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ORGANOSILICON COMPOUNDS CONTAINING A CYANO-GROUP

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CONTENTS

I. Introduction 393

II. Compounds containing a cyano-group attached directly to silicon 394
1. Methods of synthesis 394
2. Properties 395

III. Organosilicon compounds containing cyanoalkyl or cyanoaryl groups attached to silicon 396
1. Methods of synthesis 396
2. Chemical properties 400
3. Physical properties 403
4. Practical uses of cyanoalkyl compounds of silicon 404

IV. Cyanoalkoxy-derivatives of organosilicon compounds 405
1. Methods of synthesis 405
2. Properties 405

I. INTRODUCTION

Alkylated (or arylated) siloxane polymers have long been used industrially as lubricants, hydraulic liquids, rubbers, coatings, and other materials. At the present time, however, typical polysiloxane materials cannot fully satisfy the growing demand of technology. A promising and important method for the controlled modification of the special properties of siloxane polymers† is the introduction of polar substituents into the hydrocarbon radicals surrounding the siloxane chains. The problem of synthesising organosilicon compounds containing functional groups is therefore now one of the most important tasks in the organic chemistry of silicon.

One of the most polar functional groups is the cyano--group[2,3]. When introduced into other polymers, it conferred on them several valuable technical properties; examples are provided by the acrylonitrile rubbers[4]. Furthermore, nitriles are convenient starting materials for the preparation of organic compounds with various functional groups[5]. These are probably the main reasons for the rapid expansion of research on the synthesis and properties of organosilicon nitriles.

Although the first organosilicon nitriles were obtained twenty years ago, their systematic investigation began only in 1955, both in the USSR[6,7] and abroad[8-10]. General methods have now been worked out for the synthesis of silicon-containing nitriles, and their properties have been studied in detail. Several cyanoalkyl derivatives of silicon are already produced on a large scale, and materials obtained from them are finding use in important branches of technology.

Polysiloxanes containing 2-cyanoethyl and 3-cyanopropyl groups have good stability to thermal oxidation together with high resistance to oils, petrol, and frost. This fact is of fundamental importance, since it contradicts the widely held view that the only thermostable alkylpolysiloxanes are those in which the surrounding alkyl groups are small (preferably methyl).

Organosilicon compounds containing two nitrile groups will probably have many uses. These compounds, like their organic analogues, can be readily converted into

† The specific properties of siloxanes are largely determined by the low "barrier" to rotation about the Si–O bond and the extraordinarily small intermolecular forces[1].

$\alpha\omega$-dibasic acids, diamines, diesters, and other bifunctional compounds suitable for the preparation of silicon-containing polyamides, polyesters, polyurethanes, etc. It can be expected that among such organosilicon polymers, which are fundamentally different from polysiloxanes, materials having valuable technical properties will be obtained[11].

We shall consider in this review the cyanoalkyl and cyanoaryl derivatives of silicon as well as compounds of silicon with cyanoalkoxy radicals and silanes in which the cyano-group is directly linked to a silicon atom, Si[CN]. The latter compounds are now attracting attention as interesting materials for theoretical investigations, owing to the ease with which they undergo tautomeric change.

II. COMPOUNDS CONTAINING A CYANO-GROUP ATTACHED DIRECTLY TO SILICON

1. Methods of Synthesis

As early as 1941 Emeléus obtained a silicon-containing nitrile by the reaction of SiH_3I with AgCN.[12] The product was given the nitrile structure $H_3Si-C\equiv N$ without proof. Subsequently alkylsilyl cyanides, in particular $CH_3SiH_2[CN]$, were obtained from alkylsilyl iodides, and also by exchange reactions with metal cyanides[13,14].

Eaborn obtained a series of alkylsilyl cyanides[15], which boiled at lower temperatures than the corresponding iodides; on this basis he ascribed an isocyano-structure to them: $(C_2H_5)_3Si-N=C$, $(n\text{-}C_3H_7)_3Si-N=C$, $(C_2H_5)_2Si(-N=C)_2$. At the same time he found that $(n\text{-}C_3H_7)_3SiCl$ does not react with silver cyanide under the conditions of reaction (I)

$$R_n Si I_m + m\,AgCN \rightarrow R_n Si(CN)_m + m\,AgI\,. \qquad (I)$$

It was later found[16] that the corresponding $R_3Si[CN]$ compounds are formed by the reaction of silver cyanide with trialkylsilyl bromides and with $(CH_3)_3Si-S-Si(CH_3)_3$.

McBride and Beachel considered Eaborn's arguments regarding the structure of his compounds unconvincing, and made a thorough investigation of the problem[17]. They prepared the required compounds from tri- and di-methylsilyl halides and silver cyanide. They found that $SiBr_4$ and CH_3SiBr_3 do not react with silver cyanide in boiling benzene. The characteristic frequencies which they discovered in the infra-red spectra of the preparations could equally well be assigned to the structure $Si-C\equiv N$ or to a mixture of the nitrile and isocyano-structures. Several of the chemical reactions [(II), (III)] supported, in the opinion of these workers, the isocyano-structure of the preparations:

$$(CH_3)_3Si-N=C+S \xrightarrow{\text{boiling}} (CH_3)_3Si-N=C=S, \qquad (II)$$

$$(CH_3)_3Si-N=C \xrightarrow{H_2} (CH_3)_3Si-N=CH_2 \xrightarrow{H_2} (CH_3)_3SiNH_2+CH_4,$$
$$2(CH_3)_3SiNH_2 \longrightarrow (CH_3)_3Si-\underset{\displaystyle H}{N}-Si(CH_3)_3+NH_3. \qquad (III)$$

They were unable to effect the thermal rearrangement of the isocyanide into the normal nitrile, which was explained by the peculiar thermodynamic stability of the Si–N=C group.

On the basis of this work the iso-structure was accepted up to 1958 for the cyano-group linked to silicon[8,18]. In that year Bither *et al.* published a careful spectroscopic investigation[19] at various temperatures of compounds containing the Si[CN] group. Analysis of the infra-red spectra led them to conclude that a tautomeric equilibrium is present in compounds containing such groups:

$$2R_3Si-C\equiv N \rightleftarrows \left[\begin{matrix} R_3Si-C\equiv N \\ N\equiv C-SiR_3 \end{matrix}\right] \rightleftarrows 2R_3Si-N=C\,.$$

At 20° the normal form predominates, whereas at 80° the iso-form does so. Seyferth[20] has recently reported the presence of tautomerism even in the case of trimethylcyanogermane: $(CH_3)_3Ge-N=C \rightleftharpoons (CH_3)_3Ge-C\equiv N$. These conclusions agree well with experimental data on the chemical properties of these nitriles. The structure of the Si[CN] group has also been discussed in several other papers[14,21-25].

New exchange reactions (IV)–(VI) have recently been proposed for the synthesis of compounds containing Si[CN] groups[19]:

$$2R_3SiCl + K_2Hg[CN]_4 \rightarrow 2R_3Si[CN] + 2KCl \rightarrow Hg(CN)_2\,, \qquad (IV)$$

$$R_3Si-\underset{\displaystyle H}{N}-SiR_3 + 3HCN \rightarrow 2R_3Si[CN] \rightarrow NH_4[CN], \qquad (V)$$

$$R_3SiOCH_3 + (CH_3)_3C(CO)C\equiv N \xrightarrow{AlX_3} R_3Si[CN] + (CH_3)_3C(CO)OCH_3\,, \qquad (VI)$$

where R = alkyl. The compound $(CH_3)_3Si[CN]$ can be obtained from HCN, $(CH_3)_3SiCl$, and metallic lithium[14].

Existing methods have also been improved; in particular the yield of $(CH_3)_3Si[CN]$ from $(CH_3)_3SiCl$ and AgCN can be increased if the reaction is carried out under pressure[18,19] or if the AgCl formed in the reaction is removed from the reaction mixture[14].

Anderson and his coworkers[26-29] used exchange reactions to synthesise compounds of the type $R_nM[CN]_m$, where $m + n = 4$ and M = Si, Ge, Sn; no proof was given of the structure of the resulting compounds.

McBride prepared arylsilyl and alkylarylsilyl cyanides from AgCN and the corresponding arylsilyl [and alkylarylsilyl? (Ed. of Translation)] halides[23].

Prober discovered that trimethylsilyl cyanide is formed by reaction (VII):

$$(CH_3)_3SiCH_2I + AgCN \rightarrow (CH_3)_3Si[CN] + \text{other products}, \qquad (VII)$$

but he did not discuss the mechanism of this unexpected reaction. Later he noted that $(CH_3)_3Si[CN]$ is also formed by the reaction of $(CH_3)_3SiCl$ and Na with CH_3CN in ether. Petrov and Vdovin[31] showed this observation to be an example of the general reaction (VIII) for a series of trialkylsilyl halides and nitriles:

$$R(CH_3)_3SiX + R'CH_2CN + Na \xrightarrow{\text{ether}} R(CH_3)_3Si[CN] + \text{other products}, \qquad (VIII)$$

It is interesting that with $(CH_3)_2RSiCl$ and acetonitrile the yields of trialkylsilyl cyanides increased as R became larger, being 25%, 37%, and 51% when R = CH_3, C_2H_5, and C_4H_9 respectively. Since the difficultly accessible trialkylsilyl iodides or bromides and silver cyanide have usually been required in order to obtain trialkylsilyl cyanides, this last method, using readily available reagents, is of interest for such preparations.

Prober[18] suggested the following scheme for the formation of trimethylsilyl cyanide from acetonitrile:

$$2CH_3CN + 2Na \rightarrow CH_4 + NaCN + (CH_2CN)^-Na^+\,, \qquad (IX)$$

$$NaCN + (CH_3)_3SiCl \longrightarrow (CH_3)_3Si[CN] + NaCl.$$

He assumed that NaCN formed "in the nascent state" is more active than powdered NaCN, which does not interact with $(CH_3)_3SiCl$ under these conditions. However, this scheme was criticised[31], since it was inconsistent with several experimental data. The formation of compounds of the type $R_3Si[CN]$ in this case is probably the result of the decomposition of α-nitriles, $R_3SiCHRCN$, formed initially in the reaction, which are known to be unstable under the influence of various reagents (see Section III, 2).

2. Properties

Emeléus[12] found that cyanosilane is very unstable, decomposing in air with the formation of hydrogen cyanide. It was subsequently discovered[15,17,23] that trialkylsilyl (and triarylsilyl) cyanides split off the cyano-group under the influence of water, Grignard reagents, and mercuric oxide:

$$2R_3Si[CN] + H_2O \rightarrow R_3SiOSiR_3 + 2HCN, \quad (I)$$

$$R_3Si[CN] + R'MgX \rightarrow R_3SiR' + [CN]MgX, \quad (II)$$

$$2R_3Si[CN] + HgO \rightarrow R_3SiOSiR_3 + Hg[CN]_2. \quad (III)$$

where R and R′ = alkyl and aryl.

