PSEUDOHALIDES OF GROUP IIIB AND IVB ELEMENTS

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I. Introduction

This review deals with the azides, cyanides, isocyanates, and isothiocyanates of the nontransition elements of Groups III and IV, and their isomers (e.g., MNC as well as MCN) when these exist. The literature is covered to the beginning of 1966 (see also *183a*).

The aim has been to provide a substantially complete account of published work, including a general description of the chemistry for each class of pseudohalide (Sections II–V). Individual compounds, with numerical data and references, are listed in Tables I–IV.

The term "pseudohalide" was originally (*31a, 40a*) coined collectively to describe groups such as cyanide, thiocyanate, azidothiocarbonate, selenocyanate, tellurocyanate, cyanate, azide, and their structural isomers, in order to emphasize the physical and chemical resemblances between them and the halides. It is perhaps useful to consider the structural and electronic features which they have in common. These are that they are polyatomic, linear, electronegative (i.e., will exert a $-I$ effect when covalently bound to a Group IIIB or IVB element), and capable of participating in intramolecular π-bonding with a neighboring electrophilic center. This $+M$ effect is made possible by virtue of their unsaturation and/or the possession of formally nonbonding electrons on the atom which provides the donor site. With groups other than azide, the donor site may in principle be one of two (e.g., N or O in M—N═C═O and M—O—C≡N), and this presents us with the possibility of structural isomerism. A geometric consequence of strong π-interaction between the element M and the pseudohalide is linearity at the donor site; for example, in $H_3SiN{=}C{=}S$ the SiNC angle is 180°, indicating substantial Si—N multiple-bond character (see Section V). There seems to have been only a single study relating to the comparative electronic effects of halide and pseudohalide (so far only —NCO and —NCS) groups when attached to Group IIIB and IVB elements, and this is for boron compounds (*114*, *150*). Acceptor strengths, with respect to both pyridine (calorimetric data) and ethyl acetate (infrared spectroscopic data), decreased in the series $>$B—Br $>$ $>$B—Cl $>$ $>$B—NCS $>$ $>$B—NCO $>$ $>$B—F, and this probably reflects the inverse ability of these halides and pseudohalides to π-bond with boron. The same order was found also for (a) the electronegativity (from ^1H n.m.r.) of nitrogen in $(XBNC_2H_5)_3$ (e.g., 3.1 for X = F and 3.56 for X = Br), and (b) the intensity of the NH infrared stretching mode in $(XBNH)_3$. No results are yet available to throw light on relative electronegativities of the groups X. In the boron series, ^{11}B nuclear magnetic resonance measurements on both $>$B—X and $-\overset{\backslash\,-}{\underset{/}{\mathrm{B}}}\mathrm{X}$ may prove informative.

A further consequence of unsaturation in the pseudohalide group X is the possibility of addition reactions. In this way, X may behave as a functional group rather than a halide. This problem is analyzed (Section III,C).

II. Azides

A. Introduction

Hydrazoic acid was discovered in 1890 (*50*). Many inorganic and organic derivatives have been prepared. Reviews (*29*, *39*, *180b*) relating to these compounds have been published, but only recently was attention turned to the preparation of organometallic azides. Some of these have proved remarkably stable to thermal decomposition. (See Table I.)

TABLE I
DATA ON AZIDES*

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties[a]
$B(N_3)_3$	—	—	(*199*)	—
$LiB(N_3)_4$	—	—	(*200*)	—
$(Me_2N)_2BN_3$	—	38–42/2	(*128, 138a, 141*)	B (*128, 141*)
$(Et_2N)_2BN_3$	—	90–93/12	(*128, 141*)	B (*141*)
$Me_2NB(N_3)_2$	—	53–55/12	(*128, 141*)	B (*141*)
$Et_2NB(N_3)_2$	—	75–77/12	(*128, 141*)	B (*141*)
Ph_2BN_3	—	—	(*140, 140a*)	—
$Ph_2BN_3 \cdot C_5H_5N$	—	89–92/HV	(*139, 140*)	—
$PhB(N_3)_2 \cdot C_5H_5N$	—	140/HV	(*140*)	—
$B(N_3)_3 \cdot C_5H_5N$	—	130/HV	(*140*)	—
$(Cl_2BN_3)_3$	67	—	(*140a, 140b*)	B, H (*140b*)
$(Br_2BN_3)_3$	94.5	—	(*140b*)	B, H (*140b*)
$[HNB(N_3)]_3$	—	—	(*138*)	—
$[Bu^tNB(N_3)]_4$	275–7	—	(*185, 185a*)	—
$[Am^tNB(N_3)]_4$	261–3	—	(*185, 185a*)	—
$H_3N_3B_3(N_3)Cl_2$	70–73	—	(*128*)	—
$Me_3N_3B_3(N_3)Cl_2$	—	—	(*128*)	—
Et_2AlN_3	—	—	(*143a*)	—
$Al(N_3)_3$	—	—	(*100, 197*)	—
$MeAl(N_3)_2$	—	—	(*199*)	—
$MeOAl(N_3)_2$	—	—	(*199*)	—
$Ga(N_3)_3$	—	—	(*202*)	—
Me_2TlN_3	—	—	(*109b*)	—
TlN_3	c. 334	—	(*213*)	—
$PhTl(N_3)_2$	d. 200	—	(*44*)	—
Ph_2TlN_3	d. 321	—	(*30a*)	—
H_3SiN_3	−81.8	−28/760	(*61*)	—
D_3SiN_3	—	—	(*61*)	—
Me_3SiN_3	−95	92–93/760	(*32, 33, 35, 36, 47, 151, 155a, 178, 179a, 180c, 182, 196, 205*)	A, B, (*47, 180c*), D (*47*), E
Me_2SiClN_3	—	—	(*179a, 180*)	—
$MeSiCl_2N_3$	—	100.5/760	(*179a, 180*)	—
Ph_3SiN_3	79–80	—	(*36, 151, 179a, 181, 196, 203–207*)	B (*207*)
Ph_2MeSiN_3	—	196–198/47	(*155a*)	—
$PhMe_2SiN_3$	—	70/15	(*196*)	—
$2\text{-}PhC_6H_4SiMe_2N_3$[b]	—	152/65	(*80a*)	—
$Me_2Si(N_3)_2$	—	144.3/760	(*151, 178, 179a*)	B (*178*)
$MeSiCl(N_3)_2$	—	47/20	(*179a, 180*)	—
$Ph_2Si(N_3)_2$[c]	—	85–90/0.01	(*151, 179a, 203, 206*)	C (*206*)
$MeSi(N_3)_3$	—	70–73/30	(*151, 179a*)	—
$PhSi(N_3)_3$	—	63/0.01	(*151, 179a, 182*)	—

TABLE I (*Continued*)

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties[a]
$Si(N_3)_4$	—	—	*(201)*	—
Me_3GeN_3	−65	138/760	*(155, 157, 180c, 182)*	A *(182)*, B *(180c, 182)*
Ph_3GeN_3	102–103	—	*(151, 157a, 181)*	—
$Me_2Ge(N_3)_2$	−14	43.5/2	*(155, 157)*	—
Me_3SnN_3	119.5–121.5	—	*(96, 96a, 123, 180c, 182)*	A *(182)*, B *(180c, 182)*, J *(96a)*
$Bu^n{}_3SnN_3$[d]	—	118–120/0.18	*(123)*	B
$(PhCMe_2CH_2)_3SnN_3$	96–96.5	—	*(96, 151a)*	J
Ph_3SnN_3	115–116	—	*(96, 96a, 123, 151, 181)*	B *(123)*, J *(96a)*
Cl_3SnN_3	—	—	*(53)*	B
$Me_2Sn(N_3)_2$	—	—	*(154)*	—
Ph_3PbN_3	186–187	—	*(118, 119a, 151, 181)*	A *(119a, 181)*, B *(118, 181)*
$Pb_2Pb(N_3)_2$	—	—	*(119a)*	A
$Pb(N_3)_2$	—	—	*(51)*	—
Me_3PbN_3	—	—	*(180c, 182)*	A, B

[a] For all tables: A = ultraviolet; B = infrared; C = nuclear magnetic resonance; D = vapor pressure; E = heat of vaporization; F = Trouton constant; G = microwave spectrum; H = Raman spectrum; I = electron diffraction; J = Mössbauer spectrum. K = X-ray diffraction.

[b] n_D = 1.5887, 20°C. [c] n_D = 1.5097, 25°C. [d] n_D = 1.5745, 25°C.

* See data added in proof, p. 184.

B. PREPARATION

Two methods have been used for the preparation of the majority of organometallic azides, and these are summarized in Eqs. (1) and (2):

$$MH + HN_3 \rightarrow MN_3 + H_2 \tag{1}$$

$$MX + M'N_3 \rightarrow MN_3 + M'X \tag{2}$$

where M = B, Al, Ga, or Si; M′ = Li, Na, or K; and X = F or Cl.

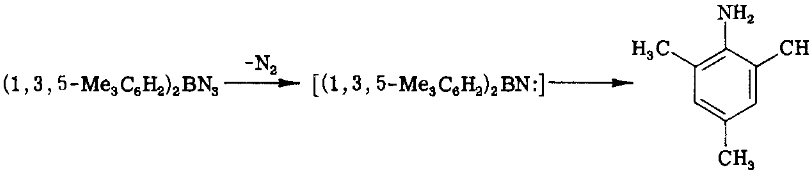
Triazidoborane was synthesized by passing diborane into a cooled ether solution containing excess hydrazoic acid and allowing the mixture to attain room temperature (*199*). Rapid evolution of hydrogen began at 20° and the reaction afforded high yields of triazidoborane:

$$B_2H_6 + 6HN_3 \rightarrow 2B(N_3)_3 + 6H_2 \tag{3}$$

Addition of trimethylamine to the ether solution gave $HB(N_3)_2$ and H_2BN_3, isolated as stable addition compounds with the amine. It has also been claimed that the acid $HB(N_3)_4$ is formed during the preparation of triazidoborane, but this was supposed stable only at low temperature.

Hydrazoic acid readily reacted with lithium borohydride yielding (90%) lithium tetraazidoborate, $LiB(N_3)_4$. The triazidoborane and lithium azide were assumed to be intermediates in the formation of this compound (*200*).

Using Eq. (2), other boron azides were prepared. The reaction of sodium azide and aluminum chloride with dimesitylfluoroborane in tetrahydrofuran yielded dimesitylazidoborane. This, however, was not isolated, but was hydrolyzed to give mesidine, thus indicating that a Curtius rearrangement had taken place (*117*):



(4)

From dialkylaminochloroboranes and lithium azide, in refluxing benzene or toluene, moderate yields of the azidoboranes were obtained (*128*, *141*); similarly prepared were Ph_2BN_3 (*140*) and Cl_2BN_3 (*140a*, *140b*), from Ph_2BCl and BCl_3, respectively:

$$(R_2N)_{3-n}BCl_n + nLiN_3 \rightarrow (R_2N)_{3-n}B(N_3)_n + nLiCl \qquad (5)$$

where R = Me or Et, and $n = 1$ or 2.

Likewise, using *B*-trichloroborazine and *B*-trichloro-*N*-trimethylborazine with one equivalent of lithium azide gave the *B*-azido-*B′*,*B″*-dichloroborazines (*128*). $[(N_3)BNH]_3$ (*138*) and two azidoborazocines (*185*, *185a*) [derivatives of $(HBNH)_4$] have been reported, the latter prepared using NaN_3 in a polar solvent.

The interaction of chlorodiphenylborane and sodium azide, using pyridine as a solvent, resulted in a 90% yield of pyridine-azidodiphenylborane, after the mixture had been stirred for several days at room temperature (*139*):

$$Ph_2BCl + NaN_3 \xrightarrow{\text{pyridine}} Ph_2BN_3{\cdot}py + NaCl \qquad (6)$$

Various aluminum azides were synthesized by using Eqs. (1) and (2). An almost quantitative yield of aluminum azide was obtained from the interaction of aluminum hydride and hydrazoic acid at −116°, using ether as a solvent. Addition compounds, such as $AlH_3{\cdot}NMe_3$ and $AlH_3{\cdot}2NMe_3$, under similar conditions, yielded insoluble (THF) products, and these were assumed (*197*) to be complex azides:

$$[R_3NH][Al(N_3)_4] \qquad \text{or} \qquad [R_3NH]_2[Al(N_3)_5]$$

Sodium azide and aluminum chloride reacted readily at 20° in tetrahydrofuran (THF) yielding (89%) aluminum triazide (*100*).

