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Preparation and Properties of Carbodi-imides and Cyanamides Containing Silicon, Germanium, Tin, and Lead

A.S.Gordetsov, V.P.Kozyukov, I.A.Vostokov, S.V.Sheludyakova, Yu.I.Dergunov, and V.F.Mironov

Information on methods of preparation and properties of carbodi-imides and cyanamides containing Group IVB elements is summarised and systematised. Reaction schemes are discussed, and several aspects of their practical application are examined. A list of 221 references is included.

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I. INTRODUCTION

Carbodi-imides and cyanamides are genetically interrelated and are functionally closely similar, but for compounds containing Group IVB elements isomeric transitions are observed between the two groups of compounds. In many cases methods of preparation and reactivities are the same. This is why hetero-organic cyanamides and carbodi-imides are considered together in this Review.

Progress in the chemistry and application of organic carbodi-imides has been repeatedly and exhaustively discussed in reviews[1-3], but information on hetero-organic carbodi-imides and cyanamides has not been fully systematised. There exist only a survey of organosilicon carbodi-imides and cyanamides[4] and a review[5] which considers organotin carbodi-imides together with other compounds containing tin–nitrogen bonds. A considerable number of papers have appeared recently which, together with earlier information, are worthy of special discussion.

The present Review aims to systematise published information on the preparation, reactivity, physicochemical properties, and applications of carbodi-imides and cyanamides containing silicon, germanium, tin, and lead. Monographs, periodical literature, and patents appearing up to 1980 are covered.

II. METHODS OF PREPARATION

1. Interaction of Cyanamide and its Derivative with Hetero-organic Compounds

The first example of a hetero-organic carbodi-imide, disilylcarbodi-imide, was obtained[6] in 25% yield by passing gaseous iodo- or bromo-silane over silver cyanamide, in conformity with the general equation

$$Ag_2N{-}C{\equiv}N + R_3MX \rightarrow AgX + R_3M{-}N{=}C{=}N{-}MR_3 \qquad (1)$$

in which M = Si, R = H, and X = Br, I. It was originally supposed that the product was the cyanamide $N{:}C.N(SiH_3)_2$. However, infrared and Raman spectral data[7-9] and also investigation of a deuterated derivative[8] showed that it had the carbodi-imide structure $H_3SiN:C:NSiH_3$. The yield of bistrimethylsilylcarbodi-imide obtained by this reaction (M = Si, R = CH_3, X = Cl) is not appreciably influenced by use of a solvent[10-12]. More severe conditions are required in the absence of a solvent (170 °C for 5 h, yields 90%) [10,11] than in ether (20 °C for 10 h, yield 80%) [12] or in benzene (yield 90%).[13]

The potential danger of explosion with dry silver cyanamide creates great difficulties in carrying out preparations[6,11,14,15]. Individual organosilicon carbodi-imides have therefore been obtained from the corresponding chlorosilanes in boiling benzene or in acetonitrile [Eqn.(1): M = Si, R_3 = $(C_2H_5)_3$, $(C_3H_7)_3$, $(C_6H_{13})_3$, $CH_3(C_6H_5)_2$, $(CH_3)_2C_6H_5$, $(C_6H_5)_3$, $(C_6H_5)_2CH_2:CH$, $(C_2H_5O)_3$; X = Hal]. The reaction in acetonitrile is accelerated by adding small quantities of water[15], but the catalytic effect decays rapidly.

Use of a mixture of two different trialkyl- or triaryl-chlorosilanes yields three different carbodi-imides[15]:

$$Me_3SiCl + Ph_3SiCl + Ag_2NCN \xrightarrow{-AgCl} Me_3SiN{=}C{=}NSiMe_3 + Me_3SiN{=}C{=}NSiPh_3 + Ph_3SiN{=}C{=}NSiPh_3$$

However, the unsymmetrical carbodi-imide cannot be isolated, because it disproportionates when distilled[15]:

$$Me_3SiN{=}C{=}NSiPh_3 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Ph_3SiN{=}C{=}NSiPh_3$$

Silver cyanamide is used to obtain several symmetrical organosilicon and organogermanium carbodi-imides of general formula $C[:NM(CH_3)_nH_{3-n}]_2$ (M = Si, Ge; n = 0–3). The corresponding chloro- or iodo-silanes and bromo- or iodo-germanes have been used as the second reactant[16]. Reaction (1) is suitable also for the preparation of symmetrical organotin carbodi-imides[17-19].

Application of an analogous reaction to silver cyanamide has enabled polymeric carbodi-imides containing silicon to be synthesised from dialkyl- and diaryl-dichlorosilanes[20]. A tetramer of dibutylbiscarbodi-imidostannane has been obtained similarly from di-n-butyltin dichloride[21]:

$$n Ag_2NC{\equiv}N + nRR'MCl_2 \rightarrow -(-MRR'-N{=}C{=}N-)_n- + 2nAgCl$$

M = Si; RR' = Me_2, Ph_2, MePh, MeVin, $(EtO)_2$;
M = Sn; RR' = Bu_2; n = 4.

In view of the high cost and explosiveness of silver cyanamide it is advisable to replace it by sodium, calcium, zinc, or lead cyanamide[15,16,22-24]. Thus bistrimethylsilylcarbodi-imide can be obtained[22] in 76% and 46% yields by passing trimethylchlorosilane through technical disodium and calcium cyanamides respectively in a lithium–potassium chloride melt:

$$Na_2NC{\equiv}N + R_3MX \rightarrow R_3MN{=}C{=}NMR_3 + NaCl \qquad (2a)$$

$$M'NC{\equiv}N + R_3MX \rightarrow R_3MN{=}C{=}NMR_3 + M'X_2 \qquad (2b)$$

where M = Si, M′ = Ca, R = CH_3, X = Cl. It has recently been shown that carbodi-imides can be obtained in high yields (80–90%) without the use of molten salts by a modified technique[6] involving passing gaseous iodides over anhydrous lead cyanamide at 25 °C [Eqn.(2b): M = Si, Ge; M′ = Pb; $R_3 = (CH_3)_nH_{3-n}$; $n = 0-3$; X = I].[16–24] Bistrimethylsilyl- and bistrimethylgermyl-carbodi-imides have been prepared by the action of trimethylchlorosilane and trimethylbromogermane respectively on lead cyanamide at 100 °C for 5 h [Eqn.(2b): M = Si, Ge; M′ = Pb; R = CH_3; X = Cl, Br].[16] The action of triphenyltin iodide on disodium cyanamide [in benzene at 80 °C for 23 h; Eqn.(2a): M = Sn, R = C_6H_5, X = I] [25] and on monosodium cyanamide[26] and that of triethyltin chloride on the latter (in ether at 0–25 °C) [27] give high yields of the corresponding organotin carbodi-imides:

$$Et_3SnCl + NaNHC{\equiv}N \xrightarrow{-NaCl} Et_3SnNHCN \rightarrow Et_3SnN{=}C{=}NSnEt_3 + H_2NCN$$

The above reactions can be successfully used to synthesise various symmetrical and unsymmetrical hetero-organic carbodi-imides and the isomeric cyanamides. Interaction of organic halides of silicon, germanium, tin, and lead with appropriate cyanamide derivatives of silver, potassium, calcium, barium, or strontium has yielded in particular $R_3SiN:C:NC_6H_5$ (R = CH_3, C_6H_5),[28] $(C_6H_5)_2Si(N:C:NC_6H_5)_2$,[28] $(C_6H_5)_3SnNCNC{\vdots}N$,[29] $R_3SnN(C_6H_5)C{\vdots}N$ (R = CH_3, C_6H_5),[30] $(C_2H_5)_3SnOC(CH_3)NCN$,[31] $R_2Sn(OCR'NCN)_2$ (R = CH_3, C_2H_5, C_4H_9, C_6H_5, $C_6H_5CH_2$; R′ = CH_3, C_6H_5),[31] $[(C_4H_9)_3SnS]_2C:N.C{\vdots}N$,[32] $(C_4H_9)_2Sn\langle S \rangle C:N.C{\vdots}N$,[32–34] $R_3MN(CN)_2$ (M = Ge, Sn, Pb; R = CH_3, C_6H_5),[35–37] and $R_2Sn[N(CH)_2]_2$ (R = CH_3, C_6H_5).[36,37].

N-Phenyl-*N*′-trimethyl[phenyl]silylcarbodi-imides can also be synthesised in 55–79% yields from phenylcyanamide[28,38–41]. The same method has since been used to obtain several other unsymmetrical organosilicon carbodi-imides[4,38–41]:

$$R_3MX + R'NHC{\equiv}N + Et_3N \rightarrow R'N{=}C{=}NSiR_3 + Et_3N{\cdot}HX$$
M = Si; R = Me, Ph; R′ = Me, Et, t-Bu, Ph, Ph_3C, EtOCO; X = Cl.
M = Sn, R = Ph, R′ = Ph_3C, X = I .

The compounds $RN:C:NSi(CH_3)_3$ are found to exist in tautomeric equilibrium with the corresponding cyanamides $RN(C{\vdots}N)Si(CH_3)_3$.[4,40,41]

Cyanamide itself also proved useful for the synthesis of carbodi-imides[12]. Thus with trimethylchlorosilane in the presence of triethylamine in ethereal solution (at ~20 °C for 1 h) a high yield of bistrimethylsilylcarbodi-imide is formed:

$$H_2NC{\equiv}N + 2R_3MX + 2Et_3N \rightarrow 2Et_3N{\cdot}HX + R_3MN{=}C{=}NMR_3$$
M = Si, R = Me, X = Cl . (3)

The first organogermanium carbodi-imide, bistributylgermylcarbodi-imide, was obtained by heating an ethereal solution of cyanamide, sodium ethoxide, and tributylgermanium chloride (yield 24%).[43] When triphenylgermanium bromide is heated with cyanamide in the presence of triethylamine in isopropyl ether, a 66% yield of bistriphenylgermylcarbodi-imide is obtained [Eqn.(3): M = Ge, R = C_6H_5, X = Br].[44]

Organotin carbodi-imides have been obtained similarly. Thus heating ethereal solutions of triethyltin chloride or triphenyltin iodide with cyanamide and triethylamine gave high fields of bistriethyl[phenyl]stannylcarbodi-imides respectively[17,25] [Eqn.(3): M = Sn, R = C_2H_5, C_6H_5; X = Cl, I].

Silylation of cyanamide with a mixture of trimethylchlorosilane and lithium in oxolan also yields bistrimethylsilylcarbodi-imide. When the duration of the reaction is increased, however, tristrimethylsilylamine and trimethylsilyl cyanide are formed[42]:

$$H_2NC{\equiv}N + 2Me_3SiCl + 2Li \xrightarrow[0-10^\circ]{\text{oxolan}} Me_3SiN{=}C{=}NSiMe_3 + 2LiCl + H_2$$
$$Me_3SiN{=}C{=}NSiMe_3 + 2Me_3SiCl + 2Li \xrightarrow{\text{oxolan}} (Me_3Si)_3N + Me_3SiCN + 2LiCl .$$

The next step in simplifying the preparation of heteroorganic carbodi-imides was to use organoelementary oxides and hydroxides as metallating agents, which made it unnecessary to introduce acceptors for hydrogen chloride and ultimately diminished the number of chemical operations. Furthermore, the yields of the final products remained high, and in isolated cases approached theoretical. Thus reaction of cyanamide with bistriethylgermyl[45], bistriethylstannyl[27,46], bistributylstannyl[47], bistriphenylstannyl[25,48], and bistris(trimethylsilylmethyl)stannyl[49] oxides gives the corresponding carbodi-imides in 80–95% yields:

$$R_3MOMR_3 + H_2NCN \rightarrow R_3MN{=}C{=}NMR_3 + H_2O$$
M = Ge, R = Et; M = Sn, R = Et, Bu, Ph, CH_2SiMe_3 .

Cyanamide reacts similarly with tin- and lead-containing hydroxides[27,46,49]:

$$R_3MOH + H_2NCN \rightarrow R_3MN{=}C{=}NMR_3 + H_2O$$
M = Sn, R = Et, Ph; M = Pb, R = Ph .

