyl group under the reaction conditions:



On treatment with Me_3SiCN, chloroformates give rise to cyanoformates[67]:

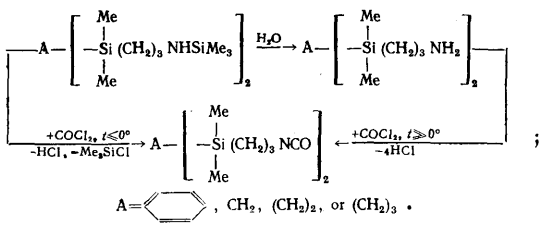
$$ROCOCl + Me_3SiCN \rightarrow ROCOCN + Me_3SiCl\ .$$

(b) *N*-Silyl-Substituted Amines

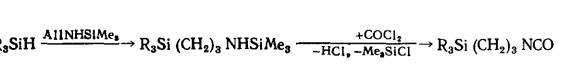
It was observed in 1969 that organosilicon di-isocyanates[9,28] are formed in high yields and under milder conditions when $COCl_2$ is allowed to react with *N*-silyl

§The uretidinedione structure has been tentatively attributed[42] to the dimethylaminoisocyanate dimer (on the basis of the analysis of the infrared and ^1H NMR spectra).

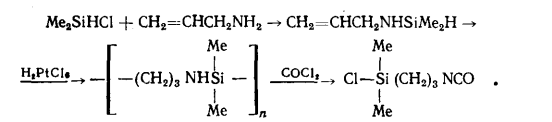
derivatives of the initial amines rather than the initial amines themselves[9,68]:



Monoisocyanates were obtained similarly[9,68-77]:

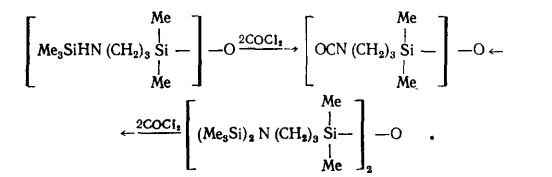


These observations made possible an exceptionally convenient procedure for the synthesis of one of the promising organosilicon monomers—γ-(chlorodimethylsilyl)propyl isocyanate—via the following mechanism[9,69,78]:

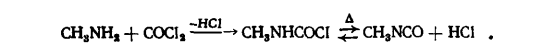


This compound had been obtained earlier as a side product in the reaction of $O-[-SiMe_2(CH_2)_3NH_2]_2$ with $COCl_2$.[9,13,14]

Subsequently it was established[9,68,69,78-83] that the reaction of phosgene with *N*-silyl-substituted primary amines is of a general type and can be used to synthesise not only organosilicon but also any other isocyanates containing groups sensitive to heat and the action of HCl, $COCl_2$, and –NHC(O)Cl. In particular, this made it possible to simplify the synthesis of di-isocyanates of the disiloxane series which has been difficult to obtain previously[9,69]:

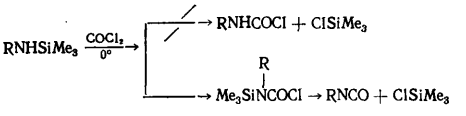


A detailed study of this new reaction in relation to many examples[9,68-84] showed that, on treatment with phosgene, any primary *N*-silyl-substituted amines give rise to high yields of the corresponding isocyanates at appreciably lower temperatures (between –60° and 0°C) than the initial free amines. The latter factor revealed particularly clearly the advantages of the above method for the synthesis of lower isocyanates[69-77]. For example, it is known that treatment of methylamine with phosgene results in the formation of methylcarbamoyl chloride, which begins to decompose at temperatures of 100°C to methyl isocyanate and hydrogen chloride:



However, the latter reaction is reversible and the separation of gaseous methyl isocyanate and hydrogen chloride is extremely difficult. The dehydrochlorination of methylcarbamoyl chloride is therefore usually carried out with the aid of organic or inorganic bases. This applies equally to the synthesis by a similar procedure of ethyl, allyl, and other low-boiling isocyanates.

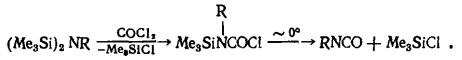
On the other hand, the reaction of *N*-silyl-substituted amines with phosgene, which leads to the formation of the extremely unstable *N*-silylcarbamoyl chloride[9,68,69,79,80], decomposing irreversibly to an alkyl isocyanate and chlorotrimethylsilanes, can serve as a new and convenient preparative method for the synthesis of lower alkyl isocyanates[9,68-83]:



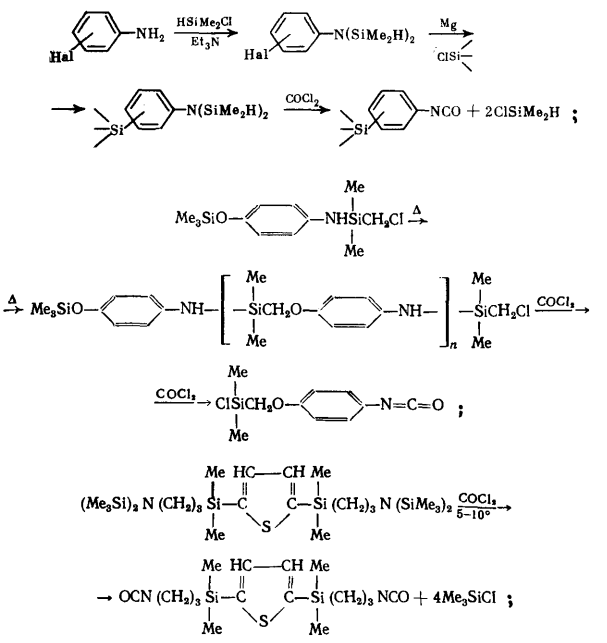
The occurrence of the reaction via the upper pathway is ruled out, since it is known that alkylcarbamoyl chlorides are stable up to ~100°C, while the above reaction takes place almost quantitatively at temperatures below zero.