Alkyl and alkoxy aluminum azides were obtained by reactions according to Eqs. (7) and (8), respectively (*199*):

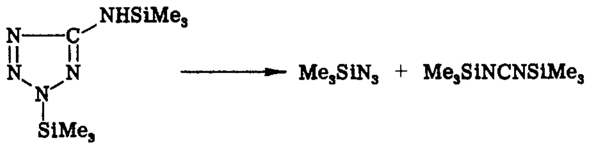
$$Me_3Al + 2HN_3 \rightarrow MeAl(N_3)_2 + 2CH_4 \tag{7}$$

$$MeAl(N_3)_2 \xrightarrow{[O]} MeOAl(N_3)_2 \tag{8}$$

A procedure identical with that used in the synthesis of aluminum triazide yielded gallium triazide from GaH_3/HN_3 (*202*); gallium hydride is stable only in complexed form.

Equation (2) has been used for all the azidosilanes prepared to date. From various silyl chlorides and sodium or lithium azide, tetraazidosilane (*201*), trimethyl- (*32, 47, 178, 196*) and triphenyl- (*196, 203, 204*) azidosilanes, dimethyl- (*178*) and diphenyl- (*204*) diazidosilanes, and phenyltriazidosilane (*203*) were obtained. Various other derivatives of silicon (*179a, 180, 205, 206*), germanium (*155, 157*), tin (*181, 182*), and lead (*151, 181, 182*) have been prepared similarly. Among the less common solvents were pyridine (*206*) and tetrahydrofuran (*205*), while from chlorosilanes and NaN_3, using molten salts as solvents, $MeCl_2SiN_3$, $MeClSi(N_3)_2$, and Me_2ClSiN_3 were obtained (*179a, 180*).

Trimethylazidosilane was also prepared by thermolysis of 1-(*N*-trimethylsilylamino)-3-trimethylsilyltetrazole [likewise, the 1,2-isomer gave Me_3SiN_3 + $Me_3SiNHCN$ (*61*)], and by interaction of hydrazoic acid and hexamethyldisilazane (*32*). Silylamine and hydrazoic acid gave H_3SiN_3 (*61*).



(9)

$$Me_3SiNHSiMe_3 + 3HN_3 \rightarrow 2Me_3SiN_3 + NH_4N_3 \tag{10}$$

Interaction of trimethylazidosilane and dimethyldichlorosilane, in the presence of aluminum chloride, gave dimethyldiazidosilane in almost quantitative yield (*178*):

$$2Me_3SiN_3 + Me_2SiCl_2 \xrightarrow{AlCl_3} Me_2Si(N_3)_2 + 2Me_3SiCl \tag{11}$$

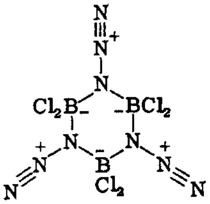
Trimethyl-, tri-*n*-butyl-, and triphenyl-tin azides were obtained from the corresponding chlorides and sodium azide (*123*). Attempts to prepare the tetraazide by the interaction of tin(IV) chloride with sodium azide resulted in the formation of $Na_2Sn(N_3)_6$ (*201*). An azidochlorostannane was made using Eq. (12) (*53*):

$$SnCl_4 + ClN_3 \xrightarrow{<20^\circ} Cl_3SnN_3 + Cl_2 \tag{12}$$

Triphenyllead(IV) azide was obtained when an ethanolic suspension of the hydroxide was treated with a chloroform solution of hydrazoic acid (*118*, *119a*); $Ph_2Pb(N_3)_2$ was prepared similarly from $(Ph_2PbO)_n$.

C. PROPERTIES

The triazides of boron, aluminum, and gallium, and tetraazidosilane are all solids, soluble in some polar organic solvents (e.g., tetrahydrofuran). They are very reactive, hydrolyze rapidly, and are extremely sensitive to percussion. The only compounds reported as oligomeric or polymeric are some tin azides and $(Cl_2BN_3)_3$ and $(Br_2BN_3)_3$ (*140a*, *140b*), for which a cyclic structure was proposed:



Some tin azides R_3SnN_3 have been regarded as polymeric in the solid state with tin in a bipyramidal five-coordinate environment and azide bridging groups, on the basis of infrared (*123*) and Mössbauer (*96a*) spectral data; the hindered $(PhCMe_2CH_2)_3SnN_3$, however, is monomeric (*151a*).

The alkyl and aryl azido compounds of silicon, tin, and lead, bisdimethylaminoazidoborane, and the azidoborazines, on the other hand, have high thermal stability. Evolution of nitrogen was slow even at elevated temperatures; thus, triphenylazidosilane was recovered quantitatively after heating at 400° in the presence of copper powder (*203*), and the azidoborazines lost nitrogen very slowly when heated at 200° (*128*).

The stability of the phenylazidosilanes was attributed to *pπ-dπ* NSi bonding, which may also be responsible for the expected linearity of the $\equiv SiN_3$ skeleton. The proton magnetic resonance spectrum of triphenylazidosilane was said to indicate a marked degree of overlap of the *d* orbitals of the silicon atom with the π-system of the benzene ring. That this is not the sole factor contributing to the stability of the azide is clear from the high stability of the alkyl derivatives. The infrared spectra of the series Me_3MN_3 (M = Si, Ge, Sn, and Pb) have been examined (*180c*).

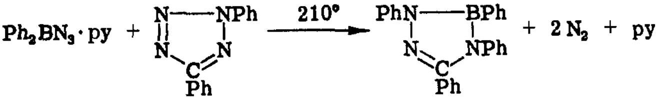
Pyridine-azidodiphenylborane underwent a number of reactions at 200°–250° in sealed tubes (*139*, *140*). A nearly quantitative yield of hexaphenylborazine was obtained from simple pyrolysis of the azide (*139*). Clearly, this involves migration of a phenyl anion from boron to nitrogen:

$$3Ph_2BN_3{\cdot}py \xrightarrow{200^\circ} (PhNBPh)_3 + 3N_2 + 3py \tag{13}$$

Heating the azide with excess dimethylamine gave a low yield of 1-phenyl-2,2-dimethylhydrazine, indicating that Ph_2BN (analogous to a carbene) may have been an intermediate in the decomposition:

$$Ph_2BN_3{\cdot}py \xrightarrow[\text{excess } Me_2NH]{250°} Ph_2BNHNMe_2 + N_2 + py \qquad (14)$$

The presence of another intermediate, PhB=NPh, was postulated (*139*) to account for the formation in low yield of 1,2,3,5-tetraphenyl-1,3,4-triaza-2-borole, when the pyrolysis was carried out in the presence of 2,5-diphenyltetrazole, which is known to be a source of the 1,3-dipole $\overset{+}{\mathrm{PhC}}{=}\mathrm{N}{-}\overset{-}{\mathrm{N}}\mathrm{Ph}$:



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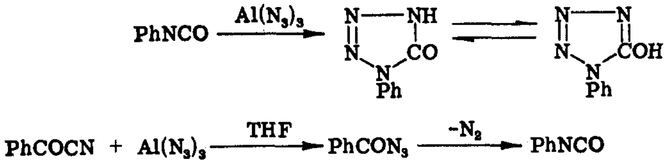
Pyrolysis of Ph_2BN_3 in the absence of pyridine gave $(PhBNPh)_2$ and nitrogen (*140*); $(Me_2N)_2BN_3$ after 17 hours at 220° gave N_2, Me_2NH, and a resin (*141*); $(Et_2N)_2BN_3$ after 18 hours at 280° afforded N_2, $B(NEt_2)_3$, and a resin; $R_2NB(N_3)_2$ (R = Me or Et) at 210° gave N_2 corresponding to one azide group; and Cl_2BN_3 at 200° yielded N_2, BCl_3, and $(ClBNCl)_3$ (*140a*).

Aluminum triazide reacted with benzonitrile to give 5-phenyltetrazole in high yield (*198*).

1-Phenyl-5(4H)-tetrazolinone was obtained from the interaction of benzoyl cyanide (Eq. 16), or phenyl isocyanate (Eq. 17), and aluminum triazide (*99*), and also from the isomerization of phenylcarbamyl azide, when aluminum azide was the catalyst (*119*).



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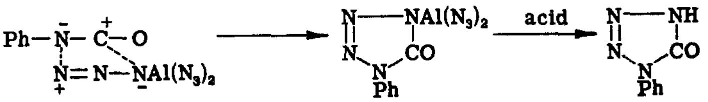

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The azidosilanes are hydrolyzed more slowly than the corresponding chlorides, and the hydrolysis is catalyzed by both acids and bases.

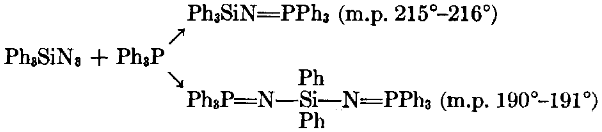
Triphenylazidosilane was completely decomposed by ultraviolet irradiation at 30°. Both photolysis and thermal degradation were believed to occur by the same mechanism as for organic azides, namely, through the formation of azene intermediates (*167*, *168*). Some doubt, however, was expressed (*47*) as to the validity of this interpretation when, from the pyrolysis of trimethylazidosilane, a complex mixture was isolated (including methane, ethane, acetylene, ethylene, hydrogen cyanide, hydrazoic acid, ammonium azide, hydrogen, and nitrogen). Azido-2-biphenyldimethylsilane, RMe_2SiN_3, upon photolysis gave nitrogen and 9,10-azasiladihydrophenanthrene (*80a*).

Azide-halogen exchange has been demonstrated for the following examples:

$$R_3SiN_3 + SbCl_5 \rightarrow R_3SiCl + Cl_4SbN_3 \tag{18}$$

$$Ph_3SiN_3 + [Et_3O]^+[BF_4]^- \rightarrow Ph_3SiF + Et_2O + N_2 + [EtHN{:}CHCH_3]^+[BF_4]^- \tag{19}$$

The phenylazidosilanes formed 1:1 complexes with triphenylphosphine (*196*). Triphenylazidosilane decomposed (*203*, *204*) slowly in benzene (50°) or ether (100°) in the presence of triphenylphosphine, to give *N*-silylphosphinimines:



$$Ph_3SiN_3 + Ph_3P \begin{cases} \nearrow Ph_3SiN{=}PPh_3 \text{ (m.p. 215°–216°)} \\ \searrow Ph_3P{=}N{-}\overset{Ph}{\underset{Ph}{Si}}{-}N{=}PPh_3 \text{ (m.p. 190°–191°)} \end{cases} \tag{20}$$

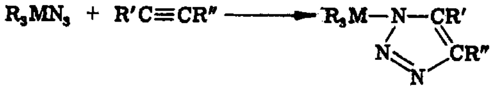
The loss of nitrogen did not follow first order kinetics, and only a maximum of 50% nitrogen was evolved. Side reactions resulting in the formation of $(Ph_3P{=}NH_2)^+N_3^-$ were postulated.

Other silicon (*35*, *181*, *194*, *206*) as well as germanium (*181*, *194*) and tin (*194*) azides also reacted with phosphines, either to form 1:1 adducts (*181*) or stable phosphinimines (*181*, *194*). However, silyl azide and halophosphines reacted by azide-halogen exchange, and the unstable azidophosphines readily lost nitrogen to afford cyclophosphazenes (*109*, *109a*).

Whereas Ph_3SiN_3 afforded $(Ph_2SiNPh)_2$ on pyrolysis, Ph_3SnN_3 and Ph_3PbN_3 gave Ph_4Sn or Ph_4Pb, respectively (*151*). It has been suggested that thermal decomposition of metallic monoazidochlorides may be utilized for preparing corresponding nitrides (*53*).