Despite the simplicity of the scheme, the reaction mechanism is quite complicated. It is assumed (in the case of organotin compounds[27]) that an organometallic cyanamide is formed initially, whose disproportionation yields the corresponding carbodi-imide and cyanamide:

$$R_3SnOSnR_3 + H_2NCN \rightarrow R_3SnNHC{\equiv}N + H_2O \quad (4a)$$

$$R_3SnNHCN \rightarrow R_3SnN{=}C{=}NSnR_3 + H_2NCN \quad (4b)$$

$$H_2NCN \rightarrow HN{=}C(NH_2)NHCN . \quad (4c)$$

It was shown later that trimethyltin, tributyltin[50], and triphenyltin[25] cyanamides could be obtained in conformity with Eqns.(4a: R = C_4H_9, C_6H_5) and

$$R_3MOH + H_2NCN \rightarrow R_3MNHC{\equiv}N + H_2O \quad (5)$$

(M = Sn, R = CH_3), and then underwent disproportionation.

Another possible mechanism in that the metallating agent may interact with the active (acidic) hydrogen atom present in the trialkyltin cyanamide $R_3SnNHCN$ formed initially, and the resulting bistrialkylstannylcyanamide may then isomerise to the corresponding carbodi-imide. Metallation may also occur with migration of the reaction centre, when the bistrialkylstannylcarbodi-imide is formed directly.

Reaction (5) has been used also for the preparation of trimethyl-lead cyanamide with alcohol as solvent[51].

Attempts to obtain silicon-containing cyanamides of type $R_3SiNHCN$ have proved unsuccessful. Thus, instead of the expected mono- and bis-trimethylsilylcyanamides, bistrimethylsilylcarbodi-imide was isolated independently of the reaction conditions[12]. It has now been shown that existence is possible only for substituted organosilicon cyanamides of type $(CH_3)_3SiN(CN)COOC_2H_5$ [52] and $RR^1R^2SiCH_2NR^3C{\vdots}N$ (R = CH_3, Cl; R^1, R^2, R^3 = Alk, Ar, AlkO).[53] Cyanamides $(CH_3)_3SiNRC{\vdots}N$ have also been synthesised, in tautomeric equilibrium with the corresponding carbodi-imides $(CH_3)_3$.SiNCNR (R = Alk, Ar).[4,40,41,54,67,68].

Cyanamide reacts with methoxytributyltin to give an 89% yield of bistributylstannylcarbodi-imide[55], the reaction being regarded as reversible:

$$H_2NCN + Bu_3SnOMe \rightleftarrows MeOH + Bu_3SnN{=}C{=}NSnBu_3 .$$

When methoxytributyltin is replaced by tributyltin isocyanate, reaction occurs only in the presence of triethylamine (at 80 °C for 48 h), and up to 68% yields of the carbodi-imide are

obtained[56]:

$$Bu_3SnN{=}C{=}O + H_2NC{\equiv}N \xrightarrow{Et_3N} Bu_3SnN{=}C{=}NSnBu_3 + HNCO .$$

A method has been proposed[57] for preparing disilylcarbodi-imide from cyanamide:

$$H_2NCN + H_3SiPH_2 \rightarrow H_3SiN{=}C{=}NSiH_3 + PH_3$$
$$H_2NCN + (H_3Si)_2S \rightarrow H_3SiN{=}C{=}NSiH_3 + H_2S .$$

Cyanamide is silylated also by hexamethyldisilazane, when the yield of bistrimethylsilylcarbodi-imide is 95%:[58,59]:

$$H_2NCN + (M_3Si)_2NH \rightarrow Me_3SiN{=}C{=}NSiMe_3 + NH_3 .$$

This method—the reaction of cyanamide and its derivatives with hetero-organic compounds—nevertheless has several important disadvantages: cyanamide is difficultly accessible, toxic, and unstable, its silver salts are explosive, large quantities of solvents are used, and in several cases the yields are comparatively low. They are almost all eliminated by replacing cyanamide by its dimer, dicyanodiamide[58-62]. The procedure is to heat the latter to 110–200 °C with a hetero-organic compound containing a bond between the heteroatom and nitrogen or oxygen, and gives very high yields of carbodi-imides containing silicon, germanium, or tin:

$$HN{=}C(NH_2)NHCN \rightarrow \begin{cases} \xrightarrow{(Me_3Si)_2NH} Me_3SiN{=}C{=}NSiMe_3 + NH_3 \\ \xrightarrow{Et_3GeNEt_2} Et_3GeN{=}C{=}NGeEt_3 + Et_2NH \\ \xrightarrow{(Bu_3Sn)_2O} Bu_3SnN{=}C{=}NSnBu_3 + H_2O \end{cases} .$$

Silylating agents used in the preparation of bistrimethylsilylcarbodi-imide have been hexamethyldisilazane, silylamines of the type $Z[NHSi(CH_3)_3]_2$ ($Z = CH_2C_6H_4CH_2$, $CH_3C_6H_3$), *N*-cyclohexyltrimethylsilylamine, tristrimethylsilylmelamine, and tristrimethylsilyl cyanurate[58-62]. Polysilylcarbodi-imides have been synthesised from dicyanodiamide and polysilazanes[62], and *N*-tributylplumbylcarbodi-imide has been obtained by the use of tributyl-lead hydroxide as metallating agent[51].

In conclusion we may state that reactions of the above type have the greatest preparative value at present because of their universality.

2. Preparation from Compounds containing Heteroatom–Nitrogen Bonds

The reactions involved comprise mainly those of cyanogen halides with silicon-containing amino-derivatives. In the preparation of organosilicon carbodi-imides cyanogen halides react with primary and secondary silylamines under milder conditions[4,63-68] than with the tertiary amines (at 50–100 and 200 °C):

$$Et_3SiNH_2 + ICN \rightarrow Et_3SiN{=}C{=}NSiEt_3 + NH_4I$$
$$(Me_3Si)_2NH + XCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Me_3SiX + NH_4X \quad (X = Cl, Br)$$
$$(Me_3Si)_3N + ClCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Me_3SiCl .$$

With organosilicon amines of types $RNHSi(CH_3)_3$ [R = CH_3, C_2H_5, iso-C_3H_7, $(CH_3)_3C$, C_6H_5] [40,60] and $RN[Si(CH_3)_3]_2$ (R = CH_3, C_4H_9, $CH_2{:}CHCH_2$) [4,40,66-68] cyanogen chloride forms unsymmetrical carbodi-imides in tautomeric equilibrium with the corresponding cyanamides:

$$RN(SiMe_3)_2 + ClCN \xrightarrow[-Me_3SiCl]{20-35^\circ} RN{=}C{=}NSiMe_3 \rightleftarrows \rightarrow Me_3Si(R)N{-}C{\equiv}N . \quad (6)$$

The action of cyanogen chloride on silicon-containing amides of carboxylic acids gives high yields of *N*-acyl-*N'*-trimethylsilylcarbodi-imides[4,66-68]:

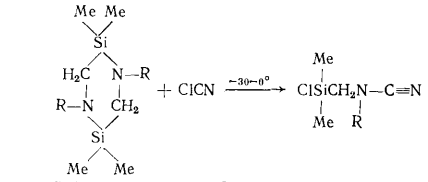
$$RC(O)N(SiMe_3)_2 + ClCN \xrightarrow{20-50^\circ} RC(O){=}N{-}C{=}NSiMe_3 + Me_3SiCl$$
(R = Me, Ph) .

These products have been obtained also by cross synthesis—reaction between acyl chlorides and bistrimethylsilylcarbodi-imide—and are shown by infrared, nuclear magnetic resonance, and mass spectral data to exist in the three tautomeric forms[4,66-68]

$$PhC(O){=}C{=}NSiMe_3 \rightleftarrows PhC(O){-}C{\equiv}N \rightleftarrows PhC(OSiMe_3){=}N{-}C{\equiv}N \quad (7)$$
(a) (b) (c)

Cyanamides containing silicon and an organic function were first obtained by the reaction of cyanogen chloride with linear and cyclic *CN*-disilylalkylamines[53,66]:

$$MeSi(R)(R')CH_2NSiMe_3 + ClCN \xrightarrow{20-60^\circ} MeSi(R)(R')CH_2N{-}C{\equiv}N + Me_3SiCl$$



(R, R' = Me, MeO, EtO; R'' = iso-Pr and iso-Bu, Ph) .

An organosilicon cyanamide is formed also by the action of cyanogen chloride on *NN*-dimethyl-*N'*-trimethylsilylhydrazine[69]:

$$Me_2N{-}NHSiMe_3 + ClCN \xrightarrow[-Me_3SiCl]{} Me_2N{-}N(SiMe_3){-}C{\equiv}N .$$

Silylamines of types $(CH_3)_2NSiH_3$, $CH_3N(SiH_3)_2$, and $(H_3Si)_3N$ apparently[70] do not form silylcarbodi-imides on treatment with cyanogen chloride.

Unsymmetrical carbodi-imides containing silicon, germanium, or tin can be obtained also from organometallic amines. Investigation of the reaction of benzoyl-t-butylcarbodi-imide with amines of types $(CH_3)_3M.N(CH_3)_2$ (M = Si, Ge, Sn) and $[(CH_3)_3M]_2NCH_3$ (M = Si, Sn) established[71,72] that the equimolecular insertion products when heated to 150 °C decomposed with the formation of unsymmetrical organo-silicon and -germanium carbodi-imides (yields 68–82%):

$$PhC(O)N{=}C{=}NCMe_3 + Me_3MN(R){-}Me \rightarrow$$
$$\rightarrow PhC(O)N(R){-}C(MMe_3){-}N(R){-}Me \xrightarrow{150^\circ} Me_3MN{=}C{=}NCMe_3 + PhC(O)N(R){-}Me$$
(M = Si, R = Me, Me_3Si; M = Ge, R = Me) .

High yields of unsymmetrical organotin carbodi-imides have been obtained[73] by the action of isothiocyanates on tristrimethylstannylamine:

$$(Me_3Sn)_3N + RN{=}C{=}S \rightarrow R{-}N{=}C{=}NSnMe_3 + (Me_3Sn)_2S$$
(R = t-Bu, C_6H_{11}, Ph) .

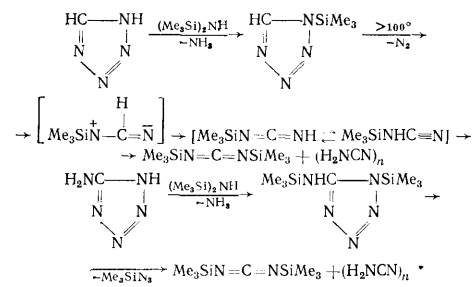
Bistrimethylsilylcarbodi-imide can be obtained in 80% yield by reaction between heptamethyldisilazane and *N*-sulphinylcyanamide[74-76], in ether at −70 °C since the latter reactant

decomposes explosively:

$$N{\equiv}C{-}N{=}S{=}O + (Me_3M)_2NMe \rightarrow$$
$$\rightarrow Me_3MN{=}C{=}NMMe_3 + MeN{=}S{=}O$$
$$M = Si, Sn .$$

Bistrimethylstannylcarbodi-imide has been obtained similarly[76].