Analogous reactions take place in the presence of silver salts[16]:

$$(C_2H_5)_3Si[CN] + AgNCO \rightarrow (C_2H_5)_3SiNCO + AgCN, \quad (IV)$$

$$(C_2H_5)_3Si[CN] + AgNCS \rightarrow (C_2H_5)_3SiNCS + AgCN. \quad (V)$$

Not only trialkylsilyl halides (VI) but also chlorides of other elements (VII) can undergo double decomposition with $R_3Si[CN]$:[19]

$$(CH_3)_3Si[CN] + R_3SiCl \rightarrow (CH_3)_3SiCl + R_3Si[CN]^{\ddagger}, \quad (VI)$$

where R = aryl or a higher alkyl group,

$$x(CH_3)_3Si[CN] + MCl_x \rightarrow x(CH_3)_3SiCl + M[CN]_x, \quad (VII)$$

where M = As, Sb, Bi, Pb, Ge, and x is the valency of the metal.

Exchange reactions take place still more readily with cyanosilane derivatives containing the $Si[CN]_2$ group[15,23]:

$$n R_2Si[CN]_2 + n H_2O \rightarrow (R_2SiO)_n + 2n HCN, \quad (VIII)$$

$$R_2Si[CN]_2 + 2R'MgX \rightarrow R_2SiR'_2 + 2XMg[CN]. \quad (IX)$$

These reactions as well as a series of other exchange reactions[14,26-30] are characteristic of organometallic compounds containing an M[CN] group (M = Si, Sn, Ge, etc.).

Several reactions undergone by the Si[CN] group without splitting off the cyano-group have been mentioned in Section I. It is interesting that hydrogenation of $(CH_3)_3Si[CN]$ in the presence of an Adams catalyst or Raney nickel[17] leads to the formation of the silazane $(CH_3)_3Si-NH-Si(CH_3)_3$, whereas reduction of $(CH_3)_3Si[CN]$ with $LiAlH_4$ yields $(CH_3)_3SiH$.[19]

The polymerisation of $CH_3SiH_2[CN]$ has been investigated[13]: above 40° it polymerises rapidly in the absence of catalysts, it remains unchanged in the presence of $Ni(CO)_4$ at 20°, and with a catalytic quantity of BF_3 it is converted even at 0° into a polymeric mass containing no BF_3.

‡ This reaction occurs so smoothly that Bither[19] regards it as the most convenient method for preparing the higher trialkylsilyl and triarylsilyl cyanides.

The following reaction has been studied[30]:

$$(CH_3)_3M[CN] + Fe(CO)_5 \xrightarrow{65°-110°} (CH_3)_3M-N=C-Fe(CO)_4, \quad (X)$$

where M = Si, Ge, Sn. High yields of adducts are obtained even at 65°–75° if M = Si (93%) or Ge (69%). When M = Sn, the yield of adduct is negligible, even after heating at 110°.

Evers and his collaborators studied the reaction of $(CH_3)_3SiCN$ and H_3SiCN with diborane and dibutylboron chloride[14,32]. At temperatures between -196° and +20° the solid complexes (A) and (B) were formed:

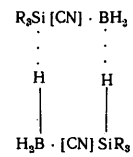
$$2H_3Si[CN] + B_2H_6 \rightarrow \underset{(A)}{2H_3Si[CN]\cdot BH_3} \quad (XI)$$

and similarly $(CH_3)_3Si[CN]$ yielded $(CH_3)_3Si[CN].BH_3$ (B). Above 70° complex (A) decomposes:

$$H_3SiCN\cdot BH_3 \rightarrow H_2B[CN] + SiH_4. \quad (XII)$$

Complex (B) decomposes similarly, but under more severe conditions, with the formation of $(CH_3)_3SiH$ and $H_2B[CN]$.

The ease with which $R_3Si[CN]$ is reduced to R_3SiH is explained by the presence of vacant 3*d* orbitals in the silicon atom, reduction probably occurring in a new complex (AA) or (BB):



where R = H, CH_3. Exchange with a dialkylboron chloride is effected in an analogous manner:

$$(n\text{-}C_4H_9)_2BCl + (CH_3)_3Si[CN] \rightarrow (n\text{-}C_4H_9)_2B[CN] + (CH_3)_3SiCl. \quad (XIII)$$

The following reactions of complex (B) have been studied:

$$B \xrightarrow{H_2O/KOH} [(CH_3)_3Si]_2O + KBO_2 + KCN + H_2O,$$

$$B \xrightarrow[[-H_2]]{HCl} (CH_3)_3Si(CN)\cdot BH_2Cl \longrightarrow (CH_3)_3SiCl + H_2B(CN)$$

$$B \xrightarrow{(CH_3)_3Si(CN)} (CH_3)_3SiH + (CH_3)_3Si(CN)\cdot BH_2(CN).$$

Several physical properties of compounds containing Si[CN] groups, including their infra-red and Raman spectra, molecular refraction, etc., have been described[14,17,19,21-25]. A sharp, unpleasant odour is a characteristic property of these organosilicon compounds. Substances containing Si[CN] groups dissolve readily in the usual organic solvents.

Since a [CN] group directly linked to a silicon atom is readily split off, polysiloxanes containing the Si[CN] group have not yet been prepared. Such materials would hardly be of interest, because of the instability of the Si–[CN] bond. Nevertheless, as a result of the great reactivity of the [CN] group, these compounds may be useful as starting materials for the synthesis of polymers consisting of silicon–nitrogen–carbon chains. At present such polymers are attracting considerable interest both on their own account and as components in the preparation of chelate polymers[33,34].

III. ORGANOSILICON COMPOUNDS CONTAINING CYANOALKYL OR CYANOARYL GROUPS ATTACHED TO SILICON

1. Methods of Synthesis

(*a*) Substitution by the cyano-group of halogen in halogenoalkyl and halogenoaryl derivatives of silicon. The double decomposition of alkyl and aryl halides with metal cyanides is the classical method for preparing alkyl and aryl cyanides. This method was, of course, tried in the first attempts to obtain organosilicon nitriles. Thus as early as 1946 Krieble and Elliott treated chloromethylpentamethylcyclotrisiloxane with sodium cyanide[35]. However, when the mixture was boiled in aqueous–alcoholic solution, the substituted methyl radical was cleaved from the silicon atom. Hauser and Harles studied the reaction of α-halogenomethyl derivatives of silicon with potassium cyanide in boiling methanol[36]. $(CH_3)_3SiCH_2Br$, $(CH_3)_3SiCHBrC_6H_5$, and $(CH_3)_3SiCBr(C_6H_5)_2$ reacted with potassium cyanide, but the normal exchange products were not isolated. The presence of trimethylmethoxysilane and of nitriles not containing silicon led these workers to suggest that α-cyanomethylated silicon derivatives are formed initially and then decompose

$$(CH_3)_3SiCHBr \xrightarrow[65^\circ]{KCN} [(CH_3)_3SiCHCN] \xrightarrow[65^\circ]{CH_3OH} (CH_3)_3SiOCH_3 + C_6H_5CH_2CN. \quad (I)$$

Formation of α-cyanomethylated silicon compounds in these cases is supported also by the fact that α-halogenomethylated silicon compounds are extremely reactive in bimolecular nucleophilic substitutions (see for example Refs. 37–40).

Prober[8] heated $(CH_3)_3SiCH_2Cl$ with NaCN in the absence of solvent at 200°, but the expected cyanomethyltrimethylsilane was obtained in low yield; $(CH_3)_3SiOSi(CH_3)_2CH_2X$, where X = Cl, I, did not react at all with NaCN under these conditions. Chloromethylated silicon compounds reacted neither with AgCN nor with CuCN at 150°–200°, whereas $(CH_3)_3SiCH_2I$ under similar conditions formed the anomalous reaction product $(CH_3)_3Si[CN]$. Klebanskii and Ponomarev report[41] that chloro(and bromo)methylheptamethylcyclotetrasiloxane reacted neither with CuCN nor with $Hg(CN)_2$ below 170°, above which considerable resinification of the products began.

In contrast to the α-halogenomethylated products, *p*-halogenophenyl compounds of silicon were successfully used for the synthesis of the corresponding cyanophenylated silanes and siloxanes[42–44] by reactions (II) and (III):

$$[p\text{-}Br{-}C_6H_4Si(CH_3)_2]_2O + CuCN \xrightarrow[10\ h]{275^\circ-300^\circ} [p\text{-}CN{-}C_6H_4Si(CH_3)_2]_2O, \quad (II)$$

$$[p\text{-}Br{-}C_6H_4]_3Si(CH_3)_2 + CuCN \xrightarrow[4\ h]{250^\circ} [p\text{-}CN{-}C_6H_4]_3Si(CH_3)_2. \quad (III)$$

In reaction (II) a 24% yield of the dinitrile was obtained, and in reaction (III) an 82% yield. Prober succeeded in preparing α-cyanomethylated derivatives by reaction (IV):[8]

$$\equiv SiCH_2MgCl + [CN]_2 \longrightarrow \equiv SiCH_2CN + ClMgCN. \quad (IV)$$

The reaction was carried out between -40° and -50°, and 38–52% yields of the α-nitriles — cyanomethyltrimethylsilane, cyanomethylpentamethyldisiloxane, and cyanomethylheptamethylcyclotetrasiloxane — were obtained from the corresponding halogenomethyl derivatives. Although the yields indicated by Prober for the last of the above α-nitriles could not be reproduced subsequently[41], replacement of the original chloromethylated cyclic tetrasiloxane by the bromomethyl derivative gave 85% yields of this α-nitrile[41].