Group IV azides react with acetylenes to form triazoles; however, $Bu^n{}_3SnN_3/HOOCC{\equiv}CCOOH$ gave $Bu^n{}_3SnOCOC{\equiv}CCOOSnBu^n{}_3$ and hydrazine (*123*).

A number of 1:1 Lewis Acid adducts of Group IVB azides, such as $Ph_3MN_3{\cdot}BBr_3$ and $Ph_3MN_3{\cdot}SnCl_4$ (M = Si, Ge, or Sn) have been prepared (*183*). The complexes $R_3SiN_3{\cdot}SbCl_5$ ($R = CH_3$ or C_6H_5) (*183*) are highly unstable (see Eq. 18) (*208*), while H_3SiN_3 and BF_3 afford SiH_4 and SiH_3F (*61*).


(21)

[M = Si (*33, 36*) or Sn (*123a*; R′ = R″ = COOEt)]

III. Cyanides and Isocyanides

A. PREPARATION

There is some doubt as to whether the covalent organometallic cyanides of Group IIIB and IVB elements have the normal cyanide (M—C≡N) or the isocyanide (M—N═C) structure. In this section (A) the formulas and names will be written as they appear in the original publications and no structural implications are intended. (See Table II.)

Eight general types of reaction (Eqs. 22–28a) are available for the preparation of organometallic cyanides:

$$\mathrm{MH + HCN \rightarrow MCN + H_2} \tag{22}$$

$$\mathrm{MH + M'CN \rightarrow MCN + M'H} \tag{23}$$

$$\mathrm{MX + M'CN \rightarrow MCN + M'X} \tag{24}$$

$$\mathrm{MX + HCN \rightarrow MCN + HX} \tag{25}$$

$$\mathrm{MOH + HCN \rightarrow MCN + H_2O} \tag{26}$$

$$\mathrm{MOM + 2HCN \rightarrow 2MCN + H_2O} \tag{27}$$

$$\mathrm{MR + HCN \rightarrow MCN + RH} \tag{28}$$

$$\mathrm{MNR_2 + 2HCN \rightarrow MCN + [R_2NH_2]^+CN^-} \tag{28a}$$

Interaction of lithium boro- (*211*) or aluminum (*210*) hydrides and hydrogen cyanide at low temperature afforded the tetracyanides of boron and aluminum:

$$\mathrm{LiBH_4 + 4HCN \rightarrow LiB(CN)_4 + 4H_2}$$

$$\mathrm{LiAlH_4 + 4HCN \rightarrow LiAl(CN)_4 + 4H_2}$$

Treatment of lithium borohydride with a dioxane solution of hydrogen cyanide at 100° afforded lithium monocyanoborohydride, crystallizing with 2 moles of dioxane and, unlike $\mathrm{LiAl(CN)_4}$, stable in aqueous solution (*210*).

Attempts (*30a, 43*) have been made to repeat the synthesis of tricyanoborane, first reported in 1931 (*142*). The reaction of trihaloboranes (Cl or Br), either with hydrogen cyanide or with silver cyanide, yields highly unstable products which cannot be characterized.

Tricyanoborazine (*40, 52*) and *P*-hexamethyl-*B*-tricyanoborophane (*191*) have been synthesized from the corresponding chloride (Eq. 29) and iodide (Eq. 30), using a polar solvent; other cyanoborazines have been obtained similarly (*94*):

$$(HNBCl)_3 + 3AgCN \xrightarrow{CH_3CN} (HNBCN)_3 + 3AgCl \qquad (29)$$

$$(Me_2PBHI)_3 + 3KCN \xrightarrow{Me_2NCOH} (Me_2PBHCN)_3 + 3KI \qquad (30)$$

Di-*n*-butyl-, di-*i*-butyl-, and di-*i*-amyl-cyanoboranes were obtained according to Eq. (31) (*135*):

$$R_2BSR' + HCN \rightarrow R_2BCN + R'SH \qquad (31)$$

Di-*n*-butylcyanoborane has been prepared from the chloride by the metathetical reactions (32) and (33) (*65a*):

$$Bu_2BCl + AgCN \rightarrow Bu_2BCN + AgCl \qquad (32)$$

$$Bu_2BCl + Me_3SiCN \rightarrow Bu_2BCN + Me_3SiCl \qquad (33)$$

Interaction of potassium cyanide and diethylthallium chloride or phenylthallium dichloride in water afforded (Eqs. 34, 35) the corresponding cyano derivatives (*31*, *44*); Me_2TlF and KCN behaved similarly (*45*):

$$Et_2TlCl + KCN \xrightarrow{H_2O} Et_2TlCN + KCl \qquad (34)$$

$$PhTlCl_2 + 2KCN \xrightarrow{H_2O} PhTl(CN)_2 + 2KCl \qquad (35)$$

Phenylthallium dichloride reacted with 4 moles of potassium cyanide to give $K[PhTl(CN)_3]$, which on boiling in water gave hydrocyanic acid and a precipitate of diphenylthallium cyanide (*44*).

Dimethylmetal cyanides of Al, Ga, In, and Tl were obtained by route (28) (*45*).

Many organocyanosilanes are known and have usually been obtained by use of reaction routes (23) and (24).

By passing the vapor of halosilanes over silver cyanide at room temperature, or by the interaction of silver or mercury(II) cyanides and halosilanes in solution, a number of cyanosilanes have been prepared. Thus, H_3SiCN (*129*), $H_2SiMeCN$ (*64*), $HSiMe_2CN$ (*111*), H_3SiSiH_2CN (*48*), and $Me_3SiSiMe_2CN$ were synthesized using the vapor phase reaction; and Me_3SiCN (*37*, *48*, *56*), Cl_3SiCN (*105*), Et_3SiNC (*37*, *56*), $Et_2Si(NC)_2$ (*176*), and $Me_2Si(CN)_2$ (*126*, *127*) were obtained by the solution technique.

It is often advantageous not to use a solvent, from the standpoints of reaction times and yields (*57*).

In the synthesis of trichlorocyanosilane from hexachlorodisilane and mercuric cyanide, pentachlorocyanodisilane was postulated as an intermediate (*105*). Cleavage of the Si—Si bond gave a polymeric chloride and

TABLE II
DATA ON CYANIDES AND ISOCYANIDES

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties[a]
$LiB(CN)_4$	—	—	—	—	—	—	*(211)*	—
$LiBH_3CN$	—	—	—	—	—	—	*(211)*	—
$NaPh_3BCN$	—	—	—	—	—	—	*(212)*	—
$(H_2BCN)n$	—	—	—	—	—	—	*(65)*	—
$B(CN)_3$	—	—	—	—	—	—	*(43, 142)*	—
$Bu^n{}_2BCN$	57–58	—	—	—	—	—	*(65a, 135)*	B *(65a, 135)*
$Bu^i{}_2BCN$	145	—	—	—	—	—	*(135)*	—
$Am^i{}_2BCN$	—	—	—	—	—	—	*(135)*	—
$(HNBCN)_3$	—	—	—	—	—	—	*(40, 52)*	—
$(MeNBCN)_3$	150	—	—	—	—	—	*(94)*	—
$(PhNBCN)_3$	220	—	—	—	—	—	*(94)*	—
$Me_3N_3B_3(CN)_2Bu^n$	40	—	—	—	—	—	*(94)*	—
$Me_3N_3B_3(CN)Bu^n{}_2$	—	130/0.001	—	—	—	—	*(94)*	—
$(Me_2PBHCN)_3$	—	—	—	—	—	—	*(191)*	—
$LiAl(CN)_4$	—	—	—	—	—	—	*(210)*	—
$Al(CN)_3$	—	—	—	—	—	—	*(210)*	—
Me_2AlCN	89	—	—	—	—	—	*(45)*	B
Me_2GaCN	79	—	—	—	—	—	*(45)*	B
$In(CN)_3$	—	—	—	—	—	—	*(98a)*	—
Me_2InCN	147	—	—	—	—	—	*(45)*	B
Me_2TlCN	275 decomp.	—	—	—	—	—	*(45, 94b)*	B *(45)*, C *(94b)*
Et_2TlCN	—	—	—	—	—	—	*(31)*	—
Ph_2TlCN	318 decomp.	—	—	—	—	—	*(44)*	—
$PhTl(CN)_2$	228	—	—	—	—	—	*(44)*	—

H_3SiCN	32.4	49.6/760	—	—	—	—	(*58, 70, 129, 137, 177*)	B (*70*), C (*58*), G (*137*)
D_3SiCN	—	—	—	—	—	—	(*120*)	—
$MeSiH_2CN$	23.1	—	—	—	—	—	(*64*)	—
Me_2SiHCN	−60.9	—	—	—	—	—	(*111*)	—
$Me_2PhSiCN$	—	230–232/760	1.49983^b	—	0.95733^b	—	(*125*)	—
Me_3SiCN	11.5	117.8/760	1.3883	26	0.7834	20	(*37, 56, 57, 65, 70, 100a, 126, 127, 162, 179, 189*)	B (*5, 70, 162*)
Et_3SiCN	5.5	182/760	1.4270	26	—	—	(*37, 56, 70, 100a*)	B (*70*)
$Pr^n{}_3SiCN$	−8	229/760	—	—	—	—	(*56, 70*)	B (*70*)
n-HeptylSiH_2CN	—	204/760	1.4349	20	0.830	20	(*26*)	—
Ph_3SiCN	135–137	210/5	—	—	—	—	(*37, 70, 125*)	B (*70*)
Cl_3SiCN	−46.2	73.2/760 (extr.)	—	—	—	—	(*105*)	—
$Me_2Si(NMe_2)CN$	—	—	—	—	—	—	(*100a*)	—
$MeSi(NMe_2)_2CN$	—	—	—	—	—	—	(*100a*)	—
$MeSi(NEt_2)_2CN$	—	—	—	—	—	—	(*100a*)	—
$Me_2Si(NEt_2)CN$	—	—	—	—	—	—	(*100a*)	—
H_3SiSiH_2CN	—	—	—	—	—	—	(*48*)	—
$Me_3SiSiMe_2CN$	—	176.4/760 (extr.)	1.4374	30	0.8136	30	(*48*)	B, D, E, F
$Me_3Si(SiMe_2)_3CN$	—	—	—	—	—	—	(*187*)	—
$Me_3Si(SiMe_2)_4CN$	—	—	—	—	—	—	(*187*)	—
$Me_2Si(CN)_2$	84–85	168–169/760	—	—	—	—	(*126, 127*)	—
$Et_2Si(CN)_2$	33	214/760	—	—	—	—	(*56*)	—
$Ph_2Si(CN)_2$	46–48	142/2	1.5599^b	—	1.0904^b	—	(*103, 125*)	—
H_3GeCN	45–46.8	—	—	—	—	—	(*85, 110, 171, 172, 175, 176*)	B (*85, 172, 175*)
D_3GeCN	—	—	—	—	—	—	(*85, 110, 175*)	B (*85, 175*)
Me_3GeCN	38–38.5	—	—	—	—	—	(*162, 172*)	B (*162, 172*)

TABLE II (*Continued*)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	D_4	°C	Reference	Other properties[a]
$\mathrm{Et_3GeCN}$	18	213/760	1.4509	20	1.111	20	(*16, 25*)	—
$\mathrm{Pr^n_3GeCN}$	−13	253/760	1.4544	20	1.041	20	(*16, 22*)	—
$\mathrm{Pr^i_3GeCN}$	—	—	—	—	—	—	(*22*)	—
$\mathrm{Bu^n_2GeHCN}$	—	108–110/8	1.4527	20	1.050	20	(*24*)	—
$\mathrm{Pr^i_2Ge(CN)_2}$	—	—	—	—	—	—	(*22*)	—
$\mathrm{Ge(CN)_4}$	—	—	—	—	—	—	(*37, 132*)	—
$\mathrm{Me_3SnCN}$	184.5–186	—	—	—	—	—	(*157a, 162*)	B (*162*), K (*157a*)
$\mathrm{Et_3SnCN}$	163.5–165	249/760	—	—	—	—	(*28, 41, 122a, 124, 162, 188*)	B
$\mathrm{Et_2Sn(CN)I}$	—	—	—	—	—	—	(*41*)	—
$\mathrm{Pr^n_3SnCN}$	—	—	—	—	—	—	(*42*)	—
$\mathrm{Bu^n_3SnCN}$	90–93	—	—	—	—	—	(*49, 122a, 124*)	—
$\mathrm{Ph_3SnCN}$	260	—	—	—	—	—	(*122a, 215*)	—
$\mathrm{Me_2Sn(CN)_2}$	>400	—	—	—	—	—	(*122a*)	B
$\mathrm{Et_2Sn(CN)_2}$	—	—	—	—	—	—	(*122a, 215*)	—
$\mathrm{Pr^n_2Sn(CN)_2}$	—	—	—	—	—	—	(*55*)	—
$\mathrm{Bu^n_2Sn(CN)_2}$	220	—	—	—	—	—	(*122a*)	B
$\mathrm{Ph_2Sn(CN)_2}$	265	—	—	—	—	—	(*122a*)	B
$\mathrm{Et_3PbCN}$	189 decomp.	—	—	—	—	—	(*95, 116a*)	—
$\mathrm{Pr^n_3PbCN}$	135	—	—	—	—	—	(*156*)	—
$\mathrm{Ph_3PbCN}$	—	—	—	—	—	—	(*63, 116a*)	B
$\mathrm{Ph_2Pb(CN)_2}$	245–255 decomp.	—	—	—	—	—	(*116a, 195*)	—
$\mathrm{Ph_2Pb(OH)CN}$	—	—	—	—	—	—	(*116a*)	—

[a] See Table I for symbols used.