Bistrimethylsilylcarbodi-imide can be isolated as either the main product or a by-product when certain compounds are heated with hexamethyldisilazane. Thus a high yield is obtained from tetrazoles[76-82]:



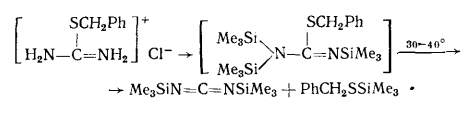
Heating hexamethyldisilazane with the polyurethane $[CONHRCH_2RNHCO_2CH_2CH_2O]_n$ ($R = p\text{-}C_6H_4$) at 197 °C for 21 h yields a mixture of bistrimethylsilylcarbodi-imide, trimethylsilyl isocyanate, hexamethyldisiloxane, and other products[83-85]. Bistrimethylsilylcarbodi-imide is formed as a by-product in the thermolysis of a mixture of the isocyanate and hexamethylenediamine[86,87]. It is obtained in good yield (85–90%) by heating isothiocyanatobistrimethylsilylamine[88]:

$$(Me_3Si)_2N{-}N{=}C{=}S \xrightarrow{110^\circ} Me_3SiN{=}C{=}NSiMe_3 + S_8 .$$

3. Reactions with Urea and Thiourea

Substituted ureas, thioureas, and isothioureas are the traditional and principal starting materials for the preparation of carbodi-imides[1,3]. However, the usual methods of dehydration of hetero-organic ureas and elimination of hydrogen sulphide from hetero-organic thioureas are unacceptable owing to the great reactivity of the resulting hetero-organic carbodi-imides[1]. Furthermore, urea and thiourea cannot be completely silylated with trimethylchlorosilane or hexamethyldisilazane[89]. An attempt to silylate urea and biuret with triethylsilane[90] was also unsuccessful, owing to the low yields and the difficulty of separating the products (triethylsilyl isocyanate, bistriethylsilylcarbodi-imide, and bistriethylsilyl ether). Therefore this route to the synthesis of hetero-organic carbodi-imides has not been developed. An exception is the direct silylation of isothiourea derivatives with a mixture of trimethylchlorosilane and triethylamine, which gives a 76% yield of bistrimethylsilylcarbodi-imide[91].

Isothiouronium salts can also be used as starting materials for the preparation of silylated carbodi-imide[91]:



There have been reports of the direct conversion of thiourea and its organic derivatives into organotin carbodi-imides[25,48], excess of the initial triphenyltin oxide being used as dehydrosulphurising agent:

$$Ph_3SnOSnPh_3 + H_2NCNH_2 \rightarrow Ph_3SnN{=}C{=}NSnPh_3 +$$
$$+ Ph_3SnSSnPh_3 + H_2O$$
$$Ph_3SnOSnPh_3 + Ph_3CNHCNH_2 \rightarrow$$
$$\rightarrow Ph_3SnN{=}C{=}NCPh_3 + Ph_3SnSSnPh_3 + H_2O .$$

This process is assumed to involve intermediate formation of triphenylstannylcyanamide, which disproportionates into the organotin carbodi-imide and dicyanodiamide (Eqns.4b, 4c).[25] Replacement of triphenylmethylated thiourea by its phenyl analogue yields an organotin cyanamide instead of the expected carbodi-imide[30]:

$$Ph_3SnOSnPh_3 + PhNHCNH_2 \rightarrow Ph_3SnNC{\equiv}N + Ph_3SnSSnPh_3 + H_2O .$$

This result was attributed[30] to differences in the steric characteristics of the phenyl and triphenylmethyl groups.

Examples of the synthesis of silylcarbodi-imides from organosilicon ureas are very few[10,11,92]. Thus reaction of bistrimethylsilylurea with phenyl-lithium followed (after boiling) by trimethylchlorosilane gives an 80% yield of bistrimethylsilylcarbodi-imide[11]:

$$(Me_3SiNH)_2CO \xrightarrow[2)Me_3SiCl]{1)PhLi} Me_3SiN{=}C{=}NSiMe_3 .$$

Replacement of phenyl-lithium by sodamide lowered the yield to 12%.[11]

Use of the silver salt of imidazole to desulphurise bistrimethylsilylthiourea gave a 50% yield of bistrimethylsilylcarbodi-imide[12]:

$$Me_3SiNHC(S)NHSiMe_3 + AgC_3H_3N_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Ag_2S + C_3H_4N_2 .$$

An organosilicon carbodi-imide containing an organic function has also been obtained from a thiourea derivative[91]:

$$Me_3SiOCH_2CH_2NHC(S)NHCH_2CH_2OSiMe_3 \xrightarrow{MeI} \rightarrow$$
$$\rightarrow [Me_3SiOCH_2CH_2NHC(SMe){=}NHCH_2CH_2OSiMe_3]^+ I^- \rightarrow$$
$$\xrightarrow[Et_3N]{Me_3SiCl} [Me_3SiOCH_2CH_2N(SiMe_3)C(SMe){=}NCH_2CH_2OSiMe_3] \rightarrow$$
$$\xrightarrow{80^\circ} Me_3SiSMe + Me_3SiOCH_2CH_2N{=}C{=}NCH_2CH_2OSiMe_3 .$$

4. Reactions with Metallated Silylamines

This differs from the preceding methods in being applied exclusively to the preparation of organosilicon carbodi-imides. Reaction of the sodium and lithium derivatives of bistrimethylsilylamine $[(CH_3)_3Si]_2NM$ with carbonyl chloride[10,11,92], carbon dioxide[10,11,93-95], carbon disulphide[93,95], silicon-containing isocyanates and isothiocyanates[10,11,96-98], cyanogen halides[12,65,99], dithiocyanogen[100], trifluoroiodomethane[93], cyanuryl chloride[13], and isocyanide dichlorides [e.g. $C_6H_5.NCCl_2$][101,102] yields organosilicon carbodi-imides. Thus on phosgenisation of the sodium derivative in boiling benzene bistrimethylsilylcarbodi-imide was isolated in 60% yield[10,11,92]. It is of interest to note for comparison that the corresponding reaction with non-metallated silazane results in isolation of another heterocumulene–trimethylsilyl isocyanate[11]:

$$(Me_3Si)_2NH + COCl_2 \rightarrow Me_3SiN{=}C{=}O + Me_3SiCl + HCl .$$

The reaction of sodium bistrimethylsilylamine with carbon dioxide has a complicated course. The gas is rapidly absorbed by a benzene solution of the sodium derivative

even at room temperature to form bistrimethylsilylcarbodi-imide[93]. By analogy with the reactions of other hetero-organic compounds it would be expected that the alkali-metal silicon-containing carbamate or its decomposition products would be formed:

$$(Me_3Si)_2NNa + CO_2 \rightarrow (Me_3Si)_2NCOONa\ .$$

Nuclear magnetic resonance spectroscopy showed that actually the reaction involved a series of consecutive processes with initial formation of a salt of carbamic acid, which broke down into sodium trimethylsiloxide and trimethylsilyl isocyanate. When carbon dioxide was passed through molten sodium bistrimethylsilylamine at 200 °C the isocyanate could be isolated before it underwent further reactions[94]. The complete series of reactions can be represented by the overall equation[93]

$$(Me_3Si)_2NNa + CO_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + \\ + (Me_3Si)_2O + NaOCN + Na_2NCN + Na_2CO_3\ .$$

Carbon disulphide reacts similarly with sodium trimethylsilylamine[93]:

$$CS_2 + (Me_3Si)_2NNa \rightarrow NaSCN + Na_2S + (Me_3Si)_2S + \\ + Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_3N\ .$$

Reaction of sodium bistrimethylsilylamine with silicon tetra-isocyanate and with trimethylsilyl isocyanate and isothiocyanate results in all cases in the formation of bistrimethylsilylcarbodi-imide, but there is a difference in behaviour between isocyanato- and isothiocyanato-silanes: whereas the isothiocyanato-group in organosilicon isothiocyanates can act in these reactions as either a pseudohalogen or a thiocarbonyl group, isocyanates behave as typical carbonyl compounds without displaying any of the pseudohalogen properties so characteristic of most of their reactions. In particular, trimethylsilyl isocyanate undergoes solely the second possible type of reaction[98]:

$$Me_3SiNCO + (Me_3Si)_2NNa \rightarrow NaOCN + (Me_3Si)_3N$$
$$Me_3SiNCO + (Me_3Si)_2NNa \rightarrow (Me_3Si)_2O + \\ + Me_3SiN{=}C{=}NSiMe_3 + NaOCN\ .$$

Trimethylsilyl isothiocyanate reacts with the sodium derivative considerably less vigorously than does the isocyanate, the proportions of the parallel reactions being respectively 65–70% and 25%:[98]

$$Me_3SiNCS + (Me_3Si)_2NNa \rightarrow \begin{cases} Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2S + NaSCN \\ (Me_3Si)_3N + NaSCN\ . \end{cases}$$

The preparative value of this reaction is limited by the difficulty of separating the product mixture due to the only slight difference in boiling point between bistrimethylsilylcarbodi-imide and bistrimethylsilyl sulphide.

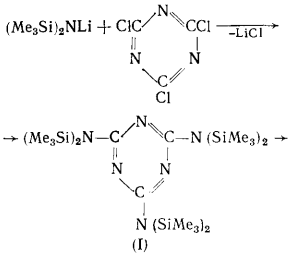
The action of sodium bistrimethylsilylamine on cyanogen halides[12,65,99], trifluoroiodomethane, and dithiocyanogen[93,100] gives high yields of bistrimethylsilylcarbodi-imide:

$$(Me_3Si)_2NNa + XCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + NaX$$
$$X = Cl,\ Br,\ I$$
$$(Me_3Si)_2NNa + ICF_3 \rightarrow NaI + NaF + Me_3SiF + Me_3SiN{=}C{=}NSiMe_3$$
$$(Me_3Si)_2NNa + (SCN)_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + \\ + NaSCN + (Me_3Si)_2NSSN(SiMe_3)_2\ .$$

As in the case of carbon dioxide, formation of the carbodi-imide in the last reaction is unexpected. It was assumed[100] to involve the series of reactions

$$(Me_3Si)_2NNa + NCS{-}SCN \rightarrow (Me_3Si)_2N{-}SCN + NaSCN$$
$$(Me_3Si)_2N{-}S{-}C{\equiv}N \rightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2NSS{-}CN$$
$$NC{-}S{-}N(SiMe_3){-}SiMe_3$$
$$(Me_3Si)_2N{-}S{-}SCN \rightarrow (Me_3Si)_2N{-}S{-}S{-}N(SiMe_3)_2 + (SCN)_2\ .$$

Reaction between lithium bistrimethylsilylamine and cyanuryl chloride in boiling oxolan gives a 25% yield of bistrimethylsilylcarbodi-imide[13] accompanied by 2,4,6-trishexamethyldisilazanyl-1,3,5-triazine, tristrimethylsilylamine, traces of hexamethyldisilazane, and an insoluble product of high melting point, which according to the infrared spectra is a lithium derivative of trimethylsilylcarbodi-imide. The reaction mechanism[13] involves initial formation of an organosilicon 1,3,5-triazine (I), its thermal decomposition, obviously to *NN*-bistrimethylsilylcyanamide, and rapid isomerisation of the latter to the carbodi-imide:

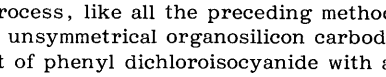


$$[(Me_3Si)_2NC{\equiv}N] \rightarrow Me_3SiN{=}C{=}NSiMe_3\ .$$

Heating pure (I) to 100 °C does actually give the carbodi-imide (85%). Formation of tristrimethylsilylamine and the lithium derivative $(CH_3)_3SiN:C:NLi$ was attributed[13] to partial interaction of lithium bistrimethylsilylamine with (I) or with bistrimethylsilylcarbodi-imide:

$$Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2NLi \rightarrow \\ \rightarrow (Me_3Si)_3N + Me_3SiN{=}C{=}NLi\ .$$

This process, like all the preceding methods, can be used to obtain unsymmetrical organosilicon carbodi-imides. Thus treatment of phenyl dichloroisocyanide with an equimolecular quantity of lithium bistrimethylsilylamine at 100 °C gives a 65% yield of *N*-phenyl-*N'*-trimethylsilylcarbodi-imide[101,102]:

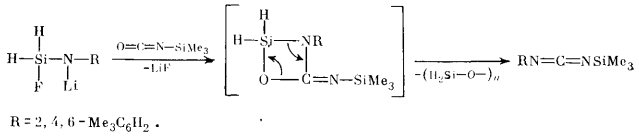


$$\xrightarrow[-Me_3SiCl]{} PhN{=}C{=}NSiMe_3\ .$$

The same compound was obtained as a by-product from the reaction of phenyl isocyanate or isothiocyanate with methyldiphenyltrimethylsilyliminophosphorane $(C_6H_5)_2P(CH_3):NSi(CH_3)_3$.[103] *N*-t-Butyl-*N'*-trimethylsilylcarbodi-imide has been prepared from t-butyl isocyanate and lithium bistrimethylsilylamine[54]:

$$t\text{-}BuN{=}C{=}O + (Me_3Si)_2NLi \rightarrow \\ \rightarrow t\text{-}BuN{=}C{=}NSiMe_3 + LiOSiMe_3\ .$$

An unsymmetrical organosilicon carbodi-imide has been obtained also by reaction between the lithium derivative of a fluorosilylamine and trimethylsilyl isocyanate[104]:



$R = 2,4,6\text{-}Me_3C_6H_2$.