(*b*) Silico-alkylation (silylation) of nitriles by halogenosilanes. Prober[18] tried to synthesise α-cyanomethyl derivatives of silicon by the following reaction:

$$(CH_3)_3SiCl + CH_3CN + Na \xrightarrow{ether} (CH_3)_3SiCH_2CN + NaCl.$$

However, the yield of the expected organosilicon nitrile was only 2%. Nevertheless, among the products were found the disilylated acetonitrile derivatives $[(CH_3)_3Si]_2CHCN$ (7%) and $(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$ (25%) as well as several others. The appearance of a ketenimine was explained by resonance of the anions (A) and (B) of the organosodium derivative $[(CH_3)_3SiCHCN]^-Na^+$:

$$[(CH_3)_3Si\overline{C}H] \longleftrightarrow [(CH_3)_3Si{-}CH{=}C{=}\overline{N}].$$
$$\quad\quad C{\equiv}N$$
$$\quad (A) \quad\quad\quad\quad (B)$$

Owing to a definite steric effect, the $(CH_3)_3SiCl$ molecule reacts mainly with form (B) (ketenimine). Under the influence of basic catalysts (H_2O, $C_6H_5NH_2$) the ketenimine readily isomerises to the nitrile. This isomerisation is probably a consequence of a molecule of the base attacking the central carbon atom, after which the $(CH_3)_3Si$ group migrates from the nitrogen to the carbon according to the scheme:

$$(CH_3)_3SiCH{=}C{=}N{-}Si(CH_3)_3 + H_2O \longrightarrow (CH_3)_3Si{-}\overset{\delta-}{C}H{-}\overset{\delta-}{C}{=}N{-}Si(CH_3)_3 \longrightarrow$$
$$\longrightarrow (CH_3)_3Si{-}CH(Si(CH_3)_3){-}C{\equiv}N + H_2O \quad (IV)$$

In the alkylation of benzyl cyanide with trimethylsilyl chloride in the presence of sodamide the expected compound, $C_6H_5CH(C{\equiv}N)Si(CH_3)_3$, was not obtained[18].

Shaw[45] made a detailed study of the alkylation of benzyl cyanide with trialkylsilyl fluorides and chlorides, and concluded that it takes place according to scheme (V) with the formation of *N*-silylated dimers of benzyl cyanide:

$$R_3SiX + 2C_6H_5CH_2CN \xrightarrow{NaNH_2} C_6H_5CH_2{-}C{=}C[CN]C_6H_5 \quad (V)$$
$$\quad\quad\quad

of the trialkyl-2-cyanoethylsilane was obtained with X = I and R = CH_3. Later these workers used the silico-alkylation of nitriles to synthesise $\alpha\omega$-bis-(trimethylsilyl)alkanes having a CN group in the hydrocarbon chain[47]:

$$(CH_3)_3Si(CH_2)_nCH_2CN + XCH_2Si(CH_3)_3 \xrightarrow[\text{ether}]{Na} (CH_3)_3Si(CH_2)_nCHCH_2Si(CH_3)_3 \quad \text{(VII)}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CN$$

where n = 1, 2 and X = Cl, Br, I.

The best yields of nitrile were obtained using iodomethyltrimethylsilane, whereas with the chloromethyl compound considerable quantities of byproducts, dimers of ω-cyanoalkyltrimethylsilanes, were formed.

The anomalous behaviour of 3-(2-cyanoethoxy)propyltrimethylsilane in this reaction is interesting. As with other nitriles, an organosodium derivative is probably formed, but it is readily decomposed in the same manner as organometallic compounds containing reactive centres in the 1,4-position[48]:

$$(CH_3)_3Si(CH_2)_3O-CH_2-\underset{\underset{C\equiv N}{|}}{CH}-H \xrightarrow[\text{ether}]{Na} \left[(CH_3)_3Si(CH_2)_3O-CH_2-\underset{\underset{CN}{|}}{CH}-Na\right] \longrightarrow \text{(VIII)}$$
$$\longrightarrow \begin{cases} (CH_3)_3Si(CH_2)_3ONa \xrightarrow{H_2O} (CH_3)_3Si(CH_2)_3OH \\ \left[CH_2=\underset{\underset{C\equiv N}{|}}{CH}\right] \longrightarrow \text{polymer.} \end{cases}$$

Several halogenomethylated silicon derivatives have been condensed with cyanoacetic ester, also under the influence of sodium[49]. De Benneville and his collaborators have reported[50,51] the alkylation of cyanoacetic ester in the presence of organic bases according to scheme (IX):

$$(CH_3)_3SiCl + \underset{\underset{CN}{|}}{CH_2}(COOC_2H_5) + (C_2H_5)_3N \longrightarrow (CH_3)_3Si\underset{\underset{CN}{|}}{CH}(COOC_2H_5) + (C_2H_5)_3N\cdot HCl \quad \text{(IX)}$$

Later they concluded[52] that the isomeric alkylation product $(CH_3)_3SiOC(OC_2H_5)=CHCN$ is formed according to scheme (VIII).

The possibility of condensing isobutyronitrile with methyltrichlorosilane in the presence of sodium to yield the α-nitrile $CH_3SiCl_2C(CH_3)_2CN$ has been mentioned in a patent[53].

Thus, in most cases the alkylation of nitriles with halogenosilanes R_3SiX does not yield the expected silicon-containing α-nitriles. Nevertheless, the silico-alkylation of nitriles with halogenomethyl (and probably other halogenoalkyl and halogenoaryl) derivatives of silicon can serve for the preparation of silicon-containing nitriles in which a cyano-group is attached to a carbon atom in the β-position to (or more remote from) the silicon atom. Silicon-containing α-nitriles $\gtrless Si-\overset{\alpha}{\underset{|}{C}}-CN$, in contrast to the β-nitriles $\gtrless Si-\overset{\alpha}{C}H_2-\overset{\beta}{\underset{|}{C}}-CN$, are unstable to heat. Their preparation is also unimportant, since they readily split off the α-cyanoalkyl group from the silicon atom under the influence of various reagents (see Section III, 2).

(*c*) Direct synthesis of cyanoalkylhalogenosilanes from ω-halogenonitriles and silicon. Petrov, Sadykh-Zade, and Vdovin studied the interaction of 2-cyanoethyl halides with silicon–copper alloys[6,31,54-56]:

$$NCCH_2CH_2X + Si \xrightarrow{Cu} X_3SiCH_2CH_2CN, \quad \text{(I)}$$

where X = Cl, Br. The reaction was carried out on a technical Si–Cu alloy under static conditions in a glass tube, and took place within a narrow temperature range (usually 370°–380°), which shifted somewhat, however, with variation in the composition of the alloy. Below 370° mainly unchanged $ClCH_2CH_2CN$ was recovered, whereas above 380° a different reaction predominated:

$$ClCH_2CH_2CN \xrightarrow[>380^\circ]{Si/Cu} \begin{cases} HCl \xrightarrow{Si/Cu} SiCl_4 + HSiCl_3 \\ + \\ CH_2=CHCN \end{cases} \quad \text{(II)}$$

The yields of $X_3SiCH_2CH_2CN$ when X = Cl and Br reached 20% and 17% respectively based on the weight of condensate obtained, and in both cases ~40% based on the halides used. By carrying out the reaction between 3-chloropropionitrile and silicon using a fluidised-bed technique, Golubtsov and his collaborators[56] were able to improve the yield to 40% of the condensate and 57% with respect to the chloride used. Chloroacetonitrile does not react with the Si–Cu alloy up to 450° (nor does it decompose appreciably under these conditions)[54].

It is interesting that 2-cyanoethyltrichlorosilane was first obtained by direct synthesis: it is an important industrial monomer which is now produced by the catalytic addition of trichlorosilane to acrylonitrile.

(*d*) Cyanoethylation of organosilicon compounds. The addition of organic compounds in general to acrylonitrile forms one of the most important methods for obtaining nitriles. This method has been successfully applied in the chemistry of organosilicon compounds as well.

Petrov *et al.*[7] and also Sommer[57] carried out cyanoethylation of silicon-containing alcohols according to the general scheme (I):

$$R_3Si(CH_2)_nOH + CH_2=CHCN \xrightarrow{\text{catalysts}} R_3Si(CH_2)_nOCH_2CH_2CN, \quad \text{(I)}$$

where R = alkyl and n = 1–3. The catalysts used were sodium methoxide, alkoxides of the initial silicon-containing alcohols, and Trilon B§, the reaction occurring even in the cold with 80–90% yields of the silicon-containing ω-cyanoalkyl ethers. Unsaturated silicon-containing alcohols of the type $R_3SiCH=CHCH_2OH$ have also been successfully cyanoethylated[58,59].

A study has been made of the cyanoethylation of amines and thiols containing silicon[60-62]:

$$(CH_3)_3SiCH_2\underset{\underset{R}{|}}{NH} + CH_2=CHCN \rightarrow (CH_3)_3SiCH_2\underset{\underset{R}{|}}{N}CH_2CH_2CN, \quad \text{(II)}$$

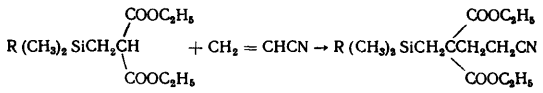
$$R_3Si(CH_2)_nSH + CH_2=CHCN \rightarrow R_3Si(CH_2)_nSCH_2CH_2CN, \quad \text{(III)}$$

where n = 1, 3 and R = alkyl.

When R = C_2H_5, reaction (II) took place in the absence of catalysts, whereas with R = C_6H_5, acetic acid acted as catalyst. When a functional group containing "active hydrogen" is directly linked to silicon (Si–OH, Si–NH_2), cyanoethylation takes place either very slowly or not at all[62-64].

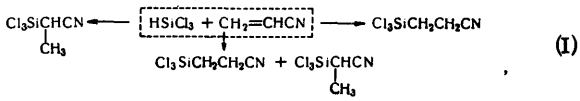
§ Tetrasodium salt of ethylenediaminetetraacetic acid (Ed. of Translation).

Examples are also known in which the cyanoethylation of organosilicon compounds takes place at a C–H bond[65-67]:



(*e*) Addition of Si–H compounds to unsaturated nitriles. This method of synthesising silicon-containing nitriles has hitherto been studied more thoroughly than others, since it is possible to obtain important industrial monomers more rapidly and more simply in this way than by other methods.

The addition of trichlorosilane to acrylonitrile was first accomplished by Petrov *et al.*[68] and independently by Japanese chemists[9,10]. These compounds can be made to react in any of three ways:



(I)

depending on the catalysts employed and the reaction conditions.

When an equimolar mixture of acrylonitrile and trichlorosilane is heated in sealed glass tubes to 180°, the β-isomer is formed, but in low yield (up to 10%)[9]. With peroxide catalysts at 160°, also in glass, the yield of the β-isomer is raised to 46%.[9] Use of Raney nickel as catalyst enables 3-trichlorosilylpropionitrile to be obtained, also in low yield[68]. Platinised asbestos or carbon at 100°–200°, either in a glass or metal apparatus[69,70], favours the formation of the β-isomer in yields of 40–60%.

Organic bases are efficient catalysts for the addition of $SiHCl_3$ to CH_2=CHCN.[9]

Table 1 gives results for the interaction of an equimolar mixture of acrylonitrile and trichlorosilane when heated in sealed glass tubes for 5 h (only the β-isomer was obtained). When the same reaction was carried out with pyridine as catalyst in an autoclave, a mixture of the α- and β-isomeric adducts was obtained. The actual catalyst here was found to be complexes of pyridine and nickel chlorides formed from the walls of the autoclave. In fact, when $NiCl_2.C_5H_5N$. .HCl, $NiCl_2.C_5H_5N$, and $NiCl_2.4C_5H_5N$ were used as catalysts in sealed glass tubes, the α-adduct was obtained.