On the other hand, the probability of ready dehydrochlorination of alkylcarbamoyl chlorides under the reaction conditions (under the influence of aminosilanes or the chlorosilanes formed) is low, and special experiments showed that, for example, methylcarbamoyl chloride does not change even after prolonged refluxing with chlorosilanes[9,69].

Nevertheless, the Si–N bond is also very readily cleaved by phosgene. For example, the reaction with *N*,*N*-disilyl-substituted amines takes place at low temperatures and the yield of the corresponding isocyanates is sometimes actually better, owing to the complete absence of hydrogen chloride, than in the reaction employing *N*-monosilyl-substituted amines[9,12,69-86]:



It must be emphasised that, when silyl-substituted amines are treated with phosgene, the corresponding silyl chloride, used to introduce a protective silyl group into the initial amines, is almost quantitatively regenerated. The above findings give rise to the hope that certain isocyanates (for example, methyl isocyanate) will be synthesised not only in the laboratory but also under industrial conditions[15]. Simple methods for the synthesis of certain organosilicon, organotin, and organogermanium isocyanates, which are of preparative value but are difficult to obtain, are presented below[9,15,78,81,82,85-89]:



$$Bu_3Sn(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} Bu_3Sn(CH_2)_3NCO\ ;$$

$$Bu_3Sn(CH_2)_3N(SiMe_3)_2 \xrightarrow{COCl_2} Bu_3Sn(CH_2)_3NCO\ ;$$

$$Et_3Ge(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} Et_3Ge(CH_2)_3NCO\ .$$

N-Silyl-substituted secondary amines undergo an exothermic reaction with phosgene, giving an almost quantitative yield of a trialkylchlorosilane and the corresponding dialkylcarbamoyl chloride[9]:

$$R_2N{-}SiMe_3 + COCl_2 \xrightarrow[-15-0^\circ]{} R_2NCOCl + Me_3SiCl\ .$$

(88%) (97%)

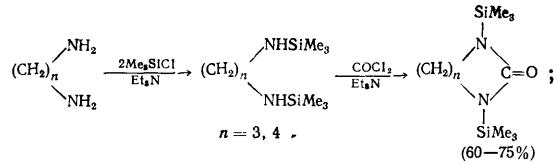
It is appropriate to mention here that the Si–N bond in aminosilanes is cleaved by acyl halides and chlorocarbonates at a much lower rate than in the case of $COCl_2$.[38, 59, 90-92] This follows, for example, from the fact that in the absence of a catalyst (concentrated H_2SO_4), the compounds ROCOCl do not interact with $R'N(SiMe_3)_2$ even on heating[38, 91]. Slow acylation of the oligomer $-[-(CH_2)_3NH.SiMe_2-]_n$ with methyl chlorocarbonate or acetyl chloride is accompanied by the competing dehydrochlorination reaction, which on treatment with phosgene takes place to only a slight extent if at all:

$$-[-(CH_2)_3NHSiMe_2-]_n- \xrightarrow{COCl_2} ClSi(Me)_2(CH_2)_3NCO$$

$$\xrightarrow{RCOCl} ClSi(Me)_2(CH_2)_3NHCOR + Me_2Si(CH_2)_3NCOR$$

R = Me, or MeO .

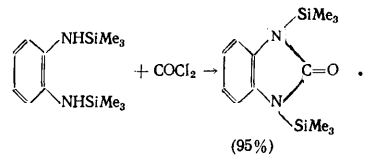
A departure from the general rule governing the interaction of phosgene is shown by certain silylated diamines[93]:



$n = 3, 4$.

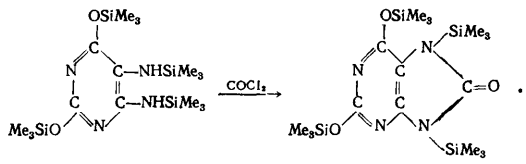
(60–75%)

Under the same conditions, *N*,*N*′-bis(trimethylsilyl)-*O*-phenylenediamine reacts with $COCl_2$ to form *N*,*N*′-bis-(trimethylsilyl)-2-benzimidazolone in a high yield[93]:

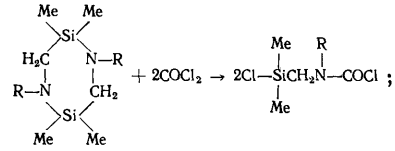


(95%)

2,4-Bis-(*O*-trimethylsilyl)-5,6-bis(trimethylsilylamino)-uracil, formed on silylation of 5,6-diaminouracil, reacts with $COCl_2$ in toluene to form tetrakistrimethylsilyluric acid[93]. Without the protection of the *N*-functional group by silylation, this reaction does not occur. The above synthesis is remarkable also because, by virtue of silylation, the reaction with 5,6-diaminouracil can be carried out in a hydrocarbon solvent[93]:

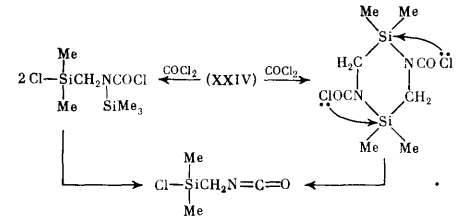


The ease of the cleavage of the 2,5-disilapiperazine ring in compound (XXIV) by phosgene combined with the complete absence of any side products makes this reaction extremely promising for preparative purposes[38]:

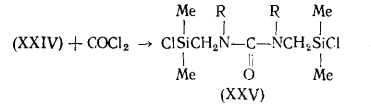


(XXIV) R=Alk, alkenyl, or Ar.