Low yields of bistrimethylsilylcarbodi-imide result from the thermal decomposition of the nitrogen-containing lithium complexes[88]

$$(Me_3Si)_3N_2Li{\cdot}COS,\ (Me_3Si)_3N_2Li{\cdot}CS_2,$$
$$(Me_3Si)_2N_2Li_2{\cdot}COS,\ (Me_3Si)_2N_2Li_2{\cdot}CS_2\ ,$$
$$(Me_3Si)_3N_2Li{\cdot}TsNCS\ .$$

5. Decarboxylation of Isocyanates

The decarboxylation of isocyanates is an important and most convenient method for obtaining organic carbodi-imides[1,3]. It is suitable also for preparing hetero-organic carbodi-imides, although very few papers have appeared on this topic. Thus, when trimethylsilyl isocyanate is passed through a quartz tube heated to ~600 °C, it undergoes partial decarboxylation to bistrimethylsilylcarbodi-imide[105,106]:

$$Me_3SiNCO \xrightarrow[-CO_2]{\Delta} Me_3SiN=C=NSiMe_3 .$$

At temperatures up to 200 °C this and other silyl isocyanates do not undergo the reaction even in the presence of decarboxylation catalysts[105,106]. In contrast, silicon-containing aromatic carbodi-imides

$$n\text{-}XC_6H_4N=C=NC_6H_4X\text{-}n \quad (X=HMe_2Si,\ Me_3Si,\ Me_3SiO)$$

have been obtained in 82–93% yields by heating the corresponding isocyanates in the presence of organo-phosphorus catalysts to 150–180 °C.[107,108].

The decarboxylation of organotin isocyanates is considerably more complicated. Thus triphenylstannyl isocyanate gives only a 19% yield of bistriphenylstannyl-carbodi-imide[109,110], which is attributed to the possibility of simultaneous disproportionation of the isocyanate to diphenylstannanediyl di-isocyanate and tetraphenyl-stannane[109–111]:

$$Ph_3SnN=C=O \begin{cases} \xrightarrow[-CO_2]{} Ph_3SnN=C=NSnPh_3 \\ \longrightarrow Ph_2Sn(NCO)_2 + Ph_4Sn \end{cases} .$$

Tributylstannyl isocyanate is extremely stable to heat, being only 4% decomposed when kept at 200 °C for 6 h; at 250 °C it breaks down into butane, butene, carbon monoxide, nitrogen, metallic tin, and an unidentified solid residue[109]. The course of the reactions is uninfluenced by the usual decarboxylation catalysts (water, hydroquinone, urea, etc.).[112] Tris(trimethylsilylmethyl)stannyl isocyanate is still more stable, breaking down at 275 °C after 6 h (yield 12%):[49]

$$(Me_3SiCH_2)_3SnNCO \rightarrow (Me_3SiCH_2)_3SnN=C=NSn(CH_2SiMe_3)_3 + CO_2 .$$

Triphenylplumbyl isocyanate is converted into the corresponding carbodi-imide $C[:NPb(C_6H_5)_3]_2$, but the yield is comparatively small[113]; the scheme of thermal decomposition has been subjected to detailed thermographic investigation[110].

Thus decarboxylation of isocyanates has at present limited value for the preparation of hetero-organic carbodi-imides.

6. Other Methods

Several papers have recently appeared on the formation of hetero-organic carbodi-imides and cyanamides by trans-metallation:

$$R_3MN=C=NMR_3 + 2R'_3M'X \rightarrow 2R_3MX + R'_3M'N=C=NM'R'_3$$

M = M′ = Si; R = Me; R′ = Et, Ph; X = Cl. M = Si; M′ = Ge;
R = Me; $R'_3 = Me_nH_{3-n}$, $n = 0-3$; X = F. M = Si; M′ = Sn;
R = Me; R′ = Ph; X = OH. M = Ge; M′ = Si; R = R′ = H; X = Br.
M = Ge; M′ = Sn; R = Et; R′ = Ph; X = Cl; M = Sn. M′ = Si;
R = Bu; R′ = Me; X = Cl . (8)

Interaction of bistrimethylsilylcarbodi-imide with triphenyl-chlorosilane at 245–250 °C [14,15] gives a 75% yield of a new carbodi-imide. The action of fluorogermane on the former reactant at room temperature results in a 95% yield of digermylcarbodi-imide[14,114]. This method has been used also to obtain organogermanium carbodi-imides of general formula $C[:NGe(CH_3)_nH_{3-n}]_2$ (yields up to 90%).[16]

Digermylcarbodi-imide in turn reacts with bromosilane at room temperature to give a quantitative yield of germyl bromide and disilylcarbodi-imide[114]. Bistrimethylsilyl-carbodi-imide has been obtained from bistributylstannyl-carbodi-imide and trimethylsilyl chloride[115] or tristrimethyl-silyl cyanurate[61], bistriethylsilylcarbodi-imide from bistrimethylsilylcarbodi-imide and triethylsilyl chloride[66]. Bistriphenylstannylcarbodi-imide is formed as a by-product in the reaction of triphenyltin hydroxide with bistrimethyl-silyl- or bistriethylgermyl-carbodi-imide[116]. In the dehydration of *NN′*-bistrimethylsilylurea with excess of phenyltri-chlorosilane bisphenyldichlorosilylcarbodi-imide is formed as a result of parallel transsilylation[66]. The interaction of equimolecular quantities of bistributylstannylcarbodi-imide and trimethylchlorosilane revealed intermediate formation of *N*-tributylstannyl-*N′*-trimethylsilylcarbodi-imide[115], which like *N*-trimethylsilyl-*N′*-triphenylsilylcarbodi-imide dis-proportionated when an attempt was made to distil it[15].

Nuclear magnetic resonance proved also the possibility of obtaining unsymmetrical germylsilylcarbodi-imides by exchange processes[117]:

$$Me_2RSiN=C=NSiRMe_2 + Me_3GeN=C=NGeMe_3 \rightleftarrows$$
$$\rightleftarrows 2Me_2RSiN=C=NGeMe_3$$
R = H, Me .

Heating bistrimethylsilylcarbodi-imide with di- and tri-halogenosilanes and with halogenated alkylsiloxanes, while the trimethylchlorosilane evolved is distilled off, yields polymeric carbodi-imides of silicon as viscous oils or rubberlike substances of high thermal stability[118–121]. Organosilicon cyanamides can also undergo transmetallation: for example, triethylchlorosilane acts on *N*-allyl-*N*-tri-methylsilylcyanamide to give an 89% yield of *N*-allyl-*N*-triethylsilylcyanamide[66].

Hetero-organic cyanamides and unsymmetrical carbodi-imides can be obtained by the interaction of $C(:NMR_3)_2$ (M = Si, Sn; R = Alk, Ar) or $R_3SnNR'C:N$ (R = Alk, Ar; R′ = H, Alk, Ar) with alkyl and aryl halides[5,112,122,123], acyl halides[4,5,124–129], and other compounds containing an active halogen atom[4,6,129–137] or a pseudohalogen group[30,66,137–139]. Carbodi-imides $(CH_3)_3SiN:C:NSO_2R$ (R = F, CF_3) have been obtained from bistrimethylsilylcarbodi-imide and the sulphonic anhydrides $(RSO_2)_2O$.[140] These reactions will be discussed in detail below.

The reaction of *N*-t-butyl-*N′*-trimethylsilylcarbodi-imide with dimethyldichlorosilane gives bis-t-butylcarbodi-imido-dimethylsilane[28]:

$$t\text{-}BuN=C=NSiMe_3 + Me_2SiCl_2 \rightarrow$$
$$\rightarrow Me_2Si\begin{matrix} N=C=NBu\text{-}t \\ N=C=NBu\text{-}t \end{matrix} + Me_3SiCl .$$

Bistrimethylsilylcarbodi-imide is formed above 120 °C from its isomer of unknown structure obtained by reaction of lithium diazomethane with trimethylchlorosilane and the arbitrarily named[141] bistrimethylsilylisodiazomethane. The structure $[(CH_3)_3Si]_2C:N^+:N^-$ was later[142,143] attributed to this last compound. Pure bistrimethylsilyldiazomethane proved to be highly thermostable, and did not rearrange into the carbodi-imide even when heated to 150 °C (in nonane for 7 days).[143] However, such rearrangement is catalysed by copper(II) sulphate and by products of secondary reactions formed in the preparation of the silylated diazomethane. Since products of the silylation of lithium diazomethane obtained by different investiga-tors[141–143] differed in properties, it was considered[144] that either a substituted diazomethane or bistrimethylsilyl aminoisocyanide $[(CH_3)_3Si]_2\ddot{N}.N^+:C:^-$ could be formed in this reaction depending on the conditions, and that either product when heated or in the presence of a catalyst isomerised into

bistrimethylsilylcarbodi-imide[144,145]. The aminoisocyanide was also obtained by an independent method[144]:

$$(Me_3Si)_2N{-}N{=}\,CCl_2 + BuLi \xrightarrow[-78^\circ]{Et_2O} \rightarrow (Me_3Si)_2\ddot{N}{-}\overset{+}{\ddot{N}}{\equiv}\overline{C}{:} + LiCl + BuCl\,.$$

Heating the product to 100 °C for 20 h did indeed give a 97% yield of bistrimethylsilylcarbodi-imide. This last compound is formed in 10–30% yields also when bistrimethylsilyl aminoisocyanide is heated with sulphur dioxide, trimethylsilylimine sulphoxide $(CH_3)_3SiN:S:O$, or bistrimethylsilylthiodi-imide $S[:NSi(CH_3)_3]_2$. The corresponding reaction with phenyl isocyanate yielded a mixture of trimethylsilyl isocyanate, *N*-phenyl-*N'*-trimethylsilylcarbodi-imide, and bistrimethylsilylcarbodi-imide in the proportions 1 : 1 : 0.3.[145]

Bistrimethylsilylcarbodi-imide has been obtained by the ultraviolet irradiation of pentacarbonyltrimethylsilylmanganese and acetonitrile at room temperature[146].

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

Carbodi-imides and cyanamides containing silicon, germanium, tin, and lead are colourless liquids or solids having a characteristic odour, fairly readily soluble in organic solvents. Hetero-organic carbodi-imides are considerably more stable, but the cyanamides are less stable, than the organic analogues: the hetero-organic carbodi-imides can be stored for many months almost without change[15], without the increase in viscosity due to polymerisation that is so characteristic of organic carbodi-imides. The hetero-organic compounds can usually be vacuum-distilled at 250 to 260 °C without decomposition. Bistriphenylsilylcarbodi-imide undergoes appreciable decomposition only above 266 °C.[15] Certain hydride and unsymmetrical carbodi-imides constitute exceptions[6,15,115,134], either breaking down or symmetrising even on slight heating.

Hetero-organic cyanamides $R_3MNR'C:N$ (M = Si, Sn; R = Alk, Ar; R' = H, Alk, Ar) are extremely unstable thermally, rapidly passing into the corresponding carbodi-imides when heated. With organotin compounds this reaction is irreversible[25,50], but with organosilicon compounds a tautomeric equilibrium is observed[4,40,41,67,68].

Polymeric organosilicon carbodi-imides $[SiRR'N:C:N]_n$ (R, R' = CH_3, C_6H_5, $CH_2:CH$) are colourless or pale brown, and are converted into viscous oils when heated above 100 °C. Their thermal stability is apparently determined by the presence of a certain number of siloxane units in the macromolecular chain[20], since some loss in weight is observed even at 200 °C. The infrared spectra remain almost unchanged even when specimens are heated in a vacuum to 350 °C for 2 h, an indication of the great thermal stability of the poly(silicon–carbodi-imide) grouping.