Catalysts proposed subsequently[71,72], tributylamine and diethylaniline, were effective enough to enable the reaction to be carried out by boiling a mixture of the reactants in flasks, resulting in the formation solely of the β-adduct in yields of 50% and above. According to Saam and Speir[73,74], high catalytic activity (formation of the β-isomer) is exhibited by *N*-substituted amides such as *NN*-dimethylformamide, *NN*-diethylformamide, *NN*-dibutylacetamide, *NN*-diethyldecanoamide, and *N*-acetyl-*p*-toluidine, etc. (yields of adducts 38–43%). Acetanilide is a somewhat less active catalyst (yield of addition product 21%). It is interesting that the corresponding amine hydrochlorides possess no catalytic activity. Dialkylcyanamides and higher phenols[75-78] are effective catalysts.

Pike and his collaborators[77-82] employed several organoelemental compounds as catalysts for the addition of $SiHCl_3$ to acrylonitrile. Table 2 gives data on the catalytic activity of some of these compounds, and Table 3 data on the effect of temperature and catalyst concentration on the yield of adducts[80]. Table 3 shows that temperature is of decisive importance in this reaction, whereas catalyst concentration and duration of heating have little effect on its extent.

The addition of alkyldichlorosilanes and of some other silicon hydrides to acrylonitrile has been considerably less studied than the cyanoethylation of trichlorosilane. It has not yet proved possible to obtain by this method a satisfactory yield of the industrially important β-adduct of CH_3SiHCl_2 to CH_2=CHCN¶. Petrov and Vdovin[83] and also Goodman *et al.*[69,70] studied the latter reaction, and found that, with both pyridine and platinised carbon, the expected $CH_3SiCl_2CH_2CH_2CN$ is formed in low yield, accompanied by the α-isomer.

TABLE 1.

Catalyst*	Reaction temp., °C	Yield of $SiCl_3CH_2CH_2CN$, %
Pyridine	185	67
Pyridine	160	69
Pyridine	130	14
Triethylamine	160	76
Piperidine	160	69
Quinoline	160	40
Dimethylaniline	160	0
Pyridine hydrochloride	150	35
Benzyltriethylammonium chloride	160	70

* Equal relative weights of the catalysts were used, with respect to the weight of the reactant mixture.

TABLE 2*

Catalyst	Conversion, %	Adducts
No catalyst	42	α
$(n\text{-}C_4H_9)_3P$	55	β
$(C_6H_5)_2PCl$	47	β
$C_6H_5PCl_2$	39	β
$(C_6H_5)_3P$	56	β
$(C_6H_5)_3N$	29.8	mixture of α and β
$(C_6H_5)_3N$	30.7	β
$(C_6H_5)_3As$	25.8	mainly α, little β
$(C_6H_5)_3B$	10.5	mixture of α and β
$(C_6H_5)_3Sb$	traces	mixture of α and β

* An equimolar mixture of the reactants was used, with 2 mole % of the catalyst; heating was carried out in a steel autoclave at 200° for 2 h.

¶ During the printing of this review Bluestein[153] described the synthesis of the β-adduct $CH_3SiCl_2CH_2CH_2CN$ from acrylonitrile and methyldichlorosilane using the ternary catalyst $(CH_3)_2NCH_2$. . $CH_2N(CH_3)_2$–$N(C_4H_9)_3$–Cu_2Cl_2, which is quite effective when a mixture of the reactants is boiled at atmospheric pressure (yield up to 80%).

TABLE 3.

Catalyst wt. %*	Temp., °C	Duration of heating, h	Conversion, %
2	200	2	56
2	150	2	65
1	150	2	67
0.5	150	2	59
1	100	0.5	71
1	100	2	70
1	75	2	13

* The catalyst was $(C_6H_5)_3P$; reaction of an equimolar mixture of $SiHCl_3$ and CH_2=CHCN was carried out in a steel autoclave.

Speir was unable to effect the addition of CH_3SiHCl_2 to acrylonitrile in the presence of chloroplatinic acid[84], or of phenylsilanes to acrylonitrile (or to allyl cyanide) in the presence of peroxides[85]. The possibility of adding CH_3SiHCl_2, $CH_3SiH(OC_2H_5)_2$, and $C_2H_5SiHCl_2$ to acrylonitrile in the presence of organophosphorus catalysts is reported in a patent[81], which also describes the preparation (II) of the interesting bifunctional compound $CH_3SiCl(CH_2CH_2CN)_2$:

$$(CH_3)H_2SiCl + 2\,CH_2{=}CHCN \xrightarrow{(C_6H_5)_3P} CH_3SiCl(CH_2CH_2CN)_2. \qquad (II)$$

Freidlina *et al.* showed[86] that CH_3SiHCl_2 and $SiH(C_2H_5)_3$ add smoothly to acrylonitrile in the presence of the catalyst $Fe(CO)_5.NiCl_2$, only the α-adducts being formed (yields up to 70%).

Trichlorosilane adds to methacrylonitrile in the presence of the catalysts used for addition to acrylonitrile[71,81]. Under the influence of H_2PtCl_6 or Pt/C catalysts various incompletely substituted silanes add smoothly to olefines containing a CN group which is not conjugated with the double bond. Thus Sommer *et al.* carried out the reaction[87]:

$$CH_3SiCl_2H + CH_2{=}CH(CH_2)_n CN \xrightarrow{Pt/C\ (20\%)} CH_3Si(Cl_2)(CH_2)_{n+2}CN, \qquad (III)$$

where n = 1, 2, and established the direction of addition of the silyl group. Allyl cyanide and 2-cyanoethyl ether react with $SiHCl_3$ and alkyldichlorosilanes in the presence of platinum catalysts even at atmospheric pressure[72,84,88-90]. Reaction with allyl cyanide slows down appreciably on passing from alkyldichlorosilanes to dialkylchlorosilanes, while with tetraalkyldisiloxanes $SiHR_2OSiHR_2$ such reaction does not take place at atmospheric pressure[72].

Alkoxysilylalkyl ω-cyanides suitable for hydrogenation to the corresponding amines can be conveniently prepared by the reaction[88]:

$$R'(RO)_2SiH + CH_2{=}CHCH_2X \xrightarrow{Pt/C\ \text{or}\ H_2PtCl_6} R'(RO)_2SiCH_2CH_2CH_2X, \qquad (IV)$$

where R' = alkyl or alkoxy-group, R = lower alkyl, and X = CN or OCH_2CH_2CN. Trichlorosilane adds on to allyl cyanide with lower yields and under more severe conditions if organophosphorus compounds[81] or $NiCl_2.4C_5H_5N$[91] are used as catalysts, the latter yielding a mixture of two isomeric adducts:

$$CH_3CH(Cl_3Si)CH_2CN \text{ and } Cl_3SiCH_2CH_2CH_2CN.$$

The addition of cyanocyclohexene to silanes has been studied[90]. Addition takes place selectively when silanes react with vinylethynyl compounds containing a cyano-group[92,93]:

$$(R')_2RSiH + CH_2{=}CH-C{\equiv}C-C(CH_3)_2OCH_2CH_2CN \xrightarrow{60°-80°;\ H_2PtCl_6} CH_2{=}CH-\underset{\displaystyle SiR(R')_2}{\underset{|}{C}}{=}CH-C(CH_3)_2OCH_2CH_2CN \qquad (V)$$

where R' = alkyl or Cl, and R = alkyl. The resulting dienes are of interest as monomers for polymerisation and copolymerisation. The addition of trichlorosilane to allyl cyanide under the influence of γ-rays has been reported[94].

The mechanism of the addition of silanes to acrylonitrile and its analogues is discussed in several papers. Goodman[70] assumes that in the presence of platinised carbon addition of silicon hydrides to acrylonitrile (and to other olefines) takes place by an ionic mechanism. He supports this view by the following arguments: (a) the reaction occurs in the presence of inhibitors of radical polymerisation; and (b) replacement of unconjugated by conjugated olefines results in a change in the orientation of addition. In Goodman's view the role of platinum consists in polarising the Si–H bond in the direction $\overset{\delta+}{\text{Si}}-\overset{\delta-}{\text{H}}$.

With unconjugated olefines electrophilic addition takes place:

$$\bar{H} - R_3Si^+ + CH_2{=}CH-R' \rightarrow [R_3\overset{+}{Si}\cdot CH_2{=}CHR']^+ H^- \rightarrow R_3SiCH_2CH_2R. \qquad (VI)$$

In conjugated systems, where the double bond is polarised by a neighbouring electronegative group, conditions are favourable for reaction by a nucleophilic mechanism:

$$\bar{H} - R_3\overset{+}{Si} + CH_2^+{=}\bar{C}HCN \rightarrow [\bar{H}\cdot CH_2{=}CH-C{\equiv}N]^-\cdot\overset{+}{Si}R_3 \rightarrow H_3C-\underset{\displaystyle SiR_3}{\underset{|}{CH}}C{\equiv}N. \qquad (VII)$$

However, Goodman himself noted that, as the negative charge on the hydrogen atom in the Si–H group increases, both reactions (VI) and (VII) should be accelerated, which was not observed on passing from $SiHCl_3$ to CH_3SiHCl_2†. Later, Goodman's views encountered still more serious objections[75,95,96].

Nozakura and Konotsune[9,10] also regard the addition of trichlorosilane to acrylonitrile in the presence of organic bases as taking place by an ionic mechanism:

$$\begin{aligned} &Cl_3SiH + B \rightarrow Cl_3\bar{Si} + HB^+, \\ &Cl_3\bar{Si} + CH_2{=}CHCN \rightarrow Cl_3SiCH_2C\bar{H}CN, \\ &Cl_3SiCH_2\bar{C}HCN + HB^+ \rightarrow Cl_3SiCH_2CH_2CN + B, \end{aligned} \qquad (VIII)$$

where B represents a basic catalyst.

This mechanism is supported by the arguments that the reaction is catalysed by bases, telomers of acrylonitrile nitrile are not formed, and polar solvents (acetonitrile)

† Goodman used nuclear magnetic resonance experiments to show that from $SiHCl_3$ to CH_3SiHCl_2 and $(CH_3)_3SiH$ there is an increase in the electronegativity of the hydrogen atom attached to silicon (owing to the decrease in the inductive effect of the Si–Cl groups).

activate the reaction appreciably. These workers are forced to explain the change in the orientation of the addition of $SiHCl_3$ to $CH_2=CHCN$ in the presence of the catalyst $4C_5H_5N.NiCl_2$ by a change in the mode of dissociation of $SiHCl_3[Cl_3Si^+ + H^-]$ under the influence of this catalyst. An ionic mechanism is also assumed by Freidlina[86] for the addition of CH_3SiHCl_2 and $(C_2H_5)_3SiH$ to acrylonitrile [with $Fe(CO)_5.NiCl_2$ as catalyst].