When R = $SiMe_3$, the reaction does not stop at the stage involving the formation of carbamoyl chloride, since its β-decomposition causes its dechlorosilylation to the isocyanate:

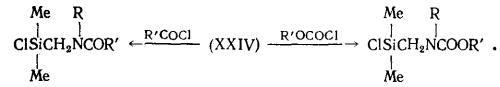


It has been shown[38] that, whereas the isocyanate is formed regardless of the order in which the reactants are mixed when R = $SiMe_3$, in the remaining cases a constant excess of $COCl_2$ must be ensured in the course of the reaction in order to obtain carbamoyl chlorides. Otherwise the ureas (XXV) are produced:



(XXV)

The disilapiperazine ring is readily cleaved by chlorocarbonates and carboxylic acid chlorides with formation of urethanes and amides respectively[38]:



(d) Silyl Derivatives of Aminoacids

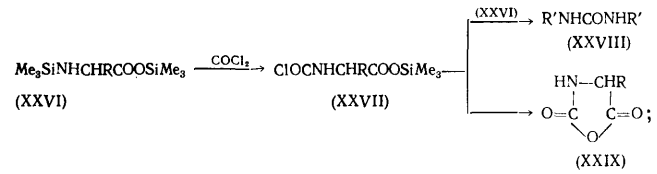
The reaction of phosgene (thiophosgene) with silyl derivatives of aminoacids is used particularly frequently in the synthesis of esters of isocyanatocarboxylic acids and *N*-carboxyanhydrides.

The interest in the esters of isocyanatocarboxylic acids is due primarily to the fact that, in combination with *N*-protected aminoacids, they can be regarded as convenient intermediates in the stepwise synthesis of di- and poly-peptides.

The silyl esters of isocyanatocarboxylic acids are much more readily hydrolysed than alkyl esters and some workers[94] have for this reason regarded them also as a potential source of free isocyanatocarboxylic acids O=C=NCH(R)COOH which had been little studied hitherto and which have been frequently mentioned in the literature as possible highly reactive monomers for the synthesis of polypeptides and polyamides (the intermediate formation of these compounds was postulated, particularly, in a study of the polymerisation of *N*-carboxyanhydrides).

N-Carboxyanhydrides of aminoacids (also referred to as oxazolidine-2,5-diones or leuchs anhydrides) are in their turn convenient and frequently employed starting compounds for the synthesis of polyaminoacids.

Thus Kricheldorf[95] showed that the trimethylsilyl esters of *N*-trimethylsilylaminoacids (XXVI) react with phosgene, eliminating Me_3SiCl and forming initially the silyl esters of *N*-chloroformylaminoacids (XXVII), which then either react with the initial substance to give urea derivatives (XXVIII) or cyclise to oxazolidine-2,5-diones (XXIX):



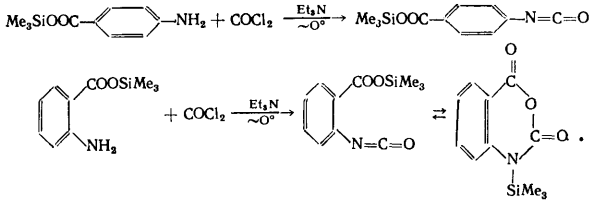
$R' = CHRCOOSiMe_3$.

The formation of the urea derivative in this reaction can be avoided by using an excess of phosgene and by adding slowly the silylated aminoacids to the latter[95]. Intramolecular cyclisation is favoured by an increased temperature and a branched structure of the hydrocarbon residue of the aminoacid.

The advantage of this method of synthesising *N*-carboxyanhydrides of aminoacids over known methods is that it does not entail the evolution of hydrogen chloride, which permits a retention of the ester groups and of the multiple bonds in the molecule. In particular, the *N*-carboxyanhydride of *O*-trimethylsilyl-L-tyrosine was obtained by this procedure in a satisfactory yield[95]. For comparison, one may note that the formation of this product by silylating the *N*-carboxyanhydride of L-tyrosine with the Me_3SiCl/Et_3N mixture cannot be achieved, because the product of this reaction polymerises after a short time.

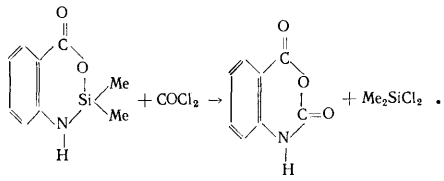
The use of silyl esters (in contrast to the *N*-benzyloxycarbonylaminoacids normally employed) also has the advantage that most of them can be vacuum distilled without decomposition[96]. Thus silylation (and subsequent distillation) can serve as a convenient method for purifying the initial aminoacids or their derivatives, which frequently show only a small capacity for crystallisation. Furthermore, in contrast to aminoacids with a free carboxy-group, silyl esters dissolve even in non-polar solvents (for example, in petroleum ether), which makes it possible to eliminate the initial substance as an impurity in the *N*-carboxyanhydride, which is precipitated[96].