Bistributylstannyl-, bistriphenylstannyl-, and bistriphenylplumbyl-carbodi-imides are completely decomposed when heated above 250 °C.[109–112].

Measurements of the Trouton constant showed that both disilyl- and bistrimethylsilyl-carbodi-imides are weakly associated in the liquid phase[6,11]. Organotin cyanamides and certain carbodi-imides are far more strongly associated and can form dimers, trimers, or tetramers even in solvents[29,31,128,147]. The fact that the coordination number of tin exceeds 4 explains the ability of these compounds to form oligomers[5,25,29,31,126,128,147].

The carbodi-imide structure of the disilyl[148], bistriphenylsilyl[149], digermyl[150,151], and bistrimethylstannyl[5,18,19] compounds has been confirmed by X-ray or gaseous electron diffraction.

The heteroatom–nitrogen bond energies in hetero-organic carbodi-imides and the increment in molecular refraction have been found only for bistriethylstannylcarbodi-imide (respectively 103 ± 6 kcal mole^{-1} and 3.44 cm^3) [152] and bistributylstannylcarbodi-imide (100 ± 5 and 3.42).[47,153]

Most workers have used infrared spectroscopy to establish the structure of the hetero-organic cyanamides and carbodi-imides they have prepared. Much information has been obtained also from study of the Raman[7,8,16,65,68,154], n.m.r.[6,15,16,20,25,30,40,41,54,68,69,71,73,76,93,102,114,123,128,130,132–135,140,141,147,155–159], and mass[16,73,136] spectra. In some cases spectral and physicochemical characteristics of other hetero-organic heterocumulenes are given for comparison with data on carbodi-imides[9,11,65,82,112–114,136,137,150–152,155,160]. Infrared spectra establish quite unambiguously the appearance of a product of carbodi-imide structure in any reaction, from the characteristic frequency $\nu_{as}(N:C:N)$—respectively 2260–2170, 2160–2130, 2090–2070, and 2060 cm^{-1} for carbodi-imides containing silicon, germanium, tin, and lead.

Relative to the infrared spectra of analogous organic carbodi-imides [$\nu_{as}(N:C:N)$ 2150–2130 cm^{-1}] the organosilicon compounds exhibit a displacement of this band to higher frequencies, close to the C:N vibrations in organic cyanamides R_2NCN (2260–2210 cm^{-1}).[11,53] Nevertheless, the carbodi-imide structure—not the cyanamide structure—was adopted for the compounds $(R_3Si)_2N_2C$, on the grounds that their spectra contain neither the bands due to symmetrical N.C:N-stretching vibrations characteristic of cyanamides (~1200 cm^{-1}) [114] nor the unsymmetrical Si.N.Si vibrations at 934 cm^{-1} usually observed with other disilyl derivatives containing an Si_2N group[11]. Nor has the $\nu_s(N.C:N)$ band been found in the spectrum of digermylcarbodi-imide[114].

For the most thoroughly studied compounds—the bistrimethylsilyl, bistriethylstannyl, and bistributylstannyl derivatives—the carbodi-imide structure was adopted also in view of the comparatively small dipole moment, respectively 1.48 [12] (1.84 [161]), 1.79 ± 0.02, and 2.74 ± 0.02 D,[152] which compare with 4.5–4.8 D,[4,152,161] in the case of disubstituted organic cyanamides.

The carbodi-imide structure of the bisdimethylsilyl compound is supported convincingly also by ^{14}N n.m.r. spectral data: the spectrum contains only one signal, at 325 ppm (relative to ammonium nitrate).[15] It may be noted for comparison that dicyclohexylcarbodi-imide also gives only one resonance signal, at 240 ppm, whereas diethylcyanamide exhibits two clearly separated signals, at 149 and 258 ppm due to nitrilo- and amino-nitrogen atoms respectively[15]. The greater positive chemical shift displayed by bistrimethylsilyl- than by dicyclohexyl-carbodi-imide can be explained by the purely inductive effect of the silicon atom, which is more electropositive than carbon.

It is noteworthy that the $\nu_{as}(N:C:N)$ frequencies of organosilicon carbodi-imides containing an organic function (2160–2130 cm^{-1}) [91,107] lie in the same region as those of their carbon analogues.

The structures of hetero-organic cyanamides and unsymmetrical carbodi-imides of silicon[28,38–41,54,66–69,71,101,102,104,115,117,130–136,140,145,158,159], germanium[35,71,117,138], tin[25,27,29–37,50,73,115,123,125–129,137,139,162], and lead[29,51] have also been determined from infrared, Raman, n.m.r., mass, and Mössbauer spectral data together with X-ray diffraction results. In some cases, however, complete certainty has not yet been achieved that the choice between cyanamide and carbodi-imide forms is correct for individual compounds, since the physicochemical data sometimes do not provide unambiguous answers to such questions. Thus, whereas there is no doubt about the structure of *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide[25,30,123] (the corresponding

cyanamide form is improbable also as a consequence of great steric hindrance), the structure of the arenesulphonyl derivatives

$$R_3SnN{=}C{=}N{-}SO_2R' \qquad R_3SnN(SO_2R'){-}C{\equiv}N$$
(A) (B)

is debatable. On the basis of the infrared spectra (2193 cm^{-1}) the cyanamide structure (B: R = CH_3, C_6H_5; R' = C_6H_5, p-$CH_3C_6H_4$, p-BrC_6H_4) has been attributed[30,126,128] to such compounds, since the ν(C:N) frequencies of organotin cyanamides of type $R_3SnNHC{:}N$ (R = CH_3, C_4H_9, C_6H_5) lie in the range 2183–2174 cm^{-1}.[25,50] On the other hand, there are good reasons for regarding such compounds as hetero-organic carbodi-imides by analogy with organic sulphonylcarbodi-imides [ν_{as}(N:C:N) 2180–2175 cm^{-1}].[163,164] Definite evidence in support of structure (A) is also the comparatively low dipole moment found for *N*-phenylsulphonyl-*N'*-tributylstannylcarbodi-imide (μ_{exp} = 5.4 ± 0.3 D, μ_{calc} = 5.04 D; for the cyanamide form μ_{calc} = 6.87 D).[129] The preparation has also been reported of *N*-phenylsulphonyl-*N'*-triethylgermylcarbodi-imide[138] and of $(CH_3)_3SiN{:}C{:}NSO_2R$ [R = F, CF_3, $(CH_3)_3SiO$],[136,140] whose carbodi-imide structure is not open to doubt; their ν_{as}(N:C:N) frequencies are respectively 2190 and 2250–2240 cm^{-1}.

Several investigations have been made recently on the structure of organosilicon cyanamides and unsymmetrical carbodi-imides[4,40,41,54,67–69]. The infrared spectra and the ^1H, ^{29}Si, and ^{13}C n.m.r. spectra have shown that the freshly prepared products of the reaction of secondary organosilicon amines with cyanogen chloride are carbodi-imides, which in time undergo a silatropic rearrangement and are converted into the corresponding cyanamides (Eqn.6). Heating again yields the original organosilicon carbodi-imides[40]. Formation of the cyanamide form is prevented by the steric effect of the t-butyl and phenyl groups.

Study of the reaction of cyanogen chloride with silylamides of carboxylic acids led to the conclusion that the products could exist in three tautomeric forms (A) ⇌ (B) ⇌ (C) (Eqn.7). The infrared spectra suggest that form (C) predominates[67,68]. In the case of the organotin analogues opinions on the structure of the products were divided. On the basis of infrared spectral data preference has been given[125,126,128] to form (B):

$$R'C(O){=}C{=}NSnR_3 \rightleftarrows R'C(O)(SnR_3){-}C{\equiv}N \rightleftarrows R'{-}C(OSnR_3){=}N{-}C{\equiv}N$$
(A) (B) (C)

R = Me, Ph; R' = Me, Et, CF_3, $PhCH_2$, p-$O_2NC_6H_4$, p-FC_6H_4, p-ClC_6H_4, MeO, EtO.

Other workers have shown[127,162] that tautomers can be formed with compounds of this type having R = C_4H_9 and R' = C_6H_5, but structure (C) is thermodynamically the most stable. The position of equilibrium in such systems is displaced under the influence of heating and additions of tributyltin chloride. Other discussions of the structures of such products have appeared[31,73].

The nitrile band in the infrared absorption spectra of organosilicon cyanamides containing an organic function $CH_3SiRR'CH_2NR''C{:}N$ (R = CH_3, C_2H_5O; R' = CH_3O, C_2H_5O; R'' = iso-C_3H_7, iso-C_4H_9, C_6H_5) [53] lies in the range 2228 to 2211 cm^{-1}. Polymeric carbodi-imides $[SiRR'NCN]_n$ [n = 6–8; RR' = $(CH_3)_2$, $(C_6H_5)_2$, $CH_3.C_6H_5$, $CH_3.CH_2{:}CH$, $(C_2H_5O)_2$] contain a strong N:C:N band at 2200–2150 cm^{-1}. The position of ν_{as}(N:C:N) is little affected by different substituents attached to the silicon atom. In the spectrum of the organotin tetramer $[(C_4H_9)_2SnN{:}C{:}N]_4$ this band has its maximum at 2063 cm^{-1}.

Study of n.m.r. spectra showed that the resonance signal of protons in organic groups attached to a silicon atom shifts upfield on passing from chlorosilanes to monomeric or polymeric organosilicon carbodi-imides. This indicates that the carbodi-imide group is less electronegative than the chlorine atom[15,20]. Thus for bistrimethylsilylcarbodi-imide and trimethylchlorosilane the difference is $\Delta\delta$ = 0.425 – 0.157 = 0.268 ppm.[20] This difference is increased when more than one chlorine atom is replaced by carbodi-imido-groups[20].

IV. CHEMICAL PROPERTIES

Hetero-organic carbodi-imides have very unusual chemical properties: in contrast to their organic analogues they can react not only at the carbodi-imide group but also at the heteroatom–nitrogen bonds. Furthermore, interaction between the N=C=N and M–N fragments results in a redistribution of electron density in the M–N=C=N system, with a consequent substantial change in reactivity of the compound as a whole. Thus the reactions of hetero-organic carbodi-imides can be divided into two main groups—(A) those accompanied by fission of heteroatom–nitrogen bonds and (B) additions at the cumulative double bonds.

The chemical properties of hetero-organic cyanamides will be considered at the same time and compared with those of the carbodi-imides.

A. Reactions with Fission of Heteroatom–Nitrogen Bonds

1. Interaction with compounds having a mobile hydrogen atom

Reactions of type (A) include primarily those of hetero-organic carbodi-imides with compounds containing a mobile hydrogen atom, e.g. water, alcohols, carboxylic acids. In contrast to organic carbodi-imides, which tend to undergo additions as a consequence of the unsaturation of the carbodi-imide group[1,3], their hetero-organic analogues are characterised by substitutions.

Hetero-organic carbodi-imides are usually quite stable towards atmospheric moisture under normal conditions. Thus bistriphenylsilylcarbodi-imide remains unchanged on contact with water for 10 days.[15] The enhanced hydrolytic stability of this class of compounds is explained by strengthening of heteroatom–nitrogen bonds due to delocalisation of electron density throughout the heterocumulene system under the influence of Group IVB elements[104,165,166]. However, prolonged heating of hetero-organic carbodi-imides with water results in fission of heteroatom–nitrogen bonds and separation of the coresponding hetero-organic oxides or hydroxides, together with cyanamide or a derivative thereof. Data have been published[11,25,28,44] on the hydrolysis of carbodi-imides containing silicon, germanium, and tin.