In the presence of peroxides[9] the cyanoethylation of $SiHCl_3$ (the β-adduct is formed) undoubtedly proceeds by a radical mechanism, as shown particularly by the formation of telomeric products.

Saam and Speir[73] assume that trichlorosilane forms complexes with compounds containing nitrogen, and in particular with *NN*-substituted amides, by means of the vacant *d* orbitals of the silicon and that these complex compounds are active intermediates in the reaction with acrylonitrile. In our view such a concept provides a more correct approach to the problem of the mechanism of this reaction, although it does not answer directly whether rupture of the Si–H bond then takes place homolytically or heterolytically. Actually, if the role of the catalysts were merely to increase the polarisation of the Si–H bond, it would be expected that only the α-isomeric products would be obtained from $Cl_3\overset{+}{S}i-\overline{H}$ and $^{+}CH_2=\overline{C}HCN$. In fact, the β-adducts are formed.

The role of organic derivatives of phosphorus, arsenic, and bismuth as catalysts[73,74,80] is probably also to form active intermediates with silanes. Such an intermediate acts as a kind of carrier of trichlorosilane in the reaction with acrylonitrile. A similar reaction mechanism has been suggested in the chemistry of the cyanoethylation of compounds not containing silicon[97]. Thus it is suggested that in the cyanoethylation of aromatic amines (with acids or copper and nickel salts as catalysts) the amines form complexes with the catalysts, the complexing agent being displaced by the acrylonitrile, after which the cycle is repeated.

The fact that reaction takes place with the intermediate formation of complex compounds, and not by the formation of kinetically independent species, affects, of course, the process as a whole. In studying the reaction mechanism, therefore, we can hardly utilise the criteria which serve as arguments in support of typical radical or ionic processes.

It is interesting that germanium and tin hydrides, whose complexing power is greater than that of organosilicon derivatives, add to acrylonitrile in the absence of any catalyst[98–100].

(*f*) Preparation of organosilicon compounds containing a cyano-group by copolymerisation. A considerable amount of detailed work has been done on the copolymerisation of acrylonitrile with silicon-containing olefines[101–104]. With the aid of radical initiators, acetyl and benzoyl peroxides, copolymers have been obtained of acrylonitrile with siloxanes, of the type

$$CH_2=CHSi[OSi(CH_3)]_m(CH_3)_n,$$

where $m + n = 3$, and the constants for the copolymerisation of the original compounds have been calculated. Increase in the concentration of the silicon-containing olefine in the monomeric mixture diminishes the rate of polymerisation and lowers the molecular weight of the polymer. A study has been made of the behaviour of olefines of the types $R_3SiCH=CH_2$ and $RSi(OR')_3$ (where R = alkenyl, for example $CH_2=CH-$ and $CH_2=CHCH_2-$, or cycloalkenyl, and R' = = lower alkyl) on copolymerisation with acrylonitrile.

The preparation of silicon-containing nitriles by the γ-irradiation (^{60}Co) of solutions of acrylonitrile in polydimethylsiloxanes[105] is of fundamental interest, the kinetic features of this case of γ-initiated graft polymerisation having been investigated.

A promising line of investigation in the chemistry of organosilicon compounds is opened up by work on bivalent silicon, which is obtainable, for example, by the reaction[106,107]

$$SiX_4 + Si \xrightarrow{>1000^\circ} 2SiX_2 \quad , \qquad (I)$$

where X = halogen.

There is an indication in a patent[106] that acrylonitrile reacts at low temperatures with difluorosilylene to form polymers in which the unit is probably

$$\left[-(SiF_2)_n-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-\right].$$

Silicon-containing butadienes readily react with acrylonitrile[108]

$$R_3SiCH=CH-CH=CH_2 + H_2C=CHCN \rightarrow R_3Si-\underset{\displaystyle CH=CH}{\overset{\displaystyle CH_2-CH-CN}{\overset{\diagup\quad\diagdown}{CH}}}\quad CH_2 \quad . \qquad (II)$$

(*g*) Other methods of preparation. Trialkylsilylalkyl ω-cyanides can be obtained by dehydrating the corresponding ω-amides by means of phosphorus pentoxide, for example[109,110]. Jex mentions in a patent[111] the possibility of obtaining 2-cyanoethyltrichlorosilane from chloropolysilanes ($Cl_3SiSiCl_3$, $SiCl_3SiCl_2SiCl_3$) and acrylonitrile.

2. Chemical Properties

(*a*) Conversion of the cyano-group into other functional groups. The following example[6] demonstrated the hydrolysis of the cyano-group in an organosilicon compound:

$$(CH_3)_3SiCH_2CH_2CN \xrightarrow{KOH/C_2H_5OH} (CH_3)_3SiCH_2CH_2COOH. \qquad (I)$$

The reaction took place, with a high yield of the acid, on boiling the compound in 40% KOH solution. Elimination of the cyanoalkyl group was not observed.

Other work[42–44,49,65–67,91,154] established that simple nitriles of the type $R_3Si[CHR]_nCN$ (R = H or CH_3, $n \geq 2$) or silicon-containing dinitriles with ω-cyanoalkyl or *p*-cyanoaryl group are also hydrolysed without appreciable cleavage of the Si–C bond. With α-nitriles ($n = 1$, R = H or CH_3) attempts to hydrolyse the cyano-group involved elimination of the cyanoalkyl group[8,10,86]. Table 4 gives data on the stability of cyanomethyl groups[8], which show that, as Si–O–Si links accumulate in the molecule, the stability of the compound increases somewhat, although it remains low in acid and especially in alkaline media.

This difference in behaviour between α- and β-nitriles is explained by the inductive ($-I$) effect of the CN group,

TABLE 4. Cleavage of Si–C bond after the mixture has been boiled for 24 h (in %).

Nitrile	H_2O	5% HCl/H_2O	5% NaOH/H_2O
Cyanomethyltrimethylsilane	100	100	100
Cyanomethylpentamethyldisiloxane	58	86	100
Cyanomethylheptamethylcyclotetrasiloxane	0	38	100

which is particularly strong in the case of α-nitriles. This effect produces an increase in the positive charge on the silicon atom, and preferential nucleophilic attack on the silicon atom becomes possible:

$$(CH_3)_3\overset{+}{S}iCH_2\overset{-}{C}N + O\overset{-}{H} \longrightarrow (CH_3)_3SiOH + C\overset{-}{H}_2CN,$$
$$^-CH_2CN + {}^+H \longrightarrow CH_3CN,\ 2(CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + H_2O. \quad (II)$$

The mechanism of cleavage in acid medium is represented by the scheme

$$(CH_3)_3SiCH_2C{\equiv}N + H^+ \rightarrow CH_3SiCH_2C{\equiv}N{:}H^+,$$
$$H_2O + (CH_3)_3SiCH_2C{\equiv}N{:}H^+ \rightarrow (CH_3)_3SiOH_2^+ + CH_2{=}C{=}NH, \quad (III)$$
$$CH_2{=}C{=}NH \rightarrow CH_3C{\equiv}N,\ (CH_3)_3SiOH_2^+ \rightarrow (CH_3)_3SiOH + H^+.$$

A β-cyano-group can be hydrolysed when it occurs in polymeric compounds, both three-dimensional[8,80,112] and linear[112,113] siloxanes:

$$O_{1/2}SiCH_2CH_2CN \xrightarrow{NaOH/H_2O} O_{1/2}SiCH_2CH_2COONa \xrightarrow{HCl/H_2O} O_{1/2}SiCH_2CH_2COOH. \quad (IV)$$
$$\xrightarrow[HCl/H_2O]{}$$

In the case of a linear silicon polymer $[-OSi(CH_3).(CH_2CH_2CN)-]_n$ sulphuric acid is used as catalyst for the hydrolysis. According to a patent[114], products of the partial hydrolysis of cyanoalkylated silicon compounds can be prepared. In this case the polymer $\{-OSiR([CH_2]_k.CHR'CN)-\}_n$ is treated with concentrated sulphuric acid and then ice, when the polymer $\{-OSiR([CH_2]_kCHR'CONH_2)-\}_n$ is obtained (in both cases R and R' are lower alkyls and $k \geq 1$). A polymer containing 1-cyanoethyl group $\{-OSi.(CH_3)[CH(CH_3)CN]-\}_n$ completely eliminates the 1-cyanoethyl group on treatment with concentrated alkalis[86].

In the presence of Grignard reagents α-cyanoalkylated silicon compounds eliminate the CN-containing group[10,83,86], whereas organosilicon compounds containing the cyano-group in the β-position (or more remote) react in the usual way[6,9,46,87,91]:

$$(CH_3)_3Si(CH)_nCN + RMgX \longrightarrow (CH_3)_3Si(CH)_nCR, \quad (V)$$
$$\quad\ R' \qquad\qquad\qquad\qquad\quad R'\ \ O$$

where R = CH_3, C_6H_5; R' = H, CH_3; $n \geq 2$.

Whereas reaction (V) takes place at room temperature, heating at 100° is required to obtain ketones from nitriles of the type $(CH_3)_3Si[CH_2]_nCH(CN)CH_2Si(CH_3)_3$ ($n \geq 1$)[47].

Several papers[44,88,109,115-118] have dealt with reduction of the cyano-group. The compound $(CH_3)_3SiCH_2CH_2CN$ is smoothly reduced to the amine by $LiAlH_4$ [109] or on hydrogenation over metallic catalysts[117]. Di-(cyanophenyl)dimethylsilane is hydrogenated in the presence of ammonia on a Raney nickel catalyst at 130°, but, in spite of the severe reaction conditions, the corresponding diamine is obtained in low yield[35]. Dinitriles of the type $O(R_2Si[CH_2]_nCN)_2$ with $n = 2, 3$ and R = CH_3, C_2H_5 are smoothly reduced to the corresponding diamines even at 75°–100° in the presence of Raney Co and Ni catalysts[115,116], the yields of the diamines reaching 92%.

Petrov, Friedlin, and their collaborators were the first to show the possibility of hydrogenating ω-cyanoalkylsilanes containing alkoxyl groups attached to the silicon atom[115]. This line of investigation was later extended by these workers[88,116,117] and by American[118] and Japanese[155] investigators.