[b] Density and refractive index measured on supercooled liquid.

trichlorocyanosilane. The hypothesis is supported by the observation that pentamethylcyanodisilane gave a high yield of trimethylcyanosilane by thermal decomposition (Eq. 36) at 115°–130° (*48*):

$$\mathrm{Me_3SiSiMe_2CN \rightarrow Me_3SiCN + Me_3Si(SiMe_2)_{\mathit{n}}SiMe_2CN} \qquad (36)$$

n-Heptylcyanosilane was obtained by reaction (37) (*26*):

$$\mathrm{2\mathit{n}\text{-}C_7H_{15}SiH_3 + 2Hg(CN)_2 \rightarrow 2\mathit{n}\text{-}C_7H_{15}SiH_2CN + 2HCN + 2Hg} \qquad (37)$$

Trimethylcyanosilane was formed (Eq. 38) when trimethylchloromethylsilane was treated with silver cyanide (*144*), and when sodium and acetonitrile were reacted (Eq. 39) with trimethylchlorosilane in ether (*145*):

$$\mathrm{Me_3SiCH_2Cl + AgCN \rightarrow Me_3SiNC + AgCl + ?} \qquad (38)$$

$$\begin{aligned}\mathrm{Me_3SiCl + Na + CH_3CN \rightarrow Me_4Si + Me_3SiCN + Me_3SiCH_2CN + (Me_3Si)_2CHCN}\\ \mathrm{+\ Me_3SiCH{=}C{=}NSiMe_3}\end{aligned} \qquad (39)$$

Dichlorosilanes and silver cyanide behave differently. Refluxing Ph_2SiCl_2 and AgCN in benzene, or in the absence of solvent, was said to provide no reaction, whereas under the same conditions, with LiCN, $Ph_2Si(CN)_2$ was obtained in 68% yield (*103*). However, R_2SiCl_2 (R_2 = Me,Ph, or Me,$CH_2{=}CH$) and AgCN in benzene or ether gave a polymeric carbodiimide, $(R_2SiNCN)_n$ ($n = 6.7$–8.4) (*147*).

Triethyl- and triphenyl-cyanosilanes have been prepared according to Eq. (40) (*37*). Methyl trimethylacetate was continuously removed by distillation:

$$\mathrm{R_3SiOMe + Me_3CCOCN \xrightarrow{AlCl_3} R_3SiNC + Me_3CCO_2CH_3} \qquad (40)$$

When hexamethyldisilazane was treated with an ethereal solution of hydrogen cyanide, trimethylcyanosilane was obtained (Eq. 41) (*37*):

$$\mathrm{(Me_3Si)_2NH + 3HCN \rightarrow 2Me_3SiNC + NH_4CN} \qquad (41)$$

From organogermanium halides and silver or mercury(II) cyanides, with or without solvent, the following cyanogermanes were obtained: $EtGe(CN)_3$ (*12*), Et_3GeCN (*16*), $Pr^n{}_3GeCN$ (*16, 22*), $Pr^i{}_3GeCN$ (*22*), Me_3GeCN (*161, 162*), H_3GeCN (*171, 176*), D_3GeCN (*175*), and $Ge(CN)_4$ (*37, 132*).

The addition of mercury(II) cyanide to $Bu^n{}_2GeH_2$ (1:2) gave di-*n*-butylcyanogermane in 74% yield (*132*).

High yields of cyanogermanes were also reported from the interaction (Eq. 42) of bis(trialkylgermanium) oxides and hydrogen cyanide (*144*):

$$\mathrm{(R_3Ge)_2O + 2HCN \rightarrow 2R_3GeCN + H_2O} \qquad (42)$$

Tetracyanogermane was obtained from trimethylcyanosilane and germanium tetrachloride (Eq. 43), by heating in xylene and removing the chlorosilane as it was formed (*37*):

$$4Me_3SiCN + GeCl_4 \rightarrow Ge(CN)_4 + 4Me_3SiCl \qquad (43)$$

Triethylgermanium sulfonate provided a source (Eq. 44) for the cyanide (*25*):

$$Et_3GeSO_3R + KCN \rightarrow Et_3GeCN + RSO_3K \qquad (44)$$

Silver cyanide was the reagent used in the synthesis (Eq. 45) of trimethyltin cyanide from trimethyltin iodide in benzene (*161*, *162*):

$$Me_3SnI + AgCN \rightarrow Me_3SnCN + AgI \qquad (45)$$

In another synthesis (Eqs. 46, 47), aqueous potassium cyanide and ethereal solutions of organotin halides were employed (*124*, *188*):

$$Et_3SnBr + KCN \rightarrow Et_3SnCN + KBr \qquad (46)$$

$$Bu^n{}_3SnCl + KCN \rightarrow Bu^n{}_3SnCN + KCl \qquad (47)$$

Absolute ethanol has also been used as a solvent (*55*).

Attempts to prepare triphenyltin cyanide from the hydroxide and aqueous hydrogen cyanide (route 26), or from triphenyltin chloride and potassium cyanide (route 24), failed. However, by passing anhydrous hydrogen cyanide into triphenyltin hydroxide and washing the product with anhydrous hydrogen cyanide, triphenyltin cyanide was obtained (Eq. 48) in 95% yield (*215*):

$$Ph_3SnOH + HCN \rightarrow Ph_3SnCN + H_2O \qquad (48)$$

Likewise, bis(triethyltin) oxide and anhydrous liquid hydrogen cyanide gave (Eq. 49) triethyltin cyanide (*28*):

$$(Et_3Sn)_2O + 2HCN \rightarrow 2Et_3SnCN + H_2O \qquad (49)$$

Interaction of anhydrous hydrogen cyanide and either R_3SnNEt_2 or $R_2Sn(NEt_2)_2$ (R = Me, Et, Bu^n, or Ph) gave diethylammonium cyanide and R_3SnCN or $R_2Sn(CN)_2$, respectively (*122a*).

Organic derivatives of silicon, germanium, and tin have been shown to interchange cyanide groups (*28*, *57*, *171*).

For the preparation of organolead cyanides, reactions (50–52) have been used (*3*, *63*, *95*, *156*):

$$R_3PbX\ (X = Cl \text{ or } I) + MCN\ (M = Ag, K, \text{ or } Na) \rightarrow R_3PbCN + MCl \qquad (50)$$

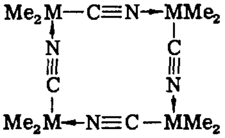
$$R_3PbOH + HCN \rightarrow R_3PbCN + H_2O \qquad (51)$$

$$R_3PbOH + NaCN \rightarrow R_3PbCN + NaOH \qquad (52)$$

B. STRUCTURES

We have here essentially three problems. These are (*i*) covalent versus ionic character [in the event, only the thallium derivatives are ionic; Me_2TlCN is soluble in water and its electrical conductance indicates it to be a strong 1:1 electrolyte, $Me_2Tl^+CN^-$ (*45*)]; (*ii*) degree of association (oligomeric and polymeric species are found only with B, Al, Ga, and In derivatives); and (*iii*), in covalent monomeric species, cyanide ($M—C{\equiv}N$) versus isocyanide ($M—N{=}C$) structures.

Tricyanoborane appears to be an unstable, polymeric solid which curiously showed no absorption band in the 2000–2300 cm^{-1} range (*43*, *94a*), while $(Bu^n{}_2BCN)_{20}$ is a low molecular weight polymer, as indicated by cryoscopy in benzene (*65a*). Compounds $(Ar_2BCN)_n$ are likewise polymeric (*114a*). The cyanodimethylmetallanes of Al, Ga, and In, on similar evidence, are tetrameric in benzene solution, and structure I has been proposed (*45*). Infrared spectra show CN stretching vibrations at 2213 (Al), 2202 (Ga), and 2101 (Tl) cm^{-1}.



(I)

The proton nuclear magnetic resonance spectra of H_3SiCN and Me_3SiCN are consistent with a normal M—CN structure, on the basis of comparative chemical shifts (within 0.02 p.p.m.), in $H_3SiC{\equiv}N$ and $H_3SiC{\equiv}CH$ (*58*). Bonding through nitrogen would probably require larger downfield shifts; thus the values in H_3SiNCO, H_3SiNCS, and $Me_3SiNCNSiMe_3$ are ~0.7 p.p.m. lower than in $H_3SiC{\equiv}CH$.

Spectroscopic evidence for H_3SiCN and D_3SiCN strongly suggested the normal structure (*120*), and this was further supported by the examination of the microwave spectrum of H_3SiCN (*137*, *165*). Similarly, infrared spectral data favored the normal structure for a number of R_3SiCN (R = H, Me, Et, *n*-Pr, Ph) derivatives (*70*). The structures of trimethylcyanosilane (*37*, *57*, *91*, *121*, *126*, *127*), trimethyl(iso)cyanogermane (*162*), and trimethyltin cyanide (*162*) have been the subject of much discussion in recent years, and it is now assumed on the basis of infrared spectra (*37*, *162*) and chemical studies (*162*) that these trimethyl derivatives may consist of equilibrium mixtures of the iso (M—NC) and normal (M—CN) structures. Comparison of the infrared spectra of Me_3SiCN and Me_3GeCN revealed two significant absorption bands in each case, at 2108 and 2198 cm^{-1} for the silicon compound, and at 2100 and 2197 cm^{-1} for the germanium compound, the first band being attributed to isocyanide, the second to the normal cyanide. The optical density of the $—C{\equiv}N$ band in trimethylcyanosilane and trimethylcyanogermane was about 4.5 times as great as that of the $—N{=}C$ band. Similar observations have been made on pentamethylcyanodisilane, where two maxima at 2183 and 2101 cm^{-1}, with the relative intensity ratio of ~3.2:1, have been noted, the former absorption band being due to the normal and the latter to the iso isomer. Triethyltin cyanide showed only one absorption band in the $—C{\equiv}N$ region at 2175 cm^{-1}. The absence of a second band does not exclude the possibility of the isocyanide isomer being present in very low concentration. The chemical and physical properties of trimethyltin cyanide are, however, more in line with those of a highly polar compound $\overset{\delta+}{Me_3Sn}—\overset{\delta-}{CN}$ rather than those of a mixture of covalent isomers, as in the case of the analogous silicon and germanium compounds, although chemical support for the iso structure in Bu_3SnNC has been forthcoming (*49*).

Evidence for the normal structure in germyl cyanide has been provided by vibrational studies on H_3GeCN and D_3GeCN, using also ^{13}C and ^{15}N enrichment (*85*); a simple linear $M—C{\equiv}N$ or $M—N{=}C$ model was taken, using a valence force field with no interaction constants. Potential energy and rotation-distortion constants and thermodynamic properties for these two molecules were calculated (*110*).