The hydrolysis of *N*-difluorophosphoryl-*N'*-trimethylsilylcarbodi-imide yields not only hexamethyldisiloxane and cyanamide but also phosphoric acid and hydrogen fluoride[132]. *N*-Phenylsulphonyl-*N'*-tributylstannylcarbodi-imide with water undergoes the reaction[129]

$$Bu_3SnN{=}C{=}NSO_2Ph \xrightarrow[-Bu_3SnOH]{H_2O} [PhSO_2NHCN] \rightarrow$$

$$\rightarrow PhSO_2NH{-}C(=N{-}C(NHSO_2Ph){=}N){-}N$$

Under similar conditions *N*-trimethylphenyl-*N'*-triphenylstannyl- and bistriphenylplumbyl-carbodi-imides do not react with water[25,49].

Hydrolysis of bistriethylgermyl- and bistriphenylgermylcarbodi-imides proceeds farther on the addition of 5–10% of sodium hydroxide to the reaction system. The final products are in the former case urea, cyanates, and hexaethyldigermoxane[45], and in the latter case urea, a mixture of cyanates, and sodium triphenylgermyl oxide[44].

Germanium-containing carbodi-imides react with water and hydrogen chalcogenides (sulphide, selenide, telluride) at room temperature[16,24]:

$$Me_nH_{3-n}GeN{=}C{=}NGeH_{3-n}Me_n + H_2El \rightarrow (Me_nH_{3-n}Ge)_2El + (H_2NCN)_2$$
$$El = O, S, Se;\ n = 0-3\ .$$

Similarly, bistriphenylplumbylcarbodi-imide is quantitatively converted by hydrogen sulphide at room temperature into bistriphenylplumbyl sulphide $S[Pb(C_6H_5)_3]_2$ and cyanamide[49]. Bistrimethylsilylcarbodi-imide, in contrast to the germanium and lead analogues, does not react with the hydrogen chalcogenides even when heated to 60–100 °C.[11-16]

Carbodi-imides containing silicon[16,116,117,168,169], germanium[114,116,117,168,169], and tin[25,55] react with alcohols and carboxylic acids to give the corresponding alkoxy- or acyloxy-derivatives together with cyanamide, dicyanodiamide, or melamine. Reaction takes place over a wide temperature range depending on the type and nature of the initial compounds. Thus digermylcarbodi-imide reacts rapidly and quantitatively with methanol at room temperature[114], whereas bistrimethylsilylcarbodi-imide requires heating to 100 °C.[116] The reaction of bistributylstannylcarbodi-imide with alcohols is reversible[55].

N-Triphenylmethyl-*N'*-triphenylstannylcarbodi-imide is decomposed by acetic acid under mild conditions to give triphenylstannyl acetate and triphenylmethylcyanamide[25].

In contrast to the above results, bistriphenylplumbylcarbodi-imide and trimethylplumbylcyanamide do not react with alcohols, and can be prepared in ethanol[49,51].

The reactions of bistrimethylsilyl- and bistriethylgermylcarbodi-imides[116] with hydroxylated compounds such as triethylsilanol and triphenyltin hydroxide also involve fission of heteroatom–nitrogen bonds, but they are complicated by simultaneous reaction between the initial carbodi-imides and water liberated on dehydration of the hydroxides:

$$R_3MN{=}C{=}NMR_3 + Ph_3SnOH \rightarrow Ph_3SnN{=}C{=}NSnPh_3 + R_3MOH$$
$$R_3MOH \xrightarrow{-H_2O} R_3MOMR_3\ .$$

The reaction of carbodi-imides containing Group IVB elements with thiols[16,117] and selenols[117,165,166,170] have a similar course to those with alcohols and lead to the separation of dicyanodiamide and the corresponding hetero-organic sulphur or selenium derivatives:

$$R_3MN{=}C{=}NMR_3 + REIH \rightarrow R_3MEIR' + (H_2NCN)_2$$
$$EL = S:\ M{=}Ge;\ R_3 = H_3,\ H_2Me,\ HMe_2,\ Me_3;$$
$$R'{=}Me,\ Et,\ Bu,\ Ph,\ Ac;\ El = Se:\ M = Si;$$
$$R{=}Me;\ R'{=}Bu;\ M{=}Ge;\ R{=}H,\ Et,\ Ph;$$
$$R'{=}Me,\ Bu,\ Ph;\ M{=}Sn;\ R{=}R'{=}Bu\ .$$

Bistrimethylsilylcarbodi-imide either does not react at all with thiols or gives insignificant [sic] 39–40% yields[16]. The SiN : C : NSi heterocumulene system is less liable to nucleophilic attack by heavy chalcogenols RSH, RSeH, and RTeH than is the corresponding GeN : C : NGe system. This is attributed to the enhanced stability of the silicon–nitrogen bond in carbodi-imides resulting from d_π–p_π interaction between the silicon and nitrogen atoms. The possibility of rupture of this bond by alcohols and acids is due to formation of the energetically more favourable silicon–oxygen bond[16]. The quantitative formation of products on treatment of germanium-containing carbodi-imides with these reagents results from the less double-bonded character of the germanium and nitrogen atoms.

The action of thioacetic acid on $C(:NSiR_3)_2$ ($R = H, CH_3$) and $C(:NGeR_3)_2$ [$R_3 = H_3, H_2CH_3, H(CH_3)_2, (CH_3)_3$] yields the corresponding thioacetates[168]. Spectral data show that in organosilicon thioacetates $R_3Si.O.CS.CH_3$ the R_3Si group is attached to the oxygen atom, whereas in the corresponding organogermanium derivatives $R_3Ge.S.CO.CH_3$ the R_3Ge group is attached to the sulphur atom.

Bistrimethylsilyl- and bistrimethylgermyl-carbodi-imides react vigorously with nitric acid at 0 °C to give the hetero-organic nitrates[171]:

$$Me_3MN{=}C{=}NMMe_3 + HNO_3 \rightarrow Me_3MONO_2 + (H_2NCN)_2\ .$$

Bistrimethylgermylcarbodi-imide reacts[117] with diphenylphosphine and phenylacetylene. The compounds $C[:NM.(CH_3)_3]_2$ (M = Si, Ge) do not react with phosphine, arsine, dimethylarsine, triphenylsilane, trimethylsilane, or pyrrole.

Bistrimethylsilylcarbodi-imide is reduced by lithium tetrahydroaluminate[15]:

$$Me_3SiN{=}C{=}NSiMe_3 + LiAlH_4 \rightarrow Me_3SiH + Li_2NCN + Al_2(NCN)_3\ .$$

Bistriphenylstannylcarbodi-imide is split by cyanamide[25]:

$$Ph_3SnN{=}C{=}NSnPh_3 + H_2NCN \rightarrow Ph_3SnNHCN\ .$$

Organosilicon carbodi-imides differ from their organic analogues in not reacting with ammonia or aniline, not adding hydrogen even in the presence of a palladium catalyst, and not causing amino-acids to condense to peptides[11].

2. Reactions with halogens and halogen-containing compounds

The action of halogens and their compounds on carbodi-imides containing silicon, germanium, and tin also involves fission of the heteroatom–nitrogen bond with formation of the corresponding hetero-organic halides and of cyanamide derivatives. Among halogen-containing compounds used have been hydrogen, alkyl, aryl, and acyl halides and Lewis acids. Only one publication[45] has described the reaction with an elementary halogen: bistriethylgermylcarbodi-imide reacts with bromine in benzene at 20 °C to give up to 70% yields of triethylgermyl bromide accompanied by dicyanodiamide and a polymer of undetermined structure. Disilylcarbodi-imide reacts with hydrogen chloride[6] to form chlorosilane and a compound to which the formula $H_2NCCl_2NH_2$ was assigned. A little later a similar reaction was accomplished with bistrimethylsilylcarbodi-imide, for which the scheme

$$R_3SiN{=}C{=}NSiR_3 + HCl \rightarrow R_3SiCl + Cl^-[H_2\overset{+}{N}{=}C{=}\overset{+}{N}H_2]\ Cl^-$$

was suggested[11].

Unsymmetrical *N*-trifluorosilyl-*N'*-trimethylsilylcarbodi-imide on treatment with excess of hydrogen chloride gives a quantitative yield of trimethylchlorosilane, chlorotrifluorosilane, and cyanamide dihydrochloride[130]:

$$Me_3SiN{=}C{=}NSiF_3 + HCl \rightarrow Me_3SiCl + F_3SiCl + H_2NCN{\cdot}2HCl\ .$$

When dry hydrogen chloride is passed through bistributylstannylcarbodi-imide at room temperature for 2 h the dihydrochloride is accompanied by tributyltin chloride (94%).[122]

Hetero-organic carbodi-imides react with metal salts of the Lewis acid type. Thus the reaction of disilylcarbodi-imide with silver chloride, bromide, and thiocyanate (at −78 °C for 18 h) gave low yields of chlorosilane, bromosilane, and isothiocyanatosilane respectively[6]. Treatment of bistriethylstannylcarbodi-imide with metal chlorides in boiling moist ether yields hydrates of the metal salts of cyanamide[5,167]:

$$Et_3SnN{=}C{=}NSnEt_3 + MCl_2 \rightarrow Et_3SnCl + MNCN\cdot nH_2O$$
$$M = Cu,\ Zn,\ Cd,\ Ca,\ Sn\ .$$

Products of the reaction with copper(II) sulphate are the monohydrate of copper(II) cyanamide $CuNCN.H_2O$ (91%) and bistriethylstannyl sulphate (98%).[167]

Hetero-organic carbodi-imides and cyanamides react very peculiarly with alkyl and aryl halides[5,112,122,123] and with arenesulphonyl chlorides[125,126,128,129,137,172]. Thus with ethyl and pentyl bromides bistributylstannylcarbodi-imide gives high yields of tributylstannyl bromide and the dialkylcyanamide[5,112,122]:

$$Bu_3SnN{=}C{=}NSnBu_3 + RBr \xrightarrow[84}{110-120^\circ}$$
$$\rightarrow Bu_3SnBr + \left[Bu_3Sn{-}N(R){-}C{\equiv}N\right] \xrightarrow{RBr} R_2NCN + Bu_3SnBr\ .$$

Bistriphenylstannylcarbodi-imide, in contrast to its butyl analogue, does not react with ethyl bromide (when boiled in acetonitrile), but with ethyl iodide triphenylstannyl iodide has been isolated[123]. With benzyl bromide it gives as final products triphenylstannyl bromide and the dibenzylcyanamide complex of the latter $(C_6H_5CH_2)_2NCN.(C_6H_5)_3SnBr$. An analogous reaction with *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide leads to isolation of the corresponding complex $(C_6H_5)_3C(C_6H_5CH_2)NCN.(C_6H_5)_3SnBr$.[123] Replacement of benzyl bromide by triphenylmethyl chloride yields either bistriphenylmethyl- or *N*-triphenylmethyl-*N'*-triphenylstannyl-carbodi-imide depending on the initial ratio of the reactants:

$$Ph_3SnN{=}C{=}NSnPh_3 \begin{cases} \xrightarrow[-Ph_3SnCl]{Ph_3CCl} Ph_3SnN{=}C{=}NCPh_3 \\ \xrightarrow[-2Ph_3SnCl]{2Ph_3CCl} Ph_3CN{=}C{=}NCPh_3 \end{cases}\ .$$

Here the usual exchange process is observed: the mechanism with migration of the reaction centre is not realised owing to the large bulk of the triphenylmethyl group[123].