The hydrogenation has been studied of nitriles of the types $NC[CH_2]_kSiR_n(OR')_{3-n}$ and $NCCH_2CH_2O[CH_2]_3SiR_n.(OR')_{3-n}$, where $k \geq 2$, and R and R' are lower alkyl radicals. Yields of up to 85% of the corresponding amines are obtained.

Raney cobalt catalysts have the most selective effect in the formation of primary amines by hydrogenation; platinum catalysts result in the formation of considerable quantities of secondary and tertiary amines. With the cobalt catalysts the yield of primary amines is increased very slightly if hydrogenation is carried out in the presence of dry ammonia[88]. Japanese investigators achieved the best results by using a Raney Ni–Pt catalyst[155].

Synthesis of one of the amines, 3-triethoxysilylpropylamine, which is now produced industrially[132], can be accomplished by three methods, (VI),[88,116-118] (VII),[119] and (VIII):[120,155]

$$(C_2H_5O)_3SiCH_2CH_2CN \xrightarrow[Raney\ Co]{H_2} (C_2H_5O)_3SiCH_2CH_2CH_2NH_2, \quad (VI)$$

$$CH_2{=}CHCH_2NH_2\cdot(CH_3)_3SiCl \xrightarrow[H_2PtCl_6]{HSi(OC_2H_5)_3}$$
$$\rightarrow (C_2H_5O)_3SiCH_2CH_2CH_2NH_2\cdot(CH_3)_3SiCl \xrightarrow{C_2H_5OH} (C_2H_5O)_3SiCH_2CH_2CH_2NH_2, \quad (VII)$$
$$(C_2H_5O)_3SiCH_2CH_2CH_2Cl + NH_3 \rightarrow (C_2H_5O)_3SiCH_2CH_2CH_2\mathbf{NH_2}, \quad (VIII)$$

method (VI) successfully competing with the other two.

Interaction of acrylonitrile with methyldichlorosilane in the presence of catalysts in steel autoclaves has been found to yield unstable products whose composition was close to that of adducts of one mole of CH_2=CHCN and two or three moles of the silane[83]. This was explained by reaction of the silanes not only at the C=C bond but also at the C≡N bond of the acrylonitrile. It was subsequently confirmed[121] that the cyano-group reacts with silanes in the presence of metal chlorides, for example, in the following manner:

$$C_6H_5CN + HSi(C_2H_5)_3 \xrightarrow{NiCl_2} C_6H_5{-}CH{=}N{-}Si(C_2H_5)_3. \quad (IX)$$

Conditions have been determined[80] for the conversion of the CN into an ester group:

$$(C_2H_5O)_3SiCH_2CH_2CN \xrightarrow{abs.\ C_2H_5OH/HCl} (C_2H_5O)_3SiCH_2CH_2COOC_2H_5 \quad (X)$$

The α- and β-isomers of cyanoethyltrimethylsilane interact differently with thioglycollic acid[9,10]:

$$(CH_3)_3SiCH_2CH_2CN \xrightarrow{HSCH_2COOH/HCl} (CH_3)_3SiCH_2CH_2CSCH_2COOH, \quad (XI)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \|$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NH\cdot HCl$$

$$(CH_3)_3SiCHCN \xrightarrow{HSCH_2COOH/HCl} (CH_3)_3SiCl + CH_2CH_2CSCH_2COOH.$$
$$\quad\ |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \|$$
$$\quad CH_3\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NH.HCl$$

Dimerisation of cyanoalkyltrimethylsilanes takes place in the presence of sodium:

$$(CH_3)_3SiCH_2CH_2CN \xrightarrow{Na} (CH_3)_3SiCH_2CH(Na)CN \xrightarrow{(CH_3)_3SiCH_2CH_2CN} \rightarrow (CH_3)_3SiCH_2CH_2C(NH_2)C{\equiv}N-CH_2Si(CH_3)_3 \quad (XII)$$

(b) Reactions of cyanoalkylsilanes in which the cyano-group is preserved. In the case of reaction (I) it has been found that the Si–X bond is more reactive than the C≡N bond towards Grignard reagents[6]:

$$Cl_3SiCH_2CH_2CN + 3\,CH_3MgX \longrightarrow (CH_3)_3SiCH_2CH_2CN. \quad (I)$$

Later this method was used to obtain from various cyanoalkylhalogenosilanes a wide variety of CN-containing silico-hydrocarbons, siloxanes, and alkylhalogenosilanes[9,31,47,72,87,91]. It is interesting that, with a Grignard reagent[10,86], an Si–Cl group in the α-nitriles $SiCl_3CH(CH_3)CN$ and $CH_3SiCl_2CH.(CH_3)CN$ can be replaced by Si–R without the cyano-group being affected.

As mentioned above, satisfactory yields of the industrially important $RSiCl_2CH_2CH_2CN$ could not be obtained by the addition of $RSiHCl_2$ to $CH_2{=}CHCN$. These bifunctional nitriles were prepared by the action of the Grignard reagent on $SiCl_3CH_2CH_2CN$.

An attempt to obtain $CH_3SiCl_2CH_2CH_2CN$ using CH_3MgX at room temperature was unsuccessful, a mixture of products $(CH_3)_nSiCl_{3-n}CH_2CH_2CN$ (n = 1–3), which were difficult to separate, being formed; the bifunctional compound was isolated in 25% yield[73,74,122]. If, however, this reaction is carried out in tetrahydrofuran at low temperatures, it takes place more selectively (see Table 5)[123].

When cyanoalkyl derivatives (from CH_3I and Zn–Cu) were made to react with $SiCl_3CH_2CH_2CN$, only $(CH_3)_3SiCH_2CH_2CN$ could be isolated from the reaction products, although equimolar proportions of the reactants were taken[113]. Yields of the bifunctional compound up to 90% are obtained by the action of $(CH_3)_2Cd$ on $SiCl_3CH_2CH_2CN$.[71,122] In this reaction the yield of $CH_3SiCl_2CH_2CH_2CN$ can be increased if alkylation is effected with CH_3MgX in the presence of tertiary amines[124,125].

Since it is difficult to isolate the dialkylmonochlorosilylalkyl ω-cyanides obtained by the alkylation of trichlorosilylalkyl or alkyldichlorosilyl alkyl ω-cyanides, the following technique has been proposed for the preparation of αω-dinitriles, which does not require the isolation of the chlorides[72,156]:

$$2\,NC(CH_2)_nSiRCl_2 \xrightarrow{R'MgX} \xrightarrow{H_2O} [NC(CH_2)_nSiRR'-]_2O, \quad (II)$$

where R and R′ are lower alkyls, and n = 2, 3.

There are several studies of the hydrolysis of cyanoalkylsilanes containing functional groups attached to the silicon atom[6,9,10,31–41,80,84,112,113]. That of 2-trichlorosilylethyl cyanide has been investigated in detail by Pike *et al.*[80] Table 6 gives comparative data on the hydrolysis of $SiCl_3.CH_2CH_2CN$ and other silicon chlorides, which show the exceptional reactivity of this compound.

The ease with which the chlorine atoms attached to silicon in $SiCl_3CH_2CH_2CN$ are replaced by OH groups is a result of the inductive effect (–*I*) of the cyano-group, owing to which an additional positive charge is induced on the silicon atom, and favourable conditions are created for nucleophilic attack on this atom:

$$NCCH_2CH_2Si^{\delta+}Cl_3 \cdots O(H)H \longrightarrow \left[NCCH_2CH_2Si(Cl)_2(OH)\right]^{+} + HCl. \quad (III)$$

The inductive effect is still greater in the case of the α-isomer, so that it is possible to obtain $\{O_{3/2}Si[CH(CH_3).CN]\}_n$ only under mild conditions, otherwise decomposition occurs at the Si–C bond (IV):[10,80]

$$NCCHSiCl_3(CH_3) \xrightarrow[0^\circ]{H_2O/ether} \left[NCCHSiO_{3/2}(CH_3)\right]_n, \quad (IV)$$

$$NCCHSiCl_3(CH_3) \xrightarrow[20^\circ]{H_2O/ether} [SiO_2]_n + CH_3CH_2CN. \quad (V)$$

The linear polysiloxane from $CH_3SiCl_2CH(CH_3)CN$ also can be obtained only under mild conditions[86]. The polymer prepared from 2-methyldichlorosilylethyl cyanide[113] is a thick oil, insoluble in the usual organic solvents but soluble in dimethylformamide; the polysiloxane from $CH_3SiCl_2CH_2.CH_2CH_2CN$ also is only partly soluble in benzene[41].

Cyanoalkylsilanes having hydrolysable groups attached to the silicon atom, in particular $SiCl_3CH_2CH_2CN$, can be cohydrolysed with other alkylsilicon chlorides, for example with $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$.[112] A rubberlike polymer has been prepared by condensing $CH_3SiCl_2CH_2CH_2CH_2CN$ with $(HO)(CH_3)_2SiOSi(CH_3)_2(OH)$.[41] Even under mild conditions of hydrolysis it was not possible to obtain the silanediol from $CH_3SiCl_2CH_2CH_2CN$, since it immediately undergoes polycondensation to an oily polymeric product[113].

TABLE 5*

RMgX	Conversion (mole %) into $RSiCl_2CH_2CH_2CN/R_2SiClCH_2CH_2CN$		
	at –50°	at –30°	at +5°
CH_3MgCl	73/7	61.6/10.6	52.4/16.1
C_2H_5MgCl	69/9		

* Equimolar proportions of RMgX and $SiCl_3CH_2CH_2CN$ were used.

TABLE 6. Relative rate of hydrolysis of the first chlorine of alkylchlorosilanes in dimethylcellosolve*.

$RSiCl_3$	At –51°	At –20°	At 0°
$C_2H_5SiCl_3$	1.0	1.0	1.0
CH_3SiCl_3	2.2	0.59	0.3
$C_6H_5SiCl_3$	4.1	2.0	1.4
$NCCH_2CH_2SiCl_3$	62.0	116.0	153.0

* Ethylene glycol dimethyl ether (Ed. of Translation).

In the presence of 2 wt.% of concentrated H_2SO_4 at 20°, CN-containing siloxanes undergo rearrangement at the Si–O–Si bonds[8]:

$$2\,(CH_3)_3Si{-}O{-}Si(CH_3)_2CH_2CN \rightarrow [NCCH_2(CH_3)_2Si]_2O + [(CH_3)_3Si]_2O. \quad (VI)$$

However, 4 wt.% of H_2SO_4 was sufficient for the cyanoalkyl group to be split off from the silicon atom when an attempt was made to obtain a linear polysiloxane from hexamethyldisiloxane and cyanomethylheptamethylcyclotetrasiloxane. In the similar reaction

$$NC(CH_2)_nSi(CH_3)_2{-}O{-}(CH_3)_2Si(CH_2)_nCN + x[(CH_3)_2SiO]_4 \xrightarrow[20^\circ]{H_2SO_4} \rightarrow$$

$$\rightarrow NC(CH_2)_nSi(CH_3)_2[OSi(CH_3)_2]_{4x}O(CH_3)_2Si(CH_2)_nCN,$$

where $n = 2, 3$ and $x = 1-4$, carried out under the influence of 2–6 wt.% of H_2SO_4, β- and γ-cyanoalkyl groups are not eliminated[156].