C. PROPERTIES

Aluminum tricyanide is stable for a short period when exposed to the atmosphere, but is hydrolyzed readily in water (*210*).

Dimethylaluminum, gallium, and indium cyanides, $(Me_2MCN)_4$, are all sensitive to moisture (*45*), while Me_2TlCN behaves as a salt in aqueous solution. $(Me_2GaCN)_4$, upon exposure to air, slowly liquefied, depositing crystals of $(Me_2GaOH)_4$; $(Me_2InCN)_4$ behaved similarly (*45*).

Trimethyl- and triethyl-cyanosilanes (*133*) and cyanogermane and its deutero analog (*175, 176*) reacted rapidly with water, according to Eqs. (53) and (54):

$$R_3SiCN + H_2O \rightarrow R_3SiOH + HCN \tag{53}$$

$$H_3GeCN + H_2O \rightarrow H_3GeOH + HCN \tag{54}$$

Study of the second reaction has been extended to hydrolysis in D_2O. Spectroscopic evidence excludes the possibility of H_3GeOD formation, as no $D—O$ absorption was observed in the 2500 cm^{-1} region. Formation of digermyl ethers was suggested (*175*).

Attempts to exploit triethyltin cyanide as a source of triethyltin carboxylic acid failed (*124*). Diethyltin dicyanide and triphenyltin cyanide decomposed (Eq. 55) readily in water (*215*). On the other hand, hydrolysis of dipropyltin dicyanide has been claimed to yield ammonia, and Eq. (56) was proposed (*55*):

$$Et_2Sn(CN)_2 + H_2O \rightarrow 1/n(Et_2SnO)_n + 2HCN \quad (55)$$

$$Pr_2Sn(CN)_2 + 4H_2O \rightarrow Pr_2Sn(COOH)_2 + 2NH_3 \quad (56)$$

Di-*n*-butylcyanoborane afforded $Bu^n{}_2BNH_2$ with ammonia (*65a*), while amines ($PhNH_2$, *n*-$BuNH_2$, or C_5H_5N) and $(R_2BCN)_n$ gave monomeric 1:1 adducts (*114a, 135*). Similar complexes were obtained from $(Me_2AlCN)_4$ or $(Me_2GaCN)_4$ and Me_3N (*45*).

Trimethyl- and triphenyl-cyanosilanes (*133*), dimethylphenylcyanosilane (*125*), and trimethylcyanogermane (*162*) readily added sulfur (Eq. 57):

$$MNC + S \rightarrow MNCS \quad (57)$$

This was taken as evidence for the presence of the iso isomers in these compounds. In contrast, cyanosilane (H_3SiCN) did not add sulfur at room temperature, but complex formation occurred upon heating (*120*). Trimethyltin cyanide was also converted to the isothiocyanate by treatment for 1 hour at 150°–160°. However, this should not be taken as support for the presence of the iso structure, since it is known that ionic cyanides react readily with sulfur at high temperatures to form thiocyanates (*166*), and tin cyanides would be expected to be highly polar [$Sn(\delta+)—CN(\delta-)$]. This is supported by data on the crystal structure of Me_3SnCN; much ionic character was indicated for Sn . . . CN bond (*157a*). The structure is polymeric, with infinite chains: . . . CN . . . Me_3Sn . . . CN . . . .

Trimethylcyanosilane and trimethyltin cyanide displaced carbon monoxide from $Fe(CO)_5$ (*161*), to give (Eq. 58) crystalline tetracarbonyl derivatives (*161*):

$$Me_3MNC + Fe(CO)_5 \rightarrow Me_3MNCFe(CO)_4 + CO \quad (58)$$

and thus resemble isonitriles (*98*).

Under high pressure and at elevated temperature using Raney nickel, reduction of trimethylcyanosilane occurred. The reaction sequence postulated (*126, 127*) was Eq. (59) or (60):

$$Me_3SiNC \xrightarrow{H_2} Me_3SiNCH_2 \xrightarrow[—CH_4]{H_2} Me_3SiNH_2 \rightarrow \tfrac{1}{2}(Me_3Si)_2NH + \tfrac{1}{2}NH_3 \quad (59)$$

$$Me_3SiNC \xrightarrow{H_2} Me_3SiNCH_2 \xrightarrow{H_2} Me_3SiNHCH_3 \xrightarrow[(—CH_4)]{H_2} Me_3SiNH_2 \rightarrow \tfrac{1}{2}(Me_3Si)_2NH + \tfrac{1}{2}NH_3 \quad (60)$$

Organocyanosilanes reacted with Grignard reagents in a manner (Eqs. 61, 62) analogous to that of the halides (*126, 127*):

$$Me_3SiNC + EtMgBr \rightarrow Me_3SiEt + Mg(CN)Br \quad (61)$$

$$Et_2Si(NC)_2 + 2MeMgI \rightarrow Et_2SiMe_2 + MgI_2 + Mg(CN)_2 \qquad (62)$$

Diborane formed addition compounds with cyanosilane (*65*), cyanogermane (*176*), and trimethylcyanosilane (*65*). The addition compounds $Me_3SiCNBH_3$ and $H_3SiCNBH_3$ decomposed (Eqs. 63, 64) at 100°, giving polymeric materials, $(H_2BCN)_n$, remarkably stable to water, oxygen, and heat (*65*):

$$Me_3SiCNBH_3 \rightarrow \frac{1}{n}(H_2BCN)_n + Me_3SiH \qquad (63)$$

$$H_3SiCNBH_3 \rightarrow \frac{1}{n}(H_2BCN)_n + SiH_4 \qquad (64)$$

Similarly (Eqs. 65, 66), haloboranes (F, Cl, and Br) reacted at low temperature with cyanosilanes (H_3SiCN and Me_3SiCN) (*65b*) and cyanogermanes [H_3GeCN (*176*) and Me_3GeCN (*162*)] (with BF_3 only), to give addition products which decomposed slowly at or below room temperature. The infrared spectra of $H_3SiCN{\cdot}BF_3$ and $H_3GeCN{\cdot}BF_3$ have been examined (*177*).

$$H_3SiCN + BX_3 \rightarrow H_3SiCNBX_3 \rightarrow (X_2BCN)_{12} + H_3SiX \qquad (65)$$

$$20Me_3SiCN + 20Bu^n{}_2BCl \rightarrow (Bu^n{}_2BCN)_{20} + 20Me_3SiCl \qquad (66)$$

The effect of heating pentamethylcyanodisilane for 7 hours at 175° has been studied (Eq. 67; $n = 3, 4$, and 7) (*187*):

$$nMe_3SiSiMe_2CN \rightarrow (n-1)Me_3SiCN + Me_3Si(SiMe_2)_nCN \qquad (67)$$

IV. Isocyanates

A. PREPARATION

The MNCO derivatives of the Group IIIB and IVB elements discussed in this section will be referred to as isocyanates, although in the original publications the normal structure may sometimes have been inferred from either their physical properties or chemical behavior. Most substances earlier described as cyanates have proved on re-examination to be the isomeric iso compounds. (See Table III.)

Four general methods (Eqs. 68–71) are available for the synthesis of organometallic isocyanates:

$$2MH + 2AgNCO \rightarrow 2MNCO + 2Ag + H_2 \qquad (68)$$

$$MX + HNCO + Base \rightarrow MNCO + Base{\cdot}HX \qquad (69)$$

$$MX + M'NCO \rightarrow MNCO + M'X \qquad (70)$$

$$MY + M'NCO \rightarrow MNCO + M'Y \qquad (71)$$

Reaction (70) refers to the transformation of a Group IIIB or IVB halide into the corresponding isocyanate, using the silver, mercury(II), lead(II), sodium, or potassium salt of cyanic acid. Reaction (71) refers to a "conversion" or "volatility" series, established for boron (*115*), silicon (*57*), germanium (*13*, *171*), and tin (*28*), whereby interchange of NCO, NCS, X, and other groups may be effected, usually by careful removal by fractionation of the most volatile component of an equilibrium mixture.

Examples of the use of reaction (70) in boron chemistry are shown in Eqs. (72–76).

In general, only with silver salts was benzene an effective solvent; sodium or lead salts reacted slowly, if at all, in nonpolar media or in the absence of a solvent such as acetonitrile or acetone (*112–115*). $Me_3N{\cdot}BCl_3$ reacted neither with silver cyanate in benzene nor with sodium cyanate in acetone, and this is probably due to the exceptionally strong N → B linkage (*150*).

$$BBr_3 + AgNCO \xrightarrow{(71)} B(NCO)_3 + 3AgBr \qquad (72)$$

$$Me_2BBr + AgNCO \xrightarrow{(87)} Me_2BNCO + AgBr \qquad (73)$$

$$(Bu^nO)_2BCl + AgNCO \xrightarrow{(112,\ 150)} (Bu^nO)_2BNCO + AgCl \qquad (74)$$

$$(MeNBCl)_3 \xrightarrow{AgNCO\ (113)} Me_3N_3B_3Cl_2NCO \xrightarrow{AgNCO} Me_3N_3B_3Cl(NCO)_2 \xrightarrow{AgNCO} (MeNBNCO)_3 \qquad (75)$$

$$py{\cdot}BCl_3 + 3AgNCO \xrightarrow{(114,\ 150)} py{\cdot}B(NCO)_3 + 3AgCl \qquad (76)$$

Reaction (68) has been demonstrated for the cases shown in Eqs. (77–79). However, an anomalous system was reaction (80).

$$2C_6H_{11}SiH_3 + 2AgNCO \xrightarrow{(23)} 2C_6H_{11}SiH_2NCO + 2Ag + H_2 \qquad (77)$$

$$2C_6H_{11}SiH_3 + 6AgNCO \xrightarrow{(23)} 2C_6H_{11}Si(NCO)_3 + 6Ag + 3H_2 \qquad (78)$$

$$(n\text{-}C_4H_9)_2GeH_2 + 2AgNCO \xrightarrow{(24)} (n\text{-}C_4H_9)_2Ge(NCO)_2 + 2Ag + H_2 \qquad (79)$$

$$IGe_2H_5 + AgNCO \xrightarrow{(131)} HNCO + GeH_4 + AgI \qquad (80)$$

Reaction (69) has so far been demonstrated only for a series of chlorosilanes, and the bases used were tertiary amines or amides (Eq. 81) (*186*, *194a*):

$$R_nSiCl_{4-n} + (4-n)HNCO + (4-n)Base \rightarrow R_nSi(NCO)_{4-n} + (4-n)Base{\cdot}HCl \qquad (81)$$

Treatment of organosilicon or germanium halides (Br or Cl) with a variety of salts of cyanic acid in solvents such as benzene, hexane, acetonitrile, and nitromethane has provided a route to isocyanates, according to Eq. (70) (*8–11*, *14*, *26*, *57*, *60*, *71*, *72*, *77*, *78*, *81*, *116*, *136*, *171*, *173*, *186*, *192*). Molten alkali halides have also been used as reaction media (*179*). No reaction took place between trimethylchlorosilane and potassium cyanate