Reaction of triphenylstannylcyanamide with triphenylmethyl chloride in the presence of triethylamine in the proportions 1 : 1 : 2 in benzene at 20 °C yields triethylamine hydrochloride (56%), bistriphenylmethylcarbodi-imide (38%), and *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide (5%).[123]

Organotin carbodi-imides and cyanamides react also with arenesulphonyl halides and pseudohalides. Thus the action of benzenesulphonyl chloride on bistributylstannylcarbodi-imide yields *N*-phenylsulphonyl-*N'*-tributylstannylcarbodi-imide and tributylstannyl chloride independently of the initial proportions of the reactants[129,137,172]; benzenesulphonyl azide reacts similarly[137,172]:

$$Bu_2SnN{=}C{=}NSnBu_3 + PhSO_2X \rightarrow Bu_3SnX + Bu_3SnN{=}C{=}NSO_2Ph$$
$$X = Cl,\ N_3\ .$$

Other publications have appeared[126,128] on the interaction of organotin carbodi-imides and arenesulphonyl chlorides, but a cyanamide structure was attributed to the products, as already mentioned:

$$R_3SnN{=}C{=}NSnR_3 + R'Cl \rightarrow R'\underset{|}{N}(C{\equiv}N)SnR_3 + R_3SnCl \qquad (9)$$
$$R = Me,\ Ph;\ R' = PhSO_2,\ p\text{-}MeC_6H_4SO_2,\ p\text{-}BrC_6H_4SO_2\ .$$

In contrast to carbodi-imides triphenylstannylcyanamide forms with benzenesulphonyl chloride in the presence of triethylamine an anionic complex[125]:

$$Ph_3SnNHC{\equiv}N + RCl + Et_3N \rightarrow [RN(CN)SnPh_3Cl]^-[Et_3NH]^+ \qquad (10)$$
$$R = Ph\ SO_2\ .$$

Reactions with acyl halides[4,5,124-129] also correspond to Eqns.(9) and (10),[125,126,128] but yield more complicated product mixtures, owing to the possibility of heterotropic rearrangements of the cyanamides (or carbodi-imides) formed. Bistrimethyl-, bistributyl-, and bistriphenylstannylcarbodi-imides react with acid chlorides at room temperature in the absence of a solvent[127,129] or in oxolan[125,126,128] to give the corresponding stannyl chlorides and cyanamide derivatives [Eqn.(9): R = CH_3, C_4H_9, C_6H_5; R' = CH_3CO, C_6H_5CO, $C_6H_5CH_2CO$, *p*-$CH_3C_6H_4CO$, *p*-$NO_2.C_6H_4CO$, *p*-ClC_6H_4CO, *p*-BrC_6H_4CO, CH_3OCO, CF_3CO]. The structure of these and the products of the reaction of bistrimethylsilylcarbodi-imide with trifluoroacetyl chloride[124] and with benzoyl chloride[4,66-68] has been discussed already (Sections II, 2 and III).

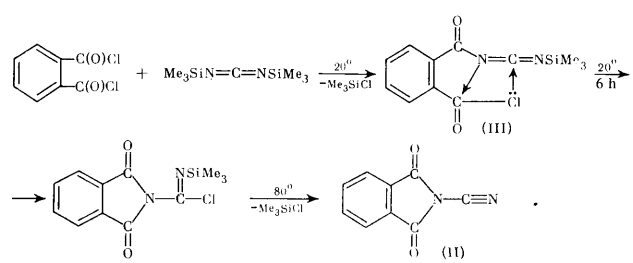
It is noteworthy that benzoyl chloride is able to react with bistributylstannylcarbodi-imide also in the proportions 2 : 1,[129] a process that is shown by the infrared spectra to take place in stages. One of the tin-nitrogen bonds is broken at room temperature within a few minutes, with formation of a substituted cyanoimine; reaction with the second molecule of benzoyl chloride takes place at 100 °C:

$$Bu_3SnN{=}C{=}NSnBu_3 + PhC(O)Cl \xrightarrow[-Bu_3SnCl]{} \left[Bu_3Sn{-}O{-}C(Ph){=}N{-}C{\equiv}N\right] \rightarrow$$
$$\rightarrow Bu_3SnO{-}C(Ph){=}N{-}C{\equiv}N \xrightarrow{PhC(O)Cl} PhC(O)O{-}C(Ph){=}N{-}C{\equiv}N$$
$$\xrightarrow{H_2O} Bu_3SnOH + PhC(O)NHC(O)NH_2\ .$$

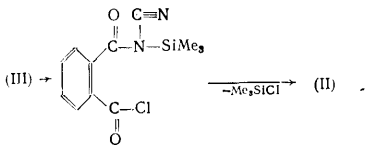
Hydrolysis of the intermediate organotin cyanamide leads to formation of benzoylurea[129].

Triphenylstannylcyanamide reacts with acid chlorides in conformity with Eqn.[(10): R = CH_3CO, C_2H_5CO, C_6H_5CO, CH_3OCO, C_2H_5OCO, $C_6H_5CH_2OCO$]. The corresponding anionic complexes were isolated as final products[125,126]. One such complex (R = CH_3CO) was obtained by cross synthesis from *N*-cyano-*N*-triphenylstannylacetamide and triethylamine hydrochloride[125]. Anionic complexes of the type $[N\vdots C.N:C(NHR).OSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+$ (R = C_2H_5, C_6H_5) have been prepared similarly[173].

The reaction of bistrimethylsilylcarbodi-imide with phthaloyl dichloride led to the isolation only of the final acylation product (II), whose formation was assumed[174] to involve the processes:



Alternatively, the reaction might involve intermediate formation of a cyanamide derivative:



The action of terephthaloyl and *p*-nitrobenzoyl chlorides on triphenylstannylcyanamide and triethylamine yields not complexes but triethylammonium salts of the corresponding acylcyanamides[125].

Organosilicon carbodi-imides are often used as intermediates in the preparation of novel hetero-organic compounds. The reaction of disilylcarbodi-imide with boron trifluoride was described as early as 1962:[7] an addition product is formed at −78 °C, which at room temperature breaks down into fluorosilane and *N*-boryl-*N*-silylcyanamide. The action of boron trifluoride on bistrimethylsilylcarbodi-imide yields trimethylfluorosilane and an unidentified polymer[117].

This communication served to initiate a large number of studies on the preparation of unsymmetrical organosilicon carbodi-imides and hetero-organic cyanoimines. Thus treatment of bistrimethylsilylcarbodi-imide with silicon tetrafluoride[130,131], phosphoryl trifluoride[132,133], thiophosphoryl trifluoride[134], $S:PF_2.N:PF_3$,[135] and $(CH_3)_3SiO_3.SCl$ [136] has yielded the corresponding halogenosilanes and carbodi-imides:

$$Me_3SiN{=}C{=}NSiMe_3 + RX \rightarrow Me_3SiN{=}C{=}NR + Me_3SiX$$
$$R = SiF_3,\ POF_2,\ PSF_2,\ S{=}PF_2N{=}PF_2;\ X = F;$$
$$R = SO_3SiMe_3;\ X = Cl\ .$$

Treatment with sulphur tetrafluoride[175,176], thionyl tetrafluoride[177,178], R_2NSF_3,[179,180] R_2NSOF_3 ($R = CH_3$, C_2H_5, C_5H_{10}),[179,181] $C_6H_5OSOF_3$,[182] $(CF_3)_2CFSF_3$,[183] $C_6H_5PF_4$, $(C_6H_5)_2PF_3$,[133,184,185] and thionyl dichloride[74-76] involves detachment of both trimethylsilyl groups to give up to 65% yields of cyanoimines:

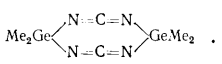
$$Me_3SiN{=}C{=}NSiMe_3 + YX_2 \rightarrow Y{=}N{-}C{\equiv}N + Me_3SiX$$
$$Y = F_2S,\ F_2SO,\ Alk_2NS(O)F;\ (CF_3)_2CFSF,\ PhPF_2,$$
$$Ph_2PF;\ X = F;\ R = SO;\ X = Cl\ .$$

Depending on the conditions treatment with sulphur tetrafluoride may yield products differing in structure[176]:

$$F_2S{=}N{-}C{\equiv}N \xleftarrow[50^\circ]{SF_4} Me_3SiN{=}C{=}NSiMe_3 \xrightarrow[200^\circ]{SF_4} F_2S{=}NSF_2N{=}SF_2\ .$$

Exchange reactions between silylcarbodi-imides and inorganic halides were partly covered in a review[186].

The reported[117] reaction of bistrimethylsilylcarbodi-imide with germanium tetrafluoride and dimethylgermanium difluoride gave as final products not only trimethylfluorosilane but also a polymer containing fluorine, germanium, and nitrogen together with the compounds bisdimethylfluorogermylcarbodi-imide and



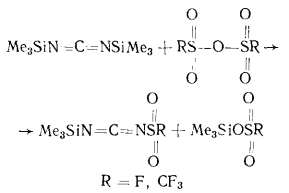
The transmetallation of hetero-organic carbodi-imides by means of organo-silicon, -germanium, and -tin halides has already been discussed in detail (Eqn.8).[1,4,14-16,66,114,115,117-121]

The reactions of unsymmetrical organosilicon carbodi-imides with hydrogen-containing compounds do not differ fundamentally from those of their symmetrical analogues. Thus the action of dimethyldichlorosilane and also of chlorine-containing sulphur compounds (sulphur dichloride and R_2NSCl) on *N*-t-butyl-*N'*-trimethylsilylcarbodi-imide has been described[158]. Elimination of trimethylchlorosilane led to isolation of the corresponding carbodi-imides:

$$t\text{-}BuN{=}C{=}NSNR_2\ (R = Me,\ Et),$$
$$t\text{-}BuN{=}C{=}NSiMe_2N{=}C{=}NBu\text{-}t,$$
$$t\text{-}BuN{=}C{=}NSN{=}C{=}NBu\text{-}t\ .$$

3. Reactions with compounds containing S–O–S and P–O–P links

Bistrimethylsilylcarbodi-imide undergoes exchange processes also with compounds containing labile S–O–S and P–O–P bonds. Thus with disulphuryl difluoride and bistrifluoromethide at room temperature the corresponding unsymmetrical organosilicon carbodi-imides are obtained[140]:

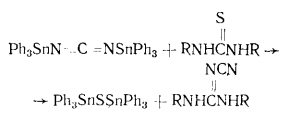


The reaction with pyrophosphoryl tetrafluoride $O(POF_2)_2$ apparently follows the same course[187], to give $(CH_3)_3.SiOPOF_2$ (85%) and an unidentified colourless solid.

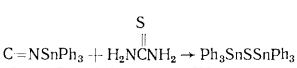
4. Interaction with thiourea derivatives and thioamides

The action of substituted thioureas and thioamides on organotin carbodi-imides and cyanamides also involves reactions of type (A).

When disubstituted thioureas are heated with bistriphenylstannylcarbodi-imides in boiling acetonitrile for 20 h, 45–74% yields of the corresponding *NN'*-disubstituted *N''*-cyanoguanidines and bistriphenylstannyl sulphide are obtained[25]:

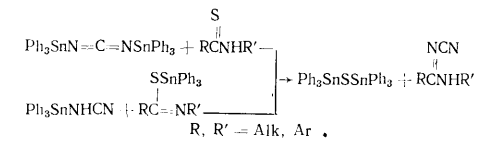


However, the use of thiourea results in the formation of triphenylstannylcyanamide, which can be explained by the scheme[25]:



Reaction of trimethyl- and triphenyl-stannylcyanamides with various isothioureas makes it possible to obtain the corresponding *N*-cyano-*S*-trialkylstannylisothioureas of general formula $R'N:C(NHCN)SSnR_3$ ($R = CH_3$, C_6H_5; $R' = CH_3$, C_6H_5, $p\text{-}FC_6H_4$, $p\text{-}NO_2C_6H_4$, $C_6H_5CH_2$, cyclo-C_6H_{11}).[188]

The reactions of bistriphenylstannylcarbodi-imide and of triphenylstannylcyanamide with *N*-substituted thioamides at room temperature in acetonitrile (63 h) or in ethanol (15 h) resulted in the same products—the corresponding *N'*-substituted cyanamidines (yields 25–67%):[189]



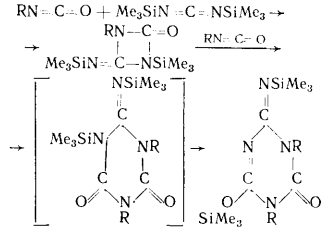
Treatment of the above carbodi-imides with thioamides in

ether or acetonitrile led to the isolation of acetonitrile or benzonitrile, bistriphenylstannyl sulphide, and dicyanodiamide. The sulphide and the organic nitrile could have been formed by decomposition of an intermediate compound of the type $(C_6H_5)_3Sn.S.CR:N.Sn(C_6H_5)_3$.[189]

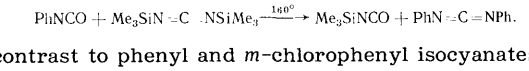
Several reactions of tin-containing carbodi-imides and cyanamides have been systematised in annual reviews on organotin compounds[190,191].