Mono- and *N*, *O*-bis-silyl derivatives of aromatic aminoacids react with phosgene to form different products, depending on the conditions. Whereas in the absence of Et_3N monosilyl derivatives form mainly polymeric compounds (or the anhydride of isatinic acid in the case of the *O*-trimethylsilyl ester of anthranilic acid), the reaction in the presence of Et_3N makes it possible to obtain high yields of trimethylsilyl esters of isocyanatocarboxylic acids whose *ortho*-derivatives show a tendency towards tautomeric transformations[87]:



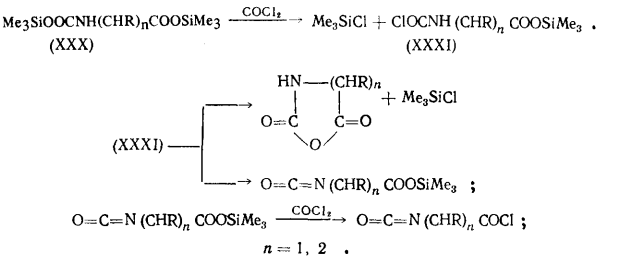
N,*O*-Bis-silyl derivatives can react with $COCl_2$ under mild conditions (0–20°C) to form trimethylsilyl esters of isocyanatocarboxylic acids also in the absence of Et_3N, whereas under more severe conditions polymeric products having tentatively the uretidine dione structure are formed[87].

The action of phosgene on 4,4-dimethyl-1,6-benzo-3-oxa-4-sila-5-aza-2-cyclohexanone leads to the virtually quantitative formation of the anhydrides of isatinic acid:



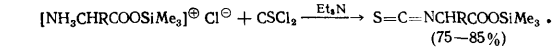
N,*O*-Bis-silylated *N*-acylaminoacids react with phosgene with difficulty at 80°C; *N*-carboxyanhydrides are formed in this case with a low yield[95]. The reactions described proceed without the inversion of configuration[95].

Above 0°C, the trimethylsilyl esters of *N*-siloxycarbonylaminoacids (XXX) react readily with phosgene, eliminating two Me_3SiCl molecules and forming *N*-carboxyanhydrides[97]. The *N*-siloxycarbonyl group then exhibits a higher reactivity than the *C*-siloxycarbonyl group, as a result of which trimethylsilyl esters of *N*-halogenocarbonylaminoacids (XXXI) are formed as intermediates, which then cyclise to form *N*-carboxyanhydrides[97,98]. The esters of halides of isocyanatocarboxylic acids are formed as side products, which predominate in the case of β-aminoacids[97]:



Since alkoxy- and aryloxy-trimethylsilyl groups are still less reactive than trimethylsiloxycarbonyl groups (the reactivity of various siloxy-groups in relation to acid chlorides diminishes in the sequence $R_2NCOOSiMe_3 > RCOOSiMe_3 > AlkOSiMe_3 > ArOSiMe_3$), [96] the reaction with phosgene by this procedure can yield *N*-carboxyanhydrides containing silyl substituted alcoholic or phenolic groups[97,98]. The above method for the synthesis of *N*-carboxyanhydrides have also the advantage that, compared with the established procedure, it makes it possible to obtain them in higher yields (>90%) and with a very high degree of purity. It is also superior to the synthesis of *N*-carboxyanhydrides from trimethylsilylesters of *N*-trimethylsilylaminoacids discussed above, since in this case the risk of the formation of urea by a side reaction is eliminated.

The interaction of thiophosgene with the hydrochlorides of the trimethylsilyl esters of aminoacids is one of the most convenient preparative methods for the synthesis of trimethylsilyl esters of isothiocyanatocarboxylic acids according to Kricheldorf's data[99]:



These acids can be used[100] as convenient intermediates in the synthesis of free isothiocyanatocarboxylic acids¶ (S=C=NCHRCOOH) and thiazolidine-2,5-diones.

On passing from trimethylsilyl esters to ordinary esters of aminoacids silylated at the nitrogen atom, the interaction with $COCl_2$ terminates with the formation of the corresponding derivatives of isocyanatocarboxylic acids[101]:

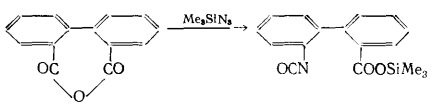
$$Me_3SiNHCHRCOOEt \xrightarrow[0^\circ]{COCl_2} OCNCHRCOOEt\ ;$$

R=Me, or iso-Pr.

The possibility of using PhOCOCl instead of $COCl_2$ for the synthesis of these compounds has been demonstrated:

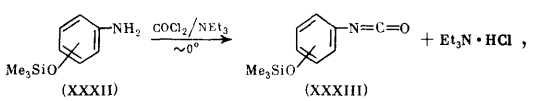
$$NH_2(CH_2)_4COOH \xrightarrow[3)\ Et_3N]{1)\ Me_3SiCl;\ 2)\ PhOCOCl} OCN(CH_2)_4COOSiMe_3 + PhOSiMe_3$$

or one can use a phosgene-free method[102]:



(e) Silyl Derivatives of Aminophenols

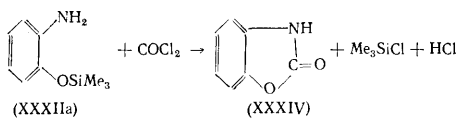
Silyl derivatives of aminophenols react vigorously with phosgene to form a wide variety of products. Thus, whereas siloxyanilines (XXXII) are converted into the corresponding isocyanates (XXXIII, a and b) on treatment with phosgene under mild conditions (~0°C) and in the presence of Et_3N, [88]



(XXXII) (XXXIII)