TABLE III
DATA ON ISOCYANATES

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties[a]
$B(NCO)_3$	—	—	—	—	—	—	*(71)*	—
Me_2BNCO	−118, −119	41.3/760 (extr.)	—	—	1.146	−78	*(87)*	B *(87)*
$(MeO)_2BNCO$	—	48/88	1.3856	20	—	—	*(115)*	—
$(Bu^nO)_2BNCO$	—	65–66/2.5	1.4155	20	0.9613	20	*(112, 115, 150)*	B *(150)*
$(Bu^nO)(Pr^i_2N)BNCO$	—	64/0.1	1.4265	20	—	—	*(115, 150)*	B *(150)*
$(Bu^tO)(Pr^i_2N)BNCO$	—	32/0.05	1.4213	20	—	—	*(115, 150)*	B *(150)*
$(C_6H_{11}O)(Pr^i_2N)BNCO$	—	90/0.25	1.4529	20	—	—	*(115, 150)*	B *(150)*
$(Me_2N)_2BNCO$	—	30/0.3	1.4499	20	—	—	*(112, 115, 150*	B *(150)*
$(Et_2N)_2BNCO$	—	61/0.1	1.4475	20	0.8678	20	*(115, 150)*	B *(150)*
$(Pr^i_2N)_2BNCO$	—	73–75/0.005	1.4502	20	0.8933	20	*(115, 150)*	B *(150)*
$(Pr^i_2N)Bu^tNHBNCO$	—	41–43/0.01	1.4453	20	—	—	*(115, 150)*	B *(150)*
$(Bu^tNH)_2BNCO$	—	72/0.1	1.4376	20	—	—	*(115, 150)*	B *(150)*
$(CH_2NPr^n)_2BNCO$	—	61/0.9	1.4575	20	—	—	*(115)*	—
$(PhMeN)(Pr^i_2N)BNCO$	—	80/0.1	1.5051	20	—	—	*(115)*	—
$o\text{-}C_6H_4O_2BNCO$	—	54/0.2	1.5277	20	—	—	*(47a, 112, 115, 150)*	A *(150)*, B *(150)*
Ph_2BNCO	—	89/0.01	1.6092	20	1.105	20	*(112, 115, 150)*	B *(150)*
$Pr^i_2NB(NCO)_2$	—	74/2	1.4529	20	—	—	*(115, 150)*	B *(150)*
$PhB(NCO)_2$	—	60/0.2	1.5527	20	1.187	20	*(112, 115, 150)*	B *(150)*
$PhB(NR_2)NCO$	—	—	—	—	—	—	*(97)*	—
$PhB(NMe_2)NCO$	—	—	—	—	—	—	*(114)*	B, C
$(HNBNCO)_3$	166	—	—	—	—	—	*(112, 113, 150)*	B *(150)*
$(MeNBNCO)_3$	85–86	112/0.03	—	—	—	—	*(113, 150)*	B *(150)*
$(EtNBNCO)_3$	36	102/0.01	—	—	—	—	*(113, 114, 150)*	B *(150)*, C *(114)*
$(Pr^nNBNCO)_3$	—	118/0.003	1.4499	20	1.094	20	*(113, 150)*	A *(150)*, B *(150)*
$(Bu^nNBNCO)_3$	30	140/0.02	—	—	—	—	*(113, 150)*	B *(150)*

$(Bu^sNBNCO)_3$	—	134/0.01	1.4901	20	1.060	20	(*113, 150*)	B (*150*)
$(PhNBNCO)_3$	151–152	—	—	—	—	—	(*113, 150*)	A (*150*), B (*150*)
$Me_3N_3B_3Cl_2(NCO)$	56–57	—	—	—	—	—	(*113, 150*)	B (*150*)
$Me_3N_3B_3Cl(NCO)_2$	95	—	—	—	—	—	(*113, 150*)	B (*150*)
$Et_3N_3B_3Cl(NCO)_2$	—	98/0.025	—	—	—	—	(*113, 150*)	B (*150*)
$[Me_2PBH(NCO)]_3$	71–72	—	—	—	—	—	(*191*)	B
$(Bu^tNBNCO)_4$	237–238	—	—	—	—	—	(*185, 185a*)	B (*185a*)
$(Am^tNBNCO)_4$	240.5/245.5	—	—	—	—	—	(*185, 185a*)	B (*185a*)
$B(NCO)_3{\cdot}C_5H_5N$	34	154/0.02	—	—	—	—	(*150*)	B
$o\text{-}C_6H_4O_2BNCO{\cdot}C_5H_5N$	—	97/0.03	—	—	—	—	(*150*)	B
$Ph_2BNCO{\cdot}C_5H_5N$	172–175	—	—	—	—	—	(*150*)	B
$PhB(NCO)_2{\cdot}C_5H_5N$	143–145	—	—	—	—	—	(*150*)	A, B
$PhB(NCO)_2{\cdot}EtOAc$	—	(dissociates at 20/15)	—	—	—	—	(*150*)	B
H_3SiNCO	—	—	—	—	—	—	(*58, 60*)	A, B, C (*58*), D, E, F
Me_3SiNCO	−49	91/760	1.3960	20	0.867	20	(*34, 78, 79, 89, 90, 106b, 146, 148, 174, 176, 179, 180c, 214*)	B (*89, 180c*), I (*106b*)
Et_3SiNCO	—	165.1/760	1.4295	20	0.889	20	(*9–11*)	—
Ph_3SiNCO	95	372/760	—	—	—	—	(*78, 79, 81*)	—
F_3SiNCO	—	−6/760	—	—	—	—	(*75*)	—
Cl_3SiNCO	−69	86.8/760	1.4262	25	1.445	25	(*3*)	—
$(MeO)_3SiNCO$	—	137.6/760	1.3839	20	1.123	20	(*72, 73*)	—
$(EtO)_3SiNCO$	—	172.9/760	1.3922	20	1.015	20	(*78, 79*)	—
$MeCOOCH_2SiMe_2NCO$	—	51/12	1.4272	20	—	—	(*34*)	—
$Me_3SiSiMe_2NCO$	—	159.4–160/760	1.4337	30	0.8537	30	(*186*)	B, D, E, F
$(OCNCH_2CH_2O)_3SiNCO$	—	—	—	—	—	—	(*66*)	—
$CyclohexylSiH_2NCO$	—	163.7/760	1.4668	20	0.990	20	(*23*)	—
$Me_2Si(NCO)_2$	−31.2	139.2/760	1.4221	20	1.076	20	(*78, 79, 89, 174, 209*)	B (*89*)
$Et_2Si(NCO)_2$	—	176.7/760	1.4348	20	1.022	20	(*9–11*)	—
$Bu^n{}_3Si(NCO)_2$	—	96/3	1.4428	25	—	—	(*194a*)	—

TABLE III (*Continued*)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties[a]
$Ph_2Si(NCO)_2$	22.9	319.6/760	1.5675	20	1.188	20	(*78, 79, 194a*)	—
$F_2Si(NCO)_2$	−75	68.6/760	1.3536	20	1.437	20	(*75*)	
$Cl_2Si(NCO)_2$	−80	117.8/760	1.4380	25	1.437	25	(*3*)	—
$(MeO)_2Si(NCO)_2$	—	152.1/760	1.4028	20	1.208	20	(*72, 73*)	—
$(EtO)_2Si(NCO)_2$	—	175.4/760	1.4046	20	1.108	20	(*78, 79, 194a*)	—
$MeSi(NCO)_3$	2.7	170.8/760	1.4430	20	1.267	20	(*78, 79, 89*)	B (*89*)
$EtSi(NCO)_3$	—	183.5/760	1.4468	20	1.219	20	(*9–11*)	—
$Pr^nSi(NCO)_3$	—	192.2/760	1.4462	20	1.173	20	(*11*)	—
$Pr^iSi(NCO)_3$	—	192/760	1.4444	20	1.163	20	(*11*)	—
$Bu^nSi(NCO)_3$	—	215.5/760	1.4479	20	1.141	20	(*78, 79*)	—
$FSi(NCO)_3$	−29.2	134.3/760	1.4161	20	1.456	20	(*75*)	—
$ClSi(NCO)_3$	−35	152/760	1.4507	—	1.437	25	(*3*)	—
$MeOSi(NCO)_3$	—	168.4/760	1.4287	20	1.313	20	(*72, 73*)	—
$EtOSi(NCO)_3$	—	179.6/760	1.4251	20	1.236	20	(*78, 79*)	—
$PhOSi(NCO)_3$	—	251.9/760	1.5210	20	1.273	20	(*78, 79, 194a*)	—
n-Heptyl$Si(NCO)_3$	—	258/760	1.4516	20	1.077	20	(*26*)	—
Cyclohexyl$Si(NCO)_3$	—	253/760	1.4787	25	1.208	—	(*23*)	—
$[(OCN)_3Si]_2O$	—	—	—	—	—	—	(*76, 89, 149*)	B (*89*)
$(Me_3Si)_2NSi(NCO)_3$	−2	81/1	1.4647	20	1.088	20	(*192*)	B
$Si(NCO)_4$	26	185.6/760	1.4610	25	1.434	25	(*71, 89, 136, 174, 194a, 179*)	A (*136*), B (*89, 136*), H (*89, 136*)
H_3GeNCO	−44 ± 0.5	71.5/760 (extr.)	—	—	—	—	(*171, 172*)	B (*172*), E (*171*), F (*171*)
Me_3GeNCO	—	122/760	—	—	—	—	(*180c*)	B
Et_3GeNCO	—	200/760	1.454	20	—	—	(*8, 15, 25*)	—
$Pr^n{}_3GeNCO$	−19	247/760	1.4574	20	1.055	20	(*15*)	—
$Pr^i{}_3GeNCO$	—	—	—	—	—	—	(*21*)	—
$Bu^n{}_3GeNCO$	—	283/760	1.4595	20	1.044	20	(*17*)	—

Cl_3GeNCO	—	112/760	—	—	—	—	*(74)*	—
$Et_2Ge(NCO)_2$	—	226/760	1.4619	20	1.330	20	*(8)*	—
$Pr^i_2Ge(NCO)_2$	—	239/760	1.464	20	1.225	20	*(104)*	—
$Bu^n_2Ge(NCO)_2$	—	273/760	1.4634	20	1.179	20	*(24)*	—
$EtGe(NCO)_3$	−31	225 4/760	1.4739	20	1.534	20	*(8)*	—
$[(OCN)_3Ge]_2O$	—	—	—	—	—	—	*(104)*	—
$Ge(NCO)_4$	−8	195–199/760	1.4793	25	1.7694	24	*(8, 72, 116, 136)*	A *(136)*, B *(136)* D *(72, 116)*, E *(116)*, H *(136)*
Me_3SnNCO	105–107	—	—	—	—	—	*(180c)*	B
Et_3SnNCO	48	120–121/11	—	—	—	—	*(28, 173a)*	B *(173a)*
Et_3SnOCN	214	—	—	—	—	—	*(20, 41, 146)*	—
Bu^n_3SnNCO	—	144–7/13	1.490	20	—	—	*(136a, 173a)*	B *(173a)*
Bu^i_3SnNCO	—	103/0.3	1.489	21	—	—	*(173a)*	—
$Me_2Sn(NCO)_2$	—	—	—	—	—	—	*(82, 154)*	—
$Bu^n_2Sn(NCO)_2$	48–51	—	—	—	—	—	*(136a)*	—
Ph_3SnNCO	98–99	—	—	—	—	—	*(136a, 173)*	—
Me_3PbNCO	220 decomp.	—	—	—	—	—	*(180c)*	B
Et_3PbNCO	—	—	—	—	—	—	*(95)*	—

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[a] See Table III for symbols used.

in a nonpolar solvent, but in the absence of solvent a good yield of isocyanatosilane resulted (*38*).

Triethyllead isocyanate has been prepared by refluxing triethyllead chloride and potassium cyanate in alcohol (*95*).

For boron compounds, the following "conversion" (Eq. 71) series has been proposed (*115*): $>\!\mathrm{BBr} \rightarrow\ >\!\mathrm{BS} \longrightarrow\ >\!\mathrm{BCN} \rightarrow\ >\!\mathrm{BCl} \rightarrow\ >\!\mathrm{BNCS} \rightarrow\ >\!\mathrm{BNCO} \rightarrow\ >\!\mathrm{BO}$—. Thus, in general, it was possible to convert a compound on the left to one further on the right by the use of either a silver or a mercury(II) salt. It should be noted, however, that the system $2>\!\mathrm{BNCS/HgO}$ provided an anhydride, $>\!\mathrm{B{-}O{-}B}\!<\!/\mathrm{Hg(NCS)_2}$, and not the isocyanate.

For triethylsilyl compounds, conversion (71) may be effected (*14*, *17*, *27*) in the following directions:

$$\equiv\mathrm{SiNPh} \rightarrow \equiv\mathrm{SiNCS} \rightarrow \equiv\mathrm{SiI} \rightarrow \equiv\mathrm{SiNCO} \rightarrow \equiv\mathrm{SiBr} \rightarrow \equiv\mathrm{SiCl}$$

Examples of other such reactions are shown in Eqs. (82) (*19*), (83) (*20*), and (84) (*25*):

$$\mathrm{R_2Si(NHPh)_2 + Ph_2Si(NCO)_2 \rightarrow R_2Si(NCO)_2 + Ph_2Si(NHPh)_2} \qquad (82)$$

$$\mathrm{MeOSi(NCO)_3 + 3(Et_3Sn)_2O \rightarrow 6Et_3SnNCO + (MeOSiO)_2O} \qquad (83)$$

$$\mathrm{Et_3GeOSO_2R + Ph_3SiNCO \rightarrow Et_3GeNCO + Ph_3SiOSO_2R} \qquad (84)$$

These reactions are not of especial value for the preparation of isocyanates, because the starting materials are usually synthesized from the halides, and these can be converted directly to the isocyanates by means of Eq. (70).