B. Additions at Cumulative Bonds of Carbodi-imides

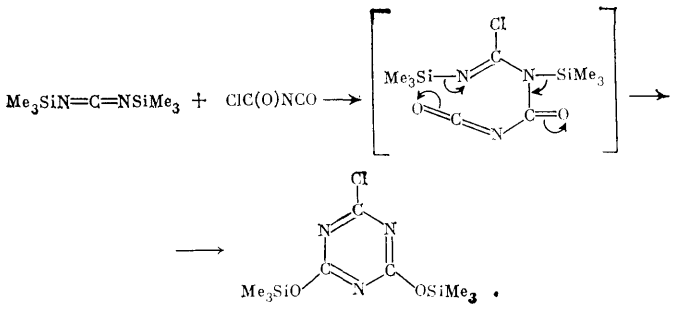
As mentioned above, addition reactions are far less characteristic of hetero-organic carbodi-imides than of the organic analogues. The first mention of reactions of this type related to that between bistrimethylsilylcarbodi-imide and fluorosulphuryl isocyanate $FSO_2N:C:O$.[192] An equimolecular adduct was formed, whose pyrolysis yielded trimethylfluorosilane. The carbodi-imide reacts with benzenesulphonyl isocyanate when heated to 100–150 °C,[138] with the formation of four- or six-membered heterocycles containing silicon depending on the initial proportions of the reactants:



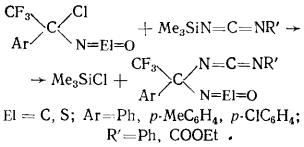
Such a scheme was suggested for the interaction of organic isocyanates with organic carbodi-imides[164,193]. In the case of phenyl isocyanate the only product of the reaction is the 1:2 adduct 2-oxo-1,3-diphenyl-4-trimethylsiloxy-6-trimethylsilylimino-1,2,3,6-tetrahydro-1,3,5-triazine (yield 82%).[194,195] A similar reaction occurs with *m*-chlorophenyl isocyanate[196]. If the low-boiling trimethylsilyl isocyanate formed is distilled off, an exchange reaction occurs with phenyl isocyanate[66]:



In contrast to phenyl and *m*-chlorophenyl isocyanates, chloroformyl isocyanate reacts with bistrimethylsilylcarbodi-imide in equimolecular proportions under mild conditions (in ether at 20 °C) to give a 64% yield of 2-chloro-4,6-bistrimethylsiloxy-1,3,5-triazine[197]:

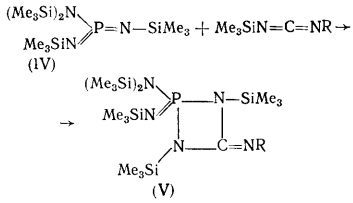


The reaction is seen to begin with electrophilic addition of the isocyanate at the carbon–nitrogen double bonds of the carbodi-imide. The product cyclises with simultaneous migration of the trimethylsilyl groups from nitrogen to oxygen atoms. Unsymmetrical organosilicon carbodi-imides undergo exchange reactions with chlorinated isocyanates; as final products have been isolated for the first time compounds having two different heterocumulene groups attached to the same carbon atom[38,39,198]:

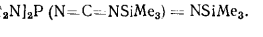


El = C, S; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; R′ = Ph, COOEt .

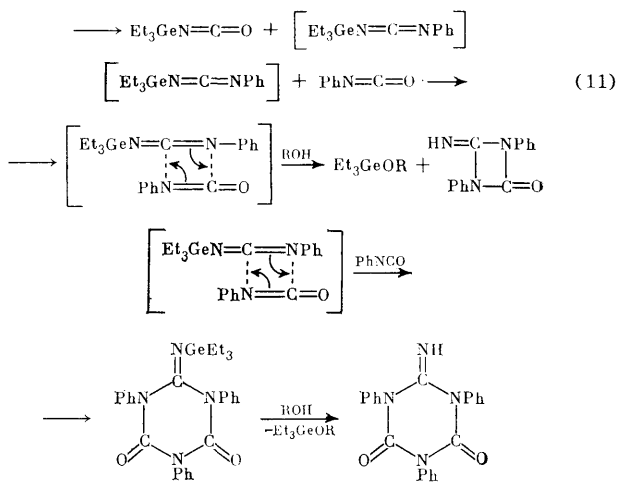
Interaction of bistrimethylsilyl- or *N*-t-butyl-*N*′-trimethylsilyl-carbodi-imide with the fully *N*-trimethylsilylated aminodiiminophosphorane (IV) at 0 °C for 2 h yielded cyclic adducts:



[R = $(CH_3)_2Si$, $(CH_3)_3C$].[159] When the reaction conditions were changed to 25 °C for 7 days, the product was not the compound [V: R = $(CH_3)_3Si$] but the carbodi-imidophosphinoimine:



The reaction of bistriethylgermylcarbodi-imide with phenyl isocyanate in the proportions 1:2 follows a rather different course[194]. Initial exchange of one of the triethylgermyl groups for phenyl is followed by cycloaddition of the resulting unsymmetrical carbodi-imide to a second phenyl isocyanate molecule; at the same time an organogermanium 1,3,5-triazine is formed to a slight extent:



(11)

R = H, Me, Et, iso-Pr .

Hydrolysis of the resulting organogermanium cycloadducts yields the corresponding organic isoammelide derivatives, as in the case of the organosilicon analogues. The action of benzenesulphonyl isocyanate involves mainly the first stage of reaction (11), which on heating is complicated by considerable resinification[138]. The final products isolated were triethylgermyl isocyanate (yield 34%) and *N*-phenylsulphonyl-*N*′-triethylgermylcarbodi-imide.

Benzenesulphonyl isocyanate reacts in just the same way when heated with bistributylstannylcarbodi-imide, giving an 83% yield of tributylstannyl isocyanate[138]. At 25 °C this carbodi-imide forms with benzenesulphonyl, phenyl, and 6-chlorohexyl isocyanates linear adducts of length depending on the initial proportions of the reactants[59,138,199,200]. Heating the adduct $C[:NSn(C_4H_9)_3]_2 \cdot 3C_6H_5NCO$ and then hydrolysing the resulting mixture yielded several products indicating a reaction mechanism similar to (11). In particular 2-imino-4,6-dioxo-1,3,5-triphenylperhydro-1,3,5-triazine and triphenyl isocyanurate were isolated in yields of 61% and 30% respectively. Formation of the latter compound is apparently due to catalytic cyclotrimerisation of phenyl isocyanate under the influence of organotin compounds, which has been studied thoroughly[201,202]. Thermal decomposition of the adduct $C[:NSn(C_4H_9)_3]_2 \cdot ClC_6H_{12}NCO$ (at 200 °C for 4–5 h) gives tributyltin chloride, tributylstannyl isocyanate, bistributylstannylcarbodi-imide, and a polymer of 6-chlorohexyl isocyanate[200].

The structure of the equimolecular adducts of phenyl isocyanate with trimethyl- and triphenyl-stannylcyanamide has not been established with certainty. It is supposed[123,139] that the stannyl group can add both to nitrogen and to oxygen atoms. More definite conclusions have been reached[123,190] concerning the structure of the products of the action of phenyl isothiocyanate on bistriphenylstannylcarbodi-imide (in benzene at 26 °C):

$$Ph_3SnN{=}C{=}NSnPh_3 + PhN{=}C{=}S \rightarrow$$
$$\rightarrow \underset{\underset{Ph_3SnN-C\equiv N}{|}}{\overset{PhN=C-SSnPh_3}{}} \xrightarrow{H_2O} \underset{\underset{HN-C\equiv N}{|}}{\overset{PhN=C-SSnPh_3}{}} .$$

An organotin derivative of cyanoisothiourea can be obtained also by the action of phenyl isothiocyanate on triphenylstannylcyanamide:

$$Ph_3SnNHCN + RN{=}C{=}S \rightarrow \underset{\underset{HN-C\equiv N}{|}}{\overset{RN=C-SSnPh_3}{}} .$$

The rate of the reaction increases with the nature of the radical in the isothiocyanate in the sequence[123,190]

$$p\text{-}O_2NC_6H_4NCS > PhNCS > PhCH_2NCS \sim$$
$$\sim p\text{-}EtOC_6H_4NCS > EtNCS .$$

N-Triphenylmethyl-*N'*-triphenylstannylcarbodi-imides had not reacted with an isothiocyanate in ether at 28 °C after 23 h.[123]

Trialkylstannylcyanamides react with yet another hetero-cumulene system--carbon disulphide[50]:

$$R_3SnNHCN + CS_2 \rightarrow HN{=}\underset{\underset{NH_2}{|}}{C}{-}NHC{\equiv}N +$$
$$+ R_3SnSSnR_3 + NCN{=}\underset{\underset{NC-NSnR_3}{|}}{C}SSnR_3$$
$$R = Me, Ph, PhCH_2 .$$

It has been reported also[117] that organogermanium carbodi-imides do not react with carbon disulphide.

V. ASPECTS OF PRACTICAL APPLICATION

Hetero-organic carbodi-imides and cyanamides have recently begun to find practical application in the synthesis of various polymers and difficultly accessible organic compounds, as well as in certain industrial chemical processes. Thus bistrimethylsilylcarbodi-imide has been successfully tried as a moisture stabiliser for polyurethanes based on complicated polyesters employed for the production of artificial leather and other purposes[203]. It has been proposed as a substitute for the most widely used for these purposes, 2,2,6,6-tetraisopropyldiphenylcarbodi-imide (Stabaksol 1). Oligomers and polymers containing a carbodi-imide group in the macromolecular chain, obtained by the interaction of organosilicon diols and isocyanatocarbodi-imides, are used for the stabilisation of polyester–urethanes to moisture and heat. Additions of 0.1–3% to polyurethanes significantly enhance their resistance to high temperatures and moisture[204].

Polymeric organosilicon carbodi-imides, obtained by the action of polychlorosilanes or chlorosilanes on bisdimethylsilylcarbodi-imide, can be used as insulating coatings, components of high-temperature colorants, etc., in cases in which high heat resistance is required[118–121]. Furthermore, such polymers are stable to irradiation, which permits their use in various types of packing operating under conditions of intense irradiation. For example, polysilylcarbodi-imide $[(C_6H_5)_2SiNCN]_n$ of molecular mass 4285 undergoes no loss in weight when heated in nitrogen to 400 °C, and retains its elasticity when exposed to an [electron irradiation] dose of 2000 MR g^{-1}.[118–121]

Organotin carbodi-imides have been suggested as heat stabilisers for polyvinyl chloride compositions[205,206]. They are also effective catalysts for urethane formation[207–211]. Thus bistributylstannylcarbodi-imide has been used as catalyst for the preparation of film-forming polyurethane coatings based on organosilicon polyols and aliphatic polyisocyanates of biuret structure[209]. Bistrimethylsilylcarbodi-imide is also a heat stabiliser for polyvinyl chloride, but considerably less effective than organotin carbodi-imide[212].

Organotin cyanamide derivatives possess antibacterial activity[139,188]. Organolead cyanamides of type $(CH_3)_3 \cdot PbNHC{:}N$ are employed as extremely efficient antioxidants and additives in lubricating and engine oils[51,213].

Hetero-organic carbodi-imides can also be employed as intermediates in the synthesis of various difficultly accessible organic compounds, e.g. dialkylcyanamides[112,122] and 1,3,5-triazines[138,194,195,197,199].

There is no doubt that the fields of practical application of hetero-organic cyanamides and carbodi-imides of Group IVB elements have not been fully studied. Further, more thorough investigation of the chemical properties of these interesting compounds will make it possible to extend considerably the range of their practical application.

* * *

During preparation of this Review for the press additional publications have appeared on the synthesis[214–219] and properties[219–221] of organosilicon and organogermanium carbodi-imides.

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