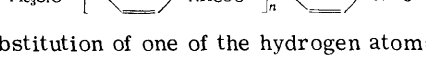
[*a*) *ortho*-isomer; *b*) *para*-isomer]

when the temperature is raised in steps (initially 20–40° and then 100–110°C), isocyanates are not formed, since the Si–OC bonds are ruptured. The main product in the reaction of (XXXIIa) is the benzoxazolinone (XXXIV)[88]:

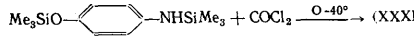


(XXXIIa) (XXXIV)

while the reaction of (XXXIIb) gives rise to an oligomer:

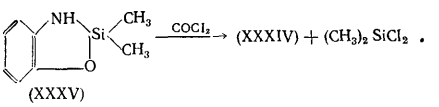


The substitution of one of the hydrogen atoms in the NH_2 group by the trimethylsilyl residue makes it possible to obtain the isocyanate (XXXIIIb) from the para-isomer[88]:



However, the yield of the product is low, since even under the mild conditions employed the reaction is accompanied by the formation of a polymer having the above structure via a side process.

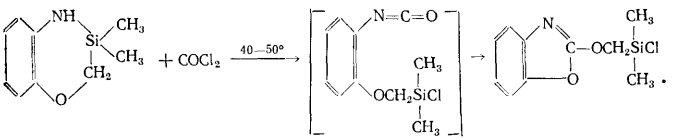
The Si–OC bond is even more readily cleaved in the cyclic compound (XXXV), whose reaction with $COCl_2$ results in its complete conversion into benzoxazolinone even at a temperature of –40°C and below:



(XXXV)

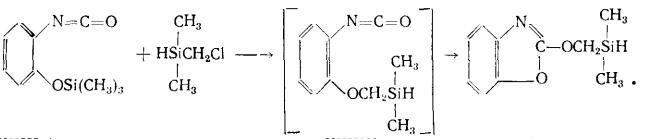
This increase of reactivity can be accounted for by the increased polarisation of the Si–O bond owing to the reduced amount of double bond character of the linkage between the O and Si atom due to the inclusion in the silicon *d* orbital of the free electron pair not only at the oxygen atom but also at the nitrogen atom.

The reaction of $COCl_2$ with the cyclic compound (XXXVI) had an unexpected course: instead of the expected isocyanate, a high yield was obtained of the isomeric product (XXXVIII). Evidently, the isocyanate (XXXVII) formed in the first stage is unstable and isomerises rapidly to (XXXVIII):



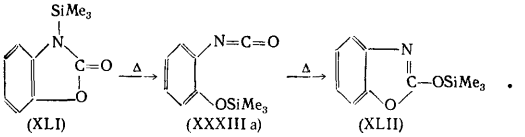
(XXXVI) (XXXVII) (XXXVIII)

The instability of isocyanates containing silylmethoxy-groups as well as Me_3SiO groups in the *ortho*-position relative to NCO was confirmed also by studies on a number of other reactions[88]. Thus the transalkylation of *o*-trimethylsiloxyphenyl isocyanate (XXXIIIa) by reaction with chloromethyldimethylsilane results in the evolution of up to 85% of the theoretical amount of Me_3SiCl, but instead of the isocyanate (XXXIX) the product is the isomeric compound (XL):



(XXXIII a) (XXXIX) (XL)

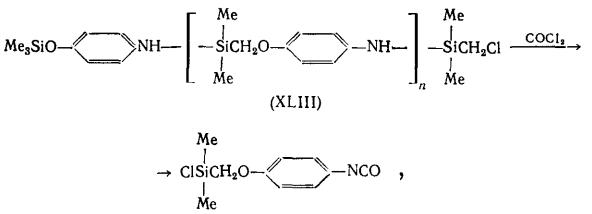
The initial product of this reaction—*o*-trimethylsiloxyphenyl isocyanate (XXXIIIa)—is the most stable of the *o*-substituted phenyl isocyanates examined. It can be isolated in an analytically pure form by vacuum distillation and is stable on storage. Nevertheless, under comparatively severe conditions this compound is capable of cyclising. For example, it has been observed that *N*-trimethylsilylbenzoxalinone (XLI), formed when benzoxalinone is treated with chlorotrimethylsilane in the presence of Et_3N, undergoes intramolecular β-elimination even under the conditions of its formation (80°C) and is converted into *o*-trimethylsiloxyphenyl isocyanate (XXXIIIa). On heating (3 h, 160–200°C), the latter isomerises to the benzoxazolinone derivative (XLII)[43,88]:



(XLI) (XXXIII a) (XLII)

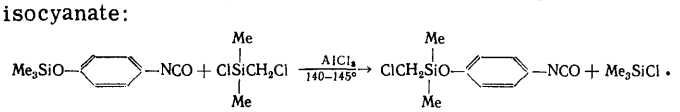
¶ β-, γ-, and ε-isothiocyanatocarboxylic acids and their silyl esters are exceptionally active physiologically, giving rise to a very severe rash. Even in very low doses, they can cause painful blisters and wounds[100].

In contrast to *o*-derivatives, *p*-siloxyphenyl isocyanates are quite stable can be obtained not only via the reactions discussed above but also on treatment of the polymer (XLIII) with phosgene[88]:



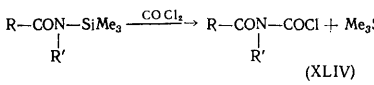
(XLIII)

and by the transalkylation of *p*-trimethylsiloxyphenyl isocyanate:



(f) *N*-Silyl-Substituted Carboxylic Acid Amides

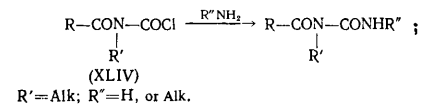
N-Acylcarbamoyl chlorides. The reaction of *N*-alkyl(aryl)-*N*-(trimethylsilyl)-amides with phosgene was found to give high yields of the first examples of a hitherto unknown class of organic compounds—*N*-alkyl-(aryl)acylcarbamoyl chlorides (XLIV)[9,43,80,84,103,104]:



(XLIV)

R′=Alk, or Ar.