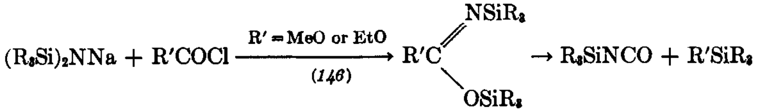
In addition to the general methods (Eqs. 68–71), isocyanatosilanes have been obtained by other routes, as illustrated in Eqs. (85–90). The urea procedure (analogous to Eq. 85) was unsuccessful in the boron field (*115*). For reaction (85), in the case of R=Me, $[\mathrm{Me_3SiNHCONH_3^+}]\mathrm{Cl^-}$

$$\mathrm{R_3SiCl + (NH_2)_2CO \xrightarrow{(81,\,90)} R_3SiNCO + NH_4Cl} \qquad (85)$$

$$\mathrm{Ph_3SiCl + NaNHCO_2Et \xrightarrow{(81)} Ph_3SiNCO + EtOH + NaCl} \qquad (86)$$

$$\mathrm{(Me_3Si)_2NH + COCl_2 \xrightarrow{(148)} Me_3SiNCO + Me_3SiCl + HCl} \qquad (87)$$

$$\mathrm{(Me_3Si)_2NH + 2PhNCO \xrightarrow{(214)} Me_3SiNCO + PhNHCONPhSiPh_3} \qquad (88)$$



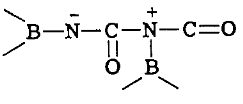
$$\mathrm{(R_3Si)_2NNa + R'COCl \xrightarrow[(146)]{R' = MeO\ or\ EtO} R'C{\genfrac{}{}{0pt}{}{\nearrow NSiR_3}{\searrow OSiR_3}} \rightarrow R_3SiNCO + R'SiR_3} \qquad (89)$$

$$\mathrm{MeCOOSiMe_2CH_2Cl + AgNCO \xrightarrow{(34)} AgCl + MeCOOCH_2SiMe_2NCO} \qquad (90)$$

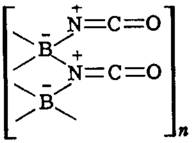
was proposed as an intermediate, while for reaction (90) the molecular rearrangement was believed to proceed by the intermediate $MeCOOSiMe_2CH_2{}^+NCO^-$. When the reagents of Eq. (88) were mixed in 1:1 stoichiometry, the product was the substituted urea. The reaction of urea with R_3SnOH or $(R_3Sn)_2O$ in a molten state (130–140°C) furnished R_3SnNCO (R = Et or Bu^i) in high yields (*173a*). With R_3SnCl, the results were poorer and $(Bu^n{}_2SnO)_n$ afforded $[Bu^n{}_2SnOSn(NCO)_2]_n$. The distannoxanes and isocyanic acid at 70–80°C gave R_3SnNCO (R = Et or Bu^n and water which was removed and an azeotrope with benzene, cyanuric acid gave the complexes $(R_3SnNCO)_3$. The urea reaction does not proceed through buret because adequate rate of reaction required more heating (160–170°C).

B. STRUCTURES

The compounds prepared to date are clearly covalent. The problem of molecular association has been seriously encountered only with derivatives of 3-coordinate boron. Propensity for polymerization among these compounds appears to decrease as follows: (*i*) $R_2BNCO > Ar_2BNCO > (R_2N)_2BNCO \geq (RO)_2BNCO$, (*ii*) $\rangle$BNCO $\geq$ $\rangle$BNCS, (*iii*) $B(NCO)_3$ (only known as a polymer) $> XB(NCO)_2 > X_2BNCO$, and (*iv*) acyclic $\geq$ cyclic (borazine) (*113–115*). These are largely qualitative observations, depending on the appearance after comparable times of solid precipitates from freshly prepared monomeric species. The relative tendencies toward polymerization (*i–iv*) would indicate that the greater the electron density at boron the greater is the stability of the monomer. Detailed information on the structures of the polymers is not available, except for infrared spectral data (*87*, *115*). These show the presence of both —NCO and C=O functions. Cyclic and linear structures are possible (*115*), but only the latter are indicated in structures II and III. Evidence in favor of polymers not directly involving boron (except in the side chains), as in structure II, is that (a) isocyanates of carbon, silicon, and phosphorus polymerize also (although less readily), (b) each of (*i*)–(*iv*) is explained, and (c) the spectral characteristics are appropriate. On the other hand, a point of contrast between boron and many other isocyanates is that the isocyanatoboranes do not depolymerize on heating. Infrared spectral data on Me_3SnNCO suggest a polymeric structure for the solid, since γ_{as} shifts to highest frequency in solution (*180c*).



(II)



(III)

The infrared spectra of Me_2BNCO (*87*), $(MeO)_2BNCO$ (*112, 114, 150*), $(HNBNCO)_3$, $(MeNBNCO)_3$, $Si(NCO)_4$ (*136*), $Me_{4-n}Si(NCO)_n$ (*89*), $(Me_3Si)_2NSi(NCO)_3$ (*192*), $Me_3SiSiMe_2NCO$ (*186*), $Ge(NCO)_4$ (*136*), and Me_3MNCO (M = Si, Ge, Sn, or Pb) (*180c*) have been recorded with full assignments of vibrational modes.

In isocyanatoboranes ν_{as}(NCO) was found at 2273 ± 30 cm^{-1} and ν_{sym}(NCO) at 1526 ± 20 cm^{-1} for a wide range of compounds (*87, 112, 114, 150*). The relatively high value for the latter mode, and calculations of force constants (*86*), have been taken as evidence for substantial BN π-bonding in B—NCO, while the intensities and band widths at half-height showed close correspondence with those found in organic isocyanates rather than cyanates (*87, 112, 114, 150*). The number of observed fundamental frequencies in Me_2BNCO agreed with that for a molecule having C_{2v} symmetry (*87*).

The infrared and Raman spectra of $Si(NCO)_4$ and $Ge(NCO)_4$ in the range 4000–80 cm^{-1} are very simple, indicating that these molecules are highly symmetrical (*89, 136*). For the former, results are consistent with a tetrahedral model, while the spectrum of $Ge(NCO)_4$ deviates slightly from that expected for a molecule belonging to the point group T_d.

The proton nuclear magnetic resonance spectrum of H_3SiNCO showed a line at lower field (~0.7 p.p.m.) than found in $H_3SiC{\equiv}CH$ and H_3SiCN, but similar to H_3SiNCS and $H_3SiNCNSiH_3$; this was taken as evidence for the $\succ$Si—N=C=O rather than the cyanato structure (*58*). The molecular structure of Me_3SiNCO in the gaseous state has been determined by electron diffraction (*106b*): $r_g(C{-}H) = 1.10 \pm 0.02$, $r_g(C{=}O) = 1.18 \pm 0.01$, $r_g(N{=}C) = 1.20 \pm 0.01$, $r_g(Si{-}N) = 1.76 \pm 0.02$, $r_g(C{-}Si) = 1.89 \pm 0.01$A, and $<(Si{-}N{-}C) = 150 \pm 3°$. It is interesting to note the substantial deviations from linearity.

C. PROPERTIES

The isocyanates of Groups IIIB and IVB vary in stability from the unstable dimethylisocyanatoborane, which polymerizes rapidly at 20°, through isocyanatogermane, stable at room temperature but decomposing at 50°–200° into polymeric hydrides and hydroacids $[_nH_3GeNCO \rightarrow (GeH_2)_n + {}_nHNCO]$, to triphenylisocyanatosilane which can be distilled at 372° without decomposition.

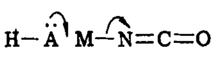
Reactions of isocyanates with protic reagents HA have been discussed (*113*). These are of interest primarily to determine whether there is a prevalence of substitution (pseudohalide behavior) or addition (functional group behavior) for a given class of compounds. This may be illustrated by Eq. (91):

$$\mathrm{HA} + \mathrm{MN{=}C{=}O}\!-\!\begin{cases} \to \mathrm{MA} + \tfrac{1}{3}(\mathrm{HNCO})_3 \\ \to \mathrm{M{\cdot}NH{\cdot}CO{\cdot}A} \end{cases} \tag{91}$$

Under S_N1 conditions, when M—N heterolysis is rate-determining, substitution will of necessity prevail; but under bimolecular conditions, product control is determined by competition between the two electrophilic sites, the central carbon atom (see Eq. 92) and M:

$$\mathrm{M{\cdot}N{:}C{:}O} + \ddot{\mathrm{A}}\mathrm{H} \rightleftharpoons \mathrm{M{\cdot}\bar{N}{\cdot}CO{\cdot}AH^+} \tag{92}$$

The nature of the transition state in the latter case depends on M, but it may in general require initial formation of a complex (as in structure V), or it may involve synchronous bond-making and bond-breaking (as in structure IV). The former is the relevant mechanism in the case of a trigonal boron pseudohalide, and the complex with a primary or secondary amine as the reagent may be pictured as in structure VI or VII. The competition between the boron atom and the carbon atom for the attacking nucleophile is affected also by the nature of the attacking reagent. This is so, because substitution at trigonal boron depends on both basicity and steric factors, whereas attack at digonal carbon is likely to be controlled largely by a combination of basicity and polarizability of the nucleophile [a simple illustration is the relative reactivity, generally $H_2O > NH_3 > R{\cdot}NH_2 > R_2NH$ for trigonal boron compounds, but $NH_3 > H_2O$ for carbonyl carbon (in *p*-nitrophenyl acetate)].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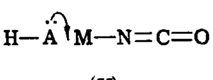
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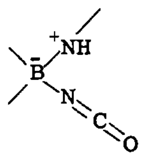
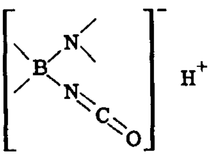
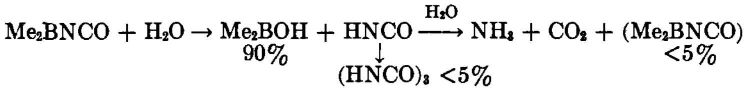

(VI)


(VII)

In order to have effective competition for the substitution, steric hindrance both in the substrate and in the reagent is helpful. From the electronic aspect, either M should not have available vacant low-energy orbitals, or the reorganization energy for change in hybridization should be high. This analysis appears to explain satisfactorily the results not only for the boron pseudohalides, but also for derivatives of other elements (as summarized in the tabulation, together with data on related isothio-



$$Me_2BNCO + H_2O \rightarrow \underset{90\%}{Me_2BOH} + \underset{\underset{(HNCO)_3\ <5\%}{\downarrow}}{HNCO} \xrightarrow{H_2O} NH_3 + CO_2 + \underset{<5\%}{(Me_2BNCO)_n} \qquad (93)$$

Behavior of Some Common Isocyanates and Isothiocyanates with Alcohols and Amines:

Class	With ROH	With R·NH$_2$	Reference
>B·NCO	>B·OR	>B·NHR	(*87, 115*)
⋗$\overset{-}{\mathrm{B}}$·NCO	>B·OR	>B·NH·CO·NHR	(*114, 150*)
(R′·N·B·NCO)$_3$	>B·OR	(R′N·B·NH·CO·NHR)$_3$	(*113*)
(R′N·B·NCS)$_3$	>B·OR	(R′N·B·NHR)$_3$	(*113*)
⋗C·NCO	⋗C·NH·CO$_2$R	⋗C·NH·CO·NHR	(*28a*)
⋗C·NCS	⋗C·NH·CS·OR	⋗C·NH·CS·NHR	(*106a*)
⋗Si·NCO	⋗Si·OR	⋗Si·NH·CO·NHR	(*88, 90*)
⋗Ge·NCO	⋗Ge·OR	—	(*8*)
>PO·NCO	>PO·NH·CO$_2$R	>PO·NH·CO·NHR	(*106c, 165a*)
>PO·NCS	>PO·NH·CS·OR	>PO·NH·CS·NHR	(*62a*)
[PN(NCS)$_2$]$_{3,4}$	(addition)	(addition)	(*180a*)
S^{VI}·NCO	S^{VI}·NH·CO$_2$R	S^{VI}·NH·CO·NHR	(*28b*)

cyanates). The lower additive reactivity of isothiocyanates than of isocyanates is attributed to the low polarity of the thiocarbonyl compared with the carbonyl bond (*113*).