According to Sommer[126], it was not possible to demethylate $(CH_3)_3SiCH_2CN$ (with sulphuric acid), because in this case the cyanoalkyl group was eliminated with the formation of $(CH_3)_3Si{-}O{-}Si(CH_3)_3$.

All cyanoalkylhalogenosilanes are smoothly alkoxylated[9,10,31,46,47,73,74,80,88,115,117,124] by anhydrous alcohols, including allyl alcohol. The reaction is carried out in the presence of substances (pyridine, ammonia) which will combine with the HCl evolved, and also in their absence, but in the latter case the yields of alkoxy-derivatives are somewhat lower, since the cyano-group also reacts to some extent with the alcohols (the HCl evolved acting as catalyst for this reaction)[80].

Acetic anhydride reacts according to (VII), the yields of the desired products exceeding 90%:[46]

$$NCCH_2CH_2SiCl_3 + 3\,CH_3CO{-}O{-}OCCH_3 \longrightarrow NCCH_2CH_2Si(OCOCH_3)_3 + 3CH_3COCl\ . \quad (VII)$$

Acyloxylation of $SiCl_3CH_2CH_2CN$ can also be effected with salts of organic acids, but lower yields are then obtained.

3. Physical Properties

Organosilicon compounds containing cyanoalkyl groups are strongly polar liquids[8,113]. Table 7 gives quantitative data enabling the properties of cyanomethyl compounds to be compared with those of analogous substances not containing cyano-groups.

The dielectric constants and dipole moments of cyanomethyl compounds in Table 7 also characterise them as polar substances. The polysiloxane $[-OSi(CH_3)(CH_2CH_2CN)-]_n$ behaves as a polar liquid[113].

As noted in parts 1 and 2 of this Section, α-nitriles, $Si{-}\overset{|}{\underset{|}{C}}{-}C{\equiv}N$, in contrast to β-, γ-, etc. nitriles, possess anomalous chemical properties. These are mainly due to the inductive effect of the cyano-group, but in some cases probably also to a steric effect or other peculiarities of molecular structure. The spectra of α-cyanoalkyl compounds also show characteristic features. Thus the infra-red absorption spectra of the first member of the series of compounds of general formula $(CH_3)_3Si[CH_2]_nCN$ (where $n = 1-3$) have the characteristic frequency of the cyano-group about 10–15 cm^{-1} below that in the β- and γ-nitriles,

TABLE 7.

Compound	Activation energy of viscous flow, kcal mole^{-1}	Heat of evaporation, kcal mole^{-1}	Entropy of evaporation, kcal mole^{-1} × × deg^{-1}
Cyanomethyltrimethylsilane	—	10.8	24.9
Tetramethylsilane	3.1	5.8[11]	19.4
Cyanomethylpentamethyldisiloxane	3.2	12.0	25.4
Hexamethyldisiloxane	2.2[9]	8.3[9]	22.2
Cyanomethylheptamethylcyclotetrasiloxane	4.5	14.0	27.6
Octamethylcyclotetrasiloxane	3.4[10]	10.0[9]	24.8

the frequency being considerably more intense than in the β-nitrile‡.[8,18,31,47]. However, in the series of nitriles

$$(CH_3)_3SiCH_2CN > (CH_3)_3SiCHCN > (CH_3)_3SiCHCN\ ,$$
$$\qquad\qquad\qquad\quad |\qquad\qquad\quad |$$
$$\qquad\qquad\qquad (CH_3)_3Si\qquad\quad CH_3$$

the frequency of the cyano-group falls, its respective values being 2240,[8,18,31] 2218,[18] and 2205 cm^{-1}.[86]

The characteristic frequencies of the CN group which have been reported[127] for nitriles not containing silicon are 2250 ± 8 cm^{-1} (unconjugated nitriles) and 2255 ± 10 cm^{-1} (conjugated nitriles). The characteristic frequency of a cyano-group attached to a β-carbon atom is also lower when the latter is a secondary carbon atom. In nitriles of the type $(CH_3)_3Si[CH_2]_nCH(CN)CH_2Si(CH_3)_3$ ($n = 1$ or 2), for example, it is 2240 cm^{-1}, whereas in $(CH_3)_3Si[CH_2]_nCN$ ($n = 2$ or 3) it is 2249 cm^{-1}.[47]

The stability of silicon polymers to thermal oxidation has been studied[80,122] (Table 8). The instability of the 1-cyanoethylsiloxane is consistent with the above results. The stability of the 2-cyanoethylsiloxane, however, is unexpected, since it is a substituted analogue of the unstable

TABLE 8. Comparison of resistance of silicone polymers to thermal oxidation in air at 250°.

Siloxane	% of initial content of carbon after 100 h
Diphenyl-	98.4
Methyl-	96.7
2-Cyanoethyl-	88.3
Dimethyl-	81.5
1-Cyanoethyl-	12.6*
1-Cyanoethyl-	1.0
3-Cyanopropyl-	94.4
2-Cyanopropyl-	75.6
Ethyl-	6.7

* After 25 h.

‡ This fact enables infra-red analysis to be used for the identification of isomeric silicon-containing α-and β-nitriles. Pike[80] also recommends analysis of mixtures of isomeric 1-and 2-cyanoethyltrichlorosilanes by infra-red spectroscopy, but his method is based on the different absorption bands of the CH and CH_2 groups in the region of the stretching vibrations.

ethylsiloxane. It is supposed that the stability of $[(NCCH_2CH_2)SiO_{3/2}]_n$ is due to the presence in the polymer molecules of intermolecular or intramolecular bonds involving the polar cyano-group.

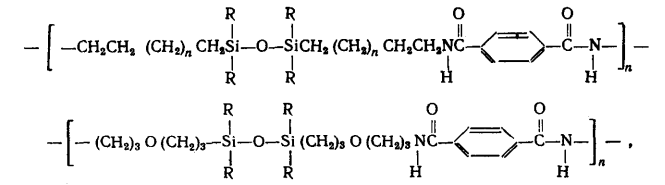
Individual cyanoalkyl compounds of silicon are soluble in the usual organic solvents, whereas the polymeric compounds are sparingly soluble in them but dissolve in dimethylformamide.

4. Practical Uses of Cyanoalkyl Compounds of Silicon

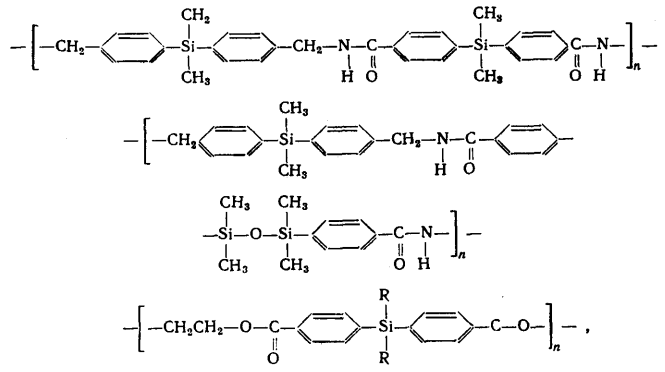
Several papers[122,128-131] show that American industry started the production of nitrile-containing siloxane rubber as early as 1958. Thanks to its valuable technical properties, this type of rubber is especially promising in the aircraft, petroleum, automobile, and radio and electrical industries[128,129]. The information in these publications deals mainly with the properties of the rubbers. The materials are dimethylpolysiloxane rubbers in which some of the methyl groups have been replaced by $[CH_2]_nCN$, the influence of the nitrile group on the properties of the rubber diminishing with increase in n.[128] Such rubbers resist the action of fuels, oils, and solvents, and are used over the temperature range from -73° to +260°.[122,128] The CN-containing groups in the rubber are apparently[122,129] 2-cyanoethyl and 3-cyanopropyl.

Table 9 and the diagram give data indicating the remarkable properties characteristic of these cyanoalkylated materials. Although the stability of nitrile-siloxane rubber to the action of petrol is about equal to that of a nitrile rubber, the advantages of the former are undisputed for work at high temperatures.

Diamines and dibasic acids obtained from $\alpha\omega$-dinitriles containing silicon have been used for the preparation of silicon-containing polyesters and polyamides, especially those having siloxane groups in the main polymer chain. For example, polymers of the following types have been obtained[43,44,115]:



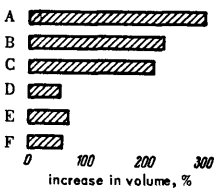
where n = 0, 1 and the R's are the same or different — CH_3 and C_2H_5.



where R = CH_3 and C_6H_5.

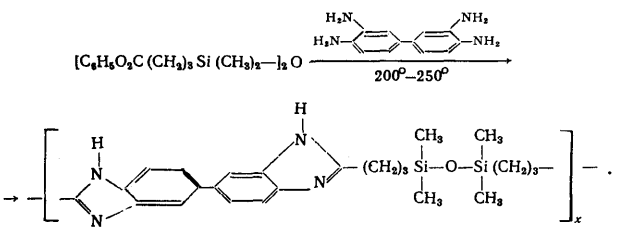
TABLE 9. Principal properties of nitrile–siloxane rubbers[129].

Property	NSR–x8701	NSR–x4803	NSR–x5602 a	NSR–x5602 b
Vulcanisation time, h	16	16	1	3
Temperature of vulcanisation, °C	232	204	149	204
Shore hardness	70±5	80±5	55±5	60±5
Tensile strength, kg cm^{-2}	45.5	59.5	77.0	70.0
Relative elongation, %	125	125	300	240
Tear strength, kg cm^{-1}	8.9	13.4	16.1	13.4
Residual shrinkage, %	55	45	—	50
Brittle point, °C	−68	−73	−73	−73
Specific gravity	1.25	1.4	—	1.121
After aging at 232° for 70 h				
Shore hardness	70±5	8025	—	65±5
Tensile strength, kg cm^{-2}	42	49	—	56.0
Relative elongation, %	100	100	—	190



Swelling of rubbers in aviation spirit:
A - natural rubber;
B - butadiene–styrene rubber;
C - general-purpose silicone rubber;
D - nitrile rubber;
E - chloroprene rubber;
F - nitrile–siloxane rubber.