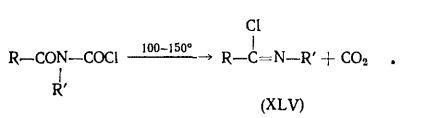
It has been shown[9,43,104] that *N*-acyl-*N*-alkylcarbamoyl chlorides (XLIV) are converted into *N*-acyl-*N*-alkylureas on treatment with aqueous ammonia:



(XLIV)

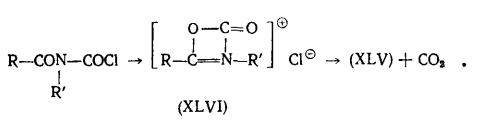
R′=Alk; R″=H, or Alk.

When acylcarbamoyl chlorides (XLIV) are heated to 100–150°C, they undergo quantitative decarboxylation to the corresponding imidochlorides (XLV)[9,43,80,84,103,104]:



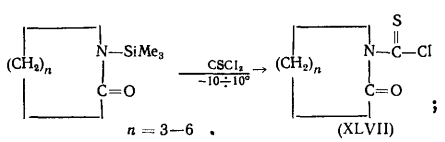
(XLV)

Presumably the decomposition of these compounds proceeds via the intermediate formation of the salt (XLVI)[43,104]:



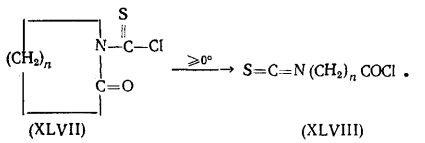
(XLVI)

Lactams silylated at the nitrogen atom, which are cyclic amides, interact with thiophosgene via a similar mechanism[105]:



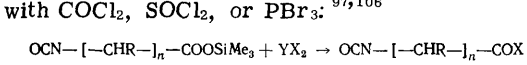
$n = 3-6$. (XLVII)

However, *N*-chlorothioformyl derivatives (XLVII) isomerise even at 0°C to the chlorides of ω-isothiocyanatocarboxylic acids (XLVIII), which can be isolated in a pure form:



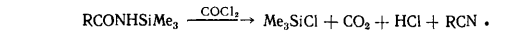
(XLVII) (XLVIII)

The oxygen analogues of the acid chlorides (XLVIII), i.e. the chlorides of isocyanatocarboxylic acids, have been obtained by treating the silyl esters of isocyanatocarboxylic acids with $COCl_2$, $SOCl_2$, or PBr_3:[97,106]

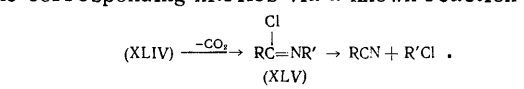


R = H or Alk; n = 1,2; X=Cl, or Br; Y=SO, CO, or PBr .

In contrast to *N*-alkyl(aryl)-*N*-silyl-substituted amides, *N*-silyl-substituted amides give rise to the corresponding nitriles on reaction with phosgene (at temperatures not exceeding room temperature)[9,43,84,103,104]:



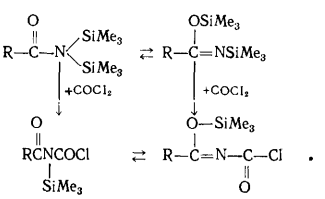
Presumably here too the reaction proceeds, as in previous instances, via the formation of acylcarbamoyl chlorides (XLIV, R′ = H), which subsequently decompose to the imidochlorides (XLV), and the latter are converted into the corresponding nitriles via a known reaction[9,103,104]:



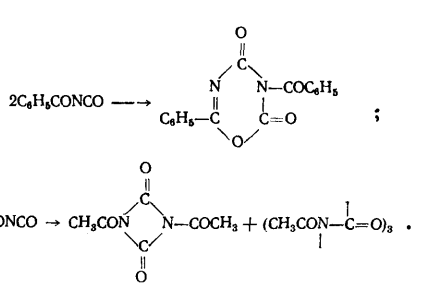
(XLV)

In contrast to compounds with R′ = alkyl or aryl, acylcarbamoyl chlorides with R′ = H apparently have extremely low thermal stabilities. Similar relations are known to be characteristic also of the imidochlorides RC(Cl)=NR′, which are also extremely unstable when R′ = H.

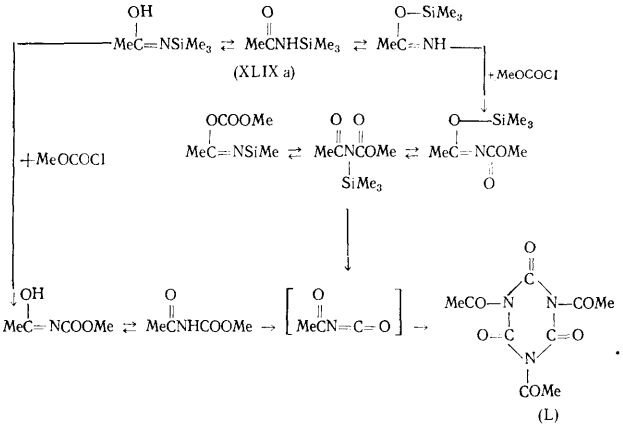
Disilyl substituted carboxylic acid amides react very vigorously with phosgene and form a mixture of di- and tri-meric forms of the acyl isocyanate[38,43,107]. The reactions probably proceed via mechanisms involving the formation of *N*-silyl substituted acylcarbamoyl chlorides with the Si–N–C–Cl system of conjugated bonds[43]:



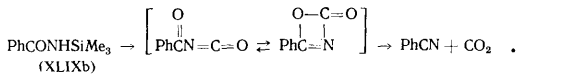
β-Decomposition of these compounds leads to acyl isocyanates, which undergo further reactions:



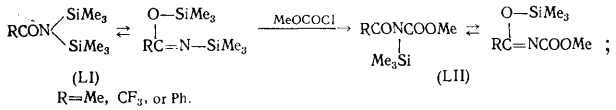
Monosilyl-substituted acetamides and benzamides react in different ways with methyl chloroformate, depending on their possible tautomeric forms: the reaction of silylated acetamide (XLIXa) led to the isolation of triacetyl isocyanurate (L) as a result of the following probably reactions:



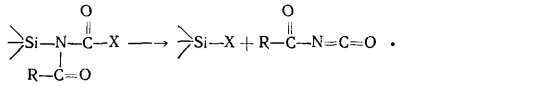
However, the monosilylbenzamide (XLIXb) is converted into benzonitrile under these conditions. The difference between the final reaction products is caused by the tendency of benzoyl isocyanate, which is stable under other conditions, to eliminate CO_2:



In the course of the study of the reaction of disilyl-substituted amides (LI) with chloroformates a new class of organo silicon compounds was obtained, namely the esters of silyl-substituted acylcarbamic acids (LII):[43]



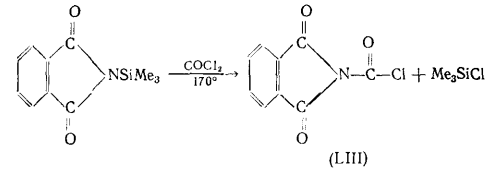
The possibility of isolating these compounds in a pure state, in contrast to the related *N*-silyl-substituted *N*-acylcarbamoyl chlorides, is due to the significantly lower electronegativity of the alkoxy- groups in the β-position relative to the silicon atom in the system of conjugated bonds $\equiv Si-\overset{|}{N}-\overset{|}{C}-X$ (X = OAlk or Cl) and the consequent lower tendency towards β-decomposition:



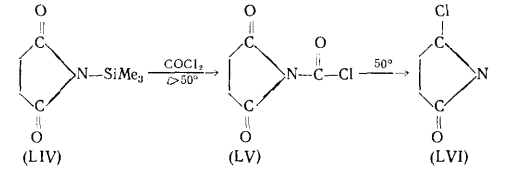
The reactivity of the amides (LI) is greatly influenced by the electronegativity of the substituent R, which is ultimately responsible, on passing from the methyl to the phenyl and trifluoromethyl groups, for the weakening of the nucleophilic properties of the molecule as a whole. Indeed, whereas bis(trimethylsilyl)acetamide (LI, R = Me) reacts readily with methyl chloroformate, the phenyl analogue (LI, R = Ph) requires the presence of catalytic amounts of H_2SO_4, as in the reaction of disilyl-substituted amines. The disilyl derivative of trifluoroacetamide does not undergo this reaction at all.

Carboxylic acid amides are known to be weaker bases than amines. Since silylation at the nitrogen atom lowers the basicity of compounds, the disilyl-substituted amides should be still weaker bases and hence should be less reactive in relation to chloroformates than the corresponding amines. The observed enhanced reactivity of disilyl derivatives of acetamide and benzamide can be accounted for by their interaction with chloroformates in the imidol form.

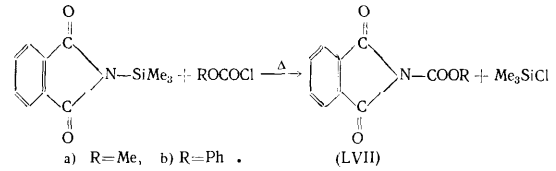
N,N-Diacylcarbamoyl chlorides[107,108]. In contrast to *N*-acyl-*N*-alkyl(aryl)carbamoyl chlorides, *N*-chlorocarbonylphthalimide (LIII), i.e. the first representative of *N,N*-diacylcarbamoyl chlorides, is formed only under very severe conditions, for example, in boiling pseudocumene on treatment of *N*-trimethylsilylphthalimide with phosgene:



On the other hand, *N*-trimethylsilylsuccinimide (LIV) reacts vigorously with $COCl_2$ and *N*-chlorocarbonylsuccinimide (LV) is decarboxylated under the reaction conditions to 2-chloro-Δ^1-5-pyrrolinone (LVI):



N-Trimethylsilylphthalimide reacts with methyl and phenyl chloroformates as well as $COCl_2$, undergoing cleavage at the Si–N bond and giving rise to the corresponding *N*-methoxycarbonyl- and *N*-phenoxycarbonylphthalimides (LVII, a and b):

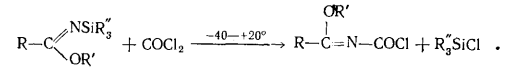


The thermal stability of the *N*-phenoxycarbonyl derivative of phthalimide is higher than that of *N*-chlorocarbonylphthalimide; it is decarboxylated only in boiling hexamethylphosphoramide (230–240°C).

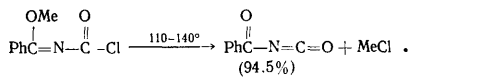
(g) *N*-Silyl-Substituted Iminoesters and Amidines

N-Silyl-substituted iminoesters proved to be much more stable than the initial iminoesters, which makes it possible to use them in reactions which had been previously difficult to control.

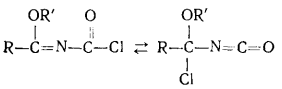
For example, it has been observed[109] that, when iminoesters are acted upon by phosgene, *N*-chlorocarbonyliminoesters are formed. The reaction of phosgene with *N*-silyliminoesters proceeds under incomparably milder conditions and leads to the formation of *N*-chlorocarbonyliminoesters in much higher yields[43,80,110]:



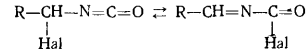
The *N*-chlorocarbonyliminoesters obtained are thermally unstable and tend to form acyl isocyanates on heating[43,80,110]:



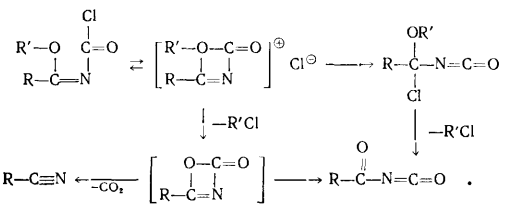
Apart from the intense absorption bands due to the C=N (1640 cm^{-1}) and C=O (1760 cm^{-1}) groups, the infrared spectra of *N*-chlorocarbonyliminoesters contain a weak absorption band due to the N=C=O group at 2252 cm^{-1}. The simultaneous presence of these bands in the spectra of compounds of this kind is explained[109] by the tautomeric equilibrium



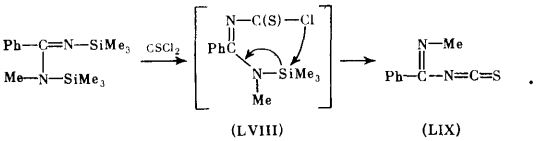
which is analogous to the familiar equilibrium of α-halogeno-substituted isocyanates[111]:



However, we believe that one cannot rule out the possibility also that *N*-chlorocarbonyliminoesters exist in the form of transitional "onium" complexes, which undergo the following reactions[43]:

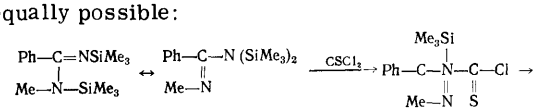


Having studied the reaction of *N*-methyl-*N*,*N*'-bis-(trimethylsilyl)benzamidine with thiophosgene, Barnikow and Ebeling[112] put forward the following mechanism for the formation of *N*-methylbenzimidoisothiocyanate (LIX):



(LVIII) (LIX)

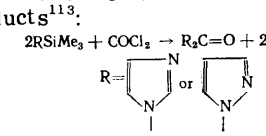
However, one should note that at least two other versions are equally possible:



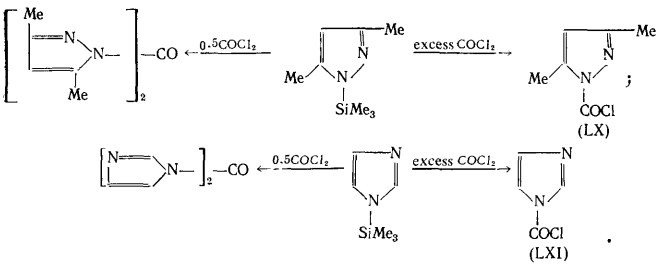
(LVIII) ↔ (LIX) .

(h) *N*-Silyl-Substituted Azoles

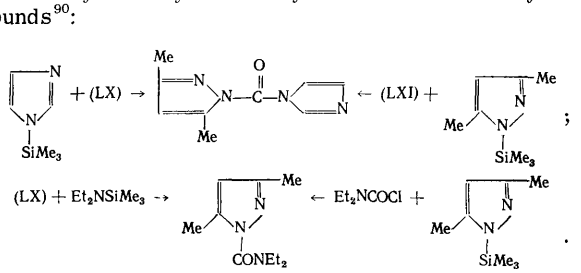
As early as 1960, Birkofer et al. showed that *N*-trimethyl-substituted diazoles react almost quantitatively with phosgene at 0–20°C to form the corresponding acylation products[113]:



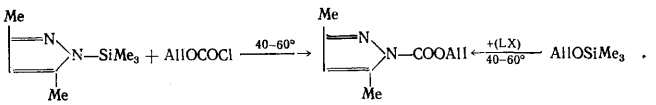
However, it was found that the nature of the final products is determined by the ratio of the initial reactants and the order in which they are introduced into the reaction:



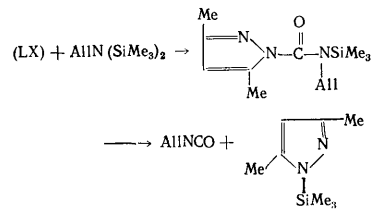
Carbamoyl chlorides (LX) and (LXI) as well as Et_2NCOCl react with *N*-silyl-substituted azoles to form symmetrically and asymetrically constructed carbonyl compounds[90]:



In contrast to $COCl_2$ and carbamoyl chlorides, allyl chlorocarbonate is less reactive in relation to *N*-trimethylsilyldiazoles and react with the latter on heating:



The carbamoyl chlorides (LX) and (LXI) react with $AllN(SiMe_3)_2$ to form the corresponding urea, whose pyrolysis under the conditions of the synthesis leads to AllNCO:



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