Some polymers of this type will, perhaps, find future application as elastic and frostproof fibres and elastomers. Derivatives of silicon-containing dinitriles have been used to introduce the siloxane group into a benzoimidazole polymer chain[154]:



The siloxane group introduces several new properties into this new class of polymers, which are interesting because of their exceptional thermal stability; its primary effect is to increase the solubility of the polymer compared with that of benzoimidazole polymers not containing silicon[157].

The production of trialkoxy(and alkyldialkoxy)silylalkyl--ω-amines§ was mastered by industry a few years ago[132]. According to patent information[118,120] these amines possess a strong fungicidal action, and are also successfully used in the preparation of glass fabrics. For example, treatment of glass fibre with a water-soluble polymer from $NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$, with subsequent application to it of a melamine–formaldehyde resin, makes it possible to obtain materials of high mechanical strength and resistance to water[120]. Glass laminates based on glass fibres finished with a γ-aminoalkyltriethoxysilane possess enhanced short--period thermal stability[133].

ω-Aminoalkyl derivatives of silicon have been patented[134-138] as intermediates for several other important technical materials.

We shall not deal in the present review with work on compositions based on CN-containing polymers and silicon--containing substances. It must be borne in mind, however, that this provides a line of research of great practical promise. Thus, for example, the introduction of silicon dioxide into a polyacrylonitrile fibre[139], or of sodium silicate into a nitrile rubber[140], substantially improves the properties of these materials.

IV. CYANOALKOXY-DERIVATIVES OF ORGANOSILICON COMPOUNDS

1. Methods of Synthesis

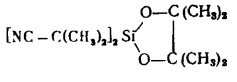
In a series of alkoxy-derivatives of silicon, →Si–[OAlk], the resistance of the Si—O bond to hydrolysis increases as Alk changes in the sequence primary, secondary, tertiary¶. In order to obtain hydrolytically stable cyanoalkoxy derivatives of silicon, therefore, investigators have usually employed secondary and tertiary alcohols, cyanohydrins of aldehydes and ketones.

Hahn[141] obtained cyanoalkoxy-derivatives of silicon by the reaction

$$NC—CRR'—OH + SiCl_4 \longrightarrow [NC—CRR'—O]_mSiCl_{4-m}, \qquad (I)$$

where R′ = CH_3, and R = C_2H_5, CH_3, cyclohexyl.

Successive treatment of silicon tetrachloride with pinacol and with acetone cyanohydrin enabled him to obtain the mixed ester



Frish and Wolf[142,143] synthesised derivatives of acetone cyanohydrin and methylchlorosilanes using pyridine and tertiary amines to combine with the hydrogen chloride evolved in the reaction. Later a thorough investigation was made of the interaction of acetone cyanohydrin with various alkyl-, aryl-, and alkenyl-chlorosilanes[144-146]. The size, structure, and number of the organic radicals attached to the silicon were found[145] to have a substantial influence on the rate of conversion of Si–Cl into $Si–O–C(CH_3)_2CN$: in the series

$$RHSiCl_2 > RSiCl_3,\ R'RSiCl_2 > R''SiCl_3,$$

where R and R′ = alkyl, while R″ = aryl, the reactivity of the Si–Cl bond decreases.

The compound $Si[O–C(CH_3)_2CN]_4$ is readily obtained by the interaction of equimolar amounts of $SiCl_4$ and acetone cyanohydrin[144]. It is interesting that for a long time the structurally analogous tetra-t-butoxysilane could not be obtained at all owing to steric hindrance; this problem was later solved only by replacing $(t\text{-}C_4H_9O)_3SiCl$ and $t\text{-}C_4H_9OH$ by the more reactive $(t\text{-}C_4H_9O)_3SiBr$ and $t\text{-}C_4H_9ONa$.[147]

Acetone cyanohydrin also proved to be considerably more reactive than $t\text{-}C_4H_9OH$ towards the Si–H bond. Whereas with R = CH_3 reaction (II) requires prolonged heating in an autoclave with catalysts (alkalis),[148] with R = CN it took place even under mild conditions of esterification of the Si–Cl bond, without catalysts[146]:

$$\equiv SiH + HOC(CH_3)_2R \longrightarrow \equiv SiOC(CH_3)_2R + H_2, \qquad (II)$$

where R = CH_3, CN.

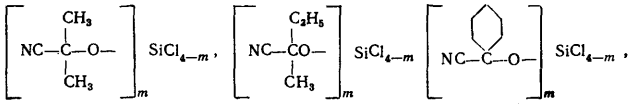
Products formed by the interaction of silicon tetrachloride cyanohydrins of aldehydes and ketones have also been described in patents[149,150].

The CN-containing ester $(t\text{-}C_4H_9O)_2Si(OCH_2CH_2CN)_2$ has been obtained from di-t-butoxydichlorosilane and 3-hydroxypropionitrile, whereas it could not be obtained from di-t--butoxysilanediol and acrylonitrile[64].

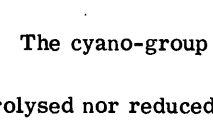
2. Properties

Individual cyanoalkoxy-derivatives of silicon are readily soluble in inert organic solvents; polymeric silicon compounds containing cyanoalkoxy-groups are considerably less soluble or do not dissolve at all in them.

Hahn[141] prepared the three series of derivatives



(A) (B) (C) †

and noted their ready hydrolysability even in moist air. The hydrolytic stability increases in the sequence (A) < < (B) < (C). The cyano-group in  could be neither hydrolysed nor reduced[141].

Cyanoalkoxy-compounds in which some of the silicon valencies are occupied by alkyl or aryl groups possess considerably hydrolytic stability[142,145]. Compounds containing no Si–Cl bonds are particularly stable, for example $C_6H_5Si[O–C(CH_3)_2CN]_3$, $C_6H_5Si[O–C(CH_3)_2CN)]_2CH_3$, $(CH_3)_3SiOC(CH_3)_2CN$, etc.; they are stable on prolonged contact with water, and are only partly hydrolysed by 5%

§ As indicated p.401 a good method for obtaining them is to hydrogenate ω-cyanoalkyl compounds of silicon.

¶ With increase in the degree of branching of the alkoxy-groups, however, it becomes difficult to attach them to the silicon atom because of steric factors.

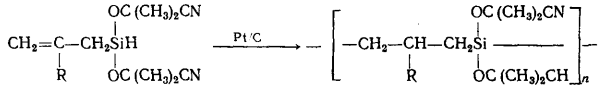
† Compound (C) is derived from cyclohexanone cyanohydrin (Ed. of Translation).

aqueous HCl or NaOH. It proved possible under mild conditions of hydrolysis to obtain the siloxanes $NCC(CH_3)_2.OSiR_2OSiR_2OC(CH_3)_2CN$ and the diol $CH_3Si(OH)_2OC(CH_3)_2CN$ from $R_2ClSiOC(CH_3)_2CN$ and $CH_3SiCl_2OC(CH_3)_2CN$ respectively[142,145].

Hydrolysis of $C_2H_5SiCl_2OC(CH_3)_2CN$ in the presence of pyridine in benzene at 0° yields a polysiloxane of low molecular weight, $\{C_2H_5SiO[O-C(CH_3)_2CN]\}_n$.[142]

Cohydrolysis of the dichlorides $RSiCl_2OC(CH_3)_2CN$ with dimethyldichlorosilane was accompanied by partial elimination of the cyanoalkyl groups[151].

Polyakova *et al.*[55,152] studied the polymerisation of alkenyl- and dialkenyl-siloxydimethylacetonitriles with peroxide catalysts[31,55]. The following reaction was also studied[55,152]:



where R = CH_3, H.

In both cases solid or oily polymeric substances are obtained, sparingly soluble in the usual organic solvents, but soluble in dimethylformamide.

With alcohols and Grignard reagents and alkylchlorosiloxydimethylacetonitriles, reaction takes place at both Si–Cl and $SiOC(CH_3)_2CN$ groups[145,146].

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ORGANIC CHARGE-TRANSFER COMPLEXES

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CONTENTS

Introduction 408
I. Nature of charge-transfer complexes 408
II. Donors 409
III. Acceptors 410
IV. Methods of investigating charge-transfer complexes and some of their properties 411
1. Optical studies on charge-transfer complexes 411
2. Investigations of the magnetic properties of charge-transfer complexes 411
3. Investigations of the electrical conductivity of charge-transfer complexes 412
V. Charge-transfer complexes and the mechanism of chemical reactions 414

INTRODUCTION

Organic molecular complexes have been known for a long time, but their systematic study which has resulted in the appearance of special monographs[1,2], is comparatively recent. During the past few years research on molecular complexes has been carried out particularly intensively not only by chemists but also by physicists and biophysicists. These complexes are formed as a result of donor–acceptor interaction between molecules, the so-called charge-transfer complexes, on which many papers have been published during the past decade, including some reviews[3-6]. The search for organic semiconductors has aroused especial interest in charge-transfer complexes. The present paper deals mainly with work on the electrical conductivity of such complexes, and on the probably related magnetic properties.

I. NATURE OF CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes are those formed by molecules or ions, or both, without a covalent bond participating in complex formation. A feature of such complexes is the transfer of an electron from one component (the donor) to the other (the acceptor). The extent of electron transfer can in principle vary from zero to complete transfer, the latter case involving the conversion of neutral molecules to radical-ions The ground state of charge-transfer complexes containing one donor molecule combined with one acceptor molecule is approximately represented by the wave function[7-13]

$$\psi_n(D,A) = a\psi_0\ (DA) + b\psi_1\ (D^+A^-)\ldots, \qquad (1)$$

where D is the donor and A the acceptor; ψ_0 is the wave function for the non-ionic state of D and A, in which they may be linked either by a hydrogen bond, by dipole–dipole interaction forces, or by any others forming part of the classical "van der Waals forces"; ψ_1 is the wave function of the combined state, corresponding to complete transfer of one electron from D to A, and a and b are coefficients. The excited state is represented by the equation

$$\psi_e(D,A) = a^*\psi_1\ (D^+A^-) - b^*\psi_0(DA). \qquad (2)$$

With complexes having a weakly ionic bond, $a \gg b$, $|a| \simeq 1$, and $|b| \simeq 0$, so that

$$\psi_n \simeq \psi_0(DA), \text{ and } \psi_e \simeq \psi_1(D^+A^-),$$

i.e. the excited state is almost completely a diradical-ion. In complexes having a stable ionic bond between the D and A species, $b > a$. Table 1 indicates the relation between the coefficients a and b for several complexes, expressed in terms of the quantity $100b^2/(a^2 + b^2)$. It follows from these data that a is nearly always greater than b.