Dimethylisocyanatoborane reacted readily (Eq. 93) with water, affording dimethylhydroxyborane, ammonia, carbon dioxide, cyanuric acid, and a polymeric boron compound (*87*). Likewise, hydrolysis of triisocyanatoborane gave boric acid, ammonium sulfate, and carbon dioxide whence the normal cyanate structure was inferred (*71*); this is clearly inappropriate, as the isocyanate would give the same products.

Silicon isocyanates are readily hydrolyzed to silanols. Some, such as triphenyl- or triethyl-isocyanatosilane, are relatively stable to water, but this stability is associated with their insolubility; thus hydrolysis is rapid when carried out in the presence of acetone or alcohol (*57, 77, 81*). Tendency for hydrolysis decreased in the series $MeSi(NCO)_3 > Me_2Si(NCO)_2 > Me_3SiNCO$, and this effect is also probably associated with a progressive decrease in the solubility of these isocyanates in water (*79*). For germanium compounds, a similar effect was observed $[Ge(NCO)_4 > EtGe(NCO)_3 > Et_2Ge(NCO)_2 > Et_3GeNCO]$ (*8*).

Dimethyltin diisocyanate was hydrolyzed according to Eq. (94). The diisocyanates of tin appear to be particularly sensitive to moisture, and hydrolysis products of types $Bu^n_8Sn_4(NCO)_4O_2$, $Bu^n_8Sn_4(NCO)_2(OH)_2O_2$, and $Ph_4Sn_2(NCO)_2(OH)_2$ have been isolated (*136a*).

$$Me_2Sn(NCO)_2 + 3H_2O \rightarrow \frac{1}{n}(Me_2SnO)_n + CO_2 + 2NH_3 \qquad (94)$$

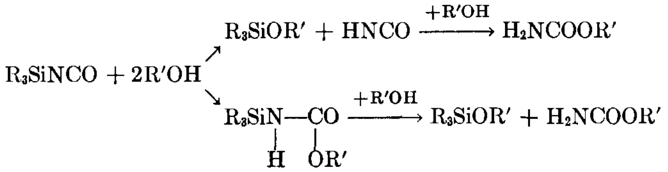
Alcoholysis of the isocyanates of boron (*87*), silicon (*34*, *90*), and germanium (*8*) proceeds readily, to afford corresponding alkoxy derivatives and substituted carbamates.

This was demonstrated for Me_2BNCO (a small yield of $(Me_2BNCO)_n$ was also obtained) (*87*), as well as for numerous other 3-coordinate mono- (*115*) and poly- (borazine derivatives) (*113*) nuclear boranes, and also for 4-coordinate species, such as $py{\cdot}B(NCO)_3$ (*114*, *150*).

The ethylisocyanatogermanes reacted quantitatively with ethanol and butanol according to Eq. (95):

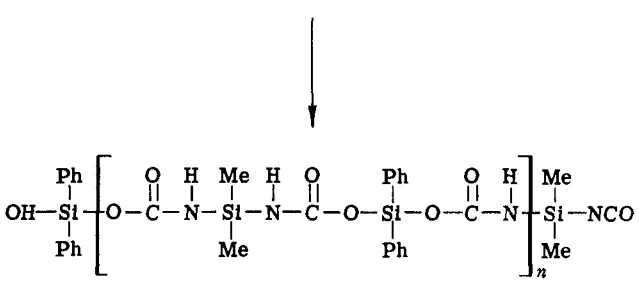
$$Et_{4-n}Ge(NCO)_n + 2nROH \rightarrow Et_{4-n}Ge(OR)_n + nH_2NCOOR \qquad (95)$$

The silicon isocyanates needed more forcing conditions. Thus, unreacted trimethylisocyanatosilane (~20%) was recovered from the reaction with excess ethanol after 3 hours at room temperature, although quantitative yields of both trimethylmethoxysilane and methyl carbamate were obtained when the reaction was carried out at a higher temperature (*90*). Change of alcohol, solvent, temperature, concentration, and molar ratios produced qualitatively the same results, i.e., no silicon urethanes were obtained. Reaction sequence (96) was postulated (*90*). With higher or more highly branched alcohols (*n*-amyl, *i*-propyl, and *t*-butyl) or phenol, reaction rates decreased. For example, after 2 hours at 70° significant proportions of starting materials may be recovered. Likewise, structural changes in the silicon substrates have similar implications; e.g., triphenylisocyanatosilane was unaffected by ethanol in boiling benzene (*81*).



$$R_3SiNCO + 2R'OH \nearrow R_3SiOR' + HNCO \xrightarrow{+R'OH} H_2NCOOR'$$
$$R_3SiNCO + 2R'OH \searrow \underset{H}{R_3SiN}{-}\underset{OR'}{CO} \xrightarrow{+R'OH} R_3SiOR' + H_2NCOOR' \qquad (96)$$

A contrasting report is provided by a patent, in which the formation of poly(silicourethanes) is claimed, prepared according to Eq. (97) (*209*):



$$nPh_2Si(OH)_2 + nMe_2Si(NCO)_2 \longrightarrow OH{-}\underset{Ph}{\overset{Ph}{Si}}{-}\left[O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}\underset{Me}{\overset{Me}{Si}}{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{Ph}{\overset{Ph}{Si}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}\right]_n{-}\underset{Me}{\overset{Me}{Si}}{-}NCO \qquad (97)$$

The reactions of isocyanatoboranes and amines have been investigated in some detail (*87*, *112–115*, *150*). In general, addition or substitution behavior may be found depending on variations in electronic and steric factors, in accordance with the general principles outlined above for MNCO/HA systems. Representative examples are shown in Eqs. (98–101). 4-Coordinate species did not invariably yield ureidoboranes. Thus, the pyridine complexes of $PhB(NCO)_2$ or Ph_2BNCO both gave the substitution products, $PhB(NHR)_2$ and Ph_2BNHR.

$$(HNBNCO)_3 + 3R_2NH \xrightarrow{(113)} (HNBNHCONR_2)_3 \qquad (98)$$

$$py{\cdot}B(NCO)_3 + 3RNH_2 \xrightarrow{(114,\ 150)} B(NHCONHR)_3 + py \qquad (99)$$

$$(Pr^i{}_2N)_2BNCO + PhMeNH \xrightarrow{(115)} (Pr^i{}_2N)(PhMeN)BNCO + Pr^i{}_2NH \qquad (100)$$

$$(Pr^i{}_2N)_2BNCO + 2Bu^tNH_2 \xrightarrow{(115)} (Bu^tNH)_2BNCO + 2Pr^i{}_2NH \qquad (101)$$

Silicon isocyanates appear invariably to give silicoureas (*88*).

The order of reactivity for various amines and isocyanato-borazines (*113*) or -silanes (*88*) was similar to that observed for organic isocyanates, i.e., $RNH_2 > R_2NH > ArNH_2 \gg ArNHR$.

Phenyllithium or phenylmagnesium bromide and triphenylisocyanatosilane gave, after hydrolysis, triphenylhydroxysilane and benzamide, according to Eq. (102) (*81*); the silicon derivative thus behaved in an analogous fashion to phenyl isocyanate. Attempts to make methylisocyanatosilanes from tetraisocyanatosilane and Grignard reagents failed (*79*), and likewise there was no reaction between triethylisocyanatosilane and methylmagnesium iodide (*57*).

$$\begin{tikzcd}
Ph_3SiNCO + PhLi \arrow[r] & Ph_3SiN = CPhOLi \arrow[d, "H_2O"] \\
Ph_3SiOH + PhCONH_2 & Ph_3SiN = CPhOH \arrow[l]
\end{tikzcd} \qquad (102)$$

Isocyanatosilanes have provided routes to silylcarbodiimides, as shown in Eqs. (103–105):

$$(Me_3Si)_2NNa + 2Si(NCO)_4 \xrightarrow{(149)} NaOCN + [(OCN)_3Si]_2O + Me_3SiNCNSiMe_3 \qquad (103)$$

$$2(Me_3Si)_2NNa + Si(NCO)_4 \xrightarrow{(193)} 2NaOCN + SiO_2 + 2Me_3SiNCNSiMe_3 \qquad (104)$$

$$2(Me_3Si)_2NNa + Me_3SiNCO \xrightarrow{(193)} NaOCN + (Me_3Si)_2O + Me_3SiNCNSiMe_3 \qquad (105)$$

Ethylene oxide was cleaved by reaction with $Si(NCO)_4$, as shown in Eq. (106) (*66*):

$$Si(NCO)_4 + 3(CH_2)_2O \rightarrow OCNSi(OCH_2CH_2NCO)_3 \qquad (106)$$

The behavior of H_3SiNCO with various acids and bases, under mild conditions, has been examined, as summarized in Eqs. (107–111) (*60*).

There was no reaction with diborane or phosphine; sodium hydroxide afforded various decomposition products, and with sulfuric acid carbon dioxide was evolved.

$$H_3SiNCO + Et_3P \rightarrow H_4Si + \text{viscous liquid} \tag{107}$$

$$H_3SiNCO + NH_3 \rightarrow H_4Si + \text{solid} \tag{108}$$

$$H_3SiNCO + HCl \rightarrow H_3SiCl + \tfrac{1}{3}(HNCO)_3 + \text{solid} \tag{109}$$

$$H_3SiNCO + MeOH \rightarrow H_4Si + HSi(OMe)_3 + Si(OMe)_4 + H_2NCOOMe \tag{110}$$

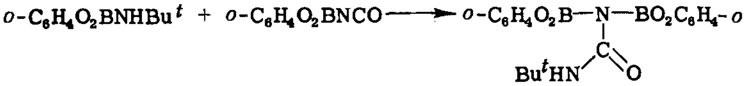
$$H_3SiNCO + BF_3 \rightarrow H_3SiF + [F_2BNCO] \rightarrow BF_3 + \text{solid} \tag{111}$$

Tetraisocyanatogermane reacted with antimony(III) fluoride according to Eq. (112), but the GeF_4 was isolated as a constant boiling mixture with $Ge(NCO)_4$ (*10, 76*):

$$3Ge(NCO)_4 + 4SbF_3 \rightarrow 3GeF_4 + 4Sb(NCO)_3 \tag{112}$$

A further reaction in which the isocyanate group behaves as a pseudohalide is exemplified by Eq. (113) (*97, 114*); on the other hand, an addition reaction has been observed in a related system (Eq. 114) (*47a*):

$$PhB(NR_2)_2 + PhB(NCO)_2 \longrightarrow 2\,PhB(NR_2)NCO \tag{113}$$



$$o\text{-}C_6H_4O_2BNHBu^t + o\text{-}C_6H_4O_2BNCO \longrightarrow o\text{-}C_6H_4O_2B{-}\underset{\substack{|\\ C(=O)NHBu^t}}{N}{-}BO_2C_6H_4\text{-}o \tag{114}$$

Pyrolysis of o-$C_6H_4O_2BNCO$ (*114*) or Ph_2BNCO (*98b*) did not lead to elimination of carbon dioxide and carbodiimide formation, even in the presence of 3-methyl-1-phenylphospholene (*98b*), and this is a further point of contrast with organic isocyanates. Ethanethiol did not react with isocyanatoboranes (*113*).

The acceptor properties of 3-coordinate isocyanatoboranes toward ligands such as ethyl acetate or pyridine, relative to related compounds, are $\rangle$BBr > $\rangle$BCl > $\rangle$BNCS > $\rangle$BNCO > $\rangle$BF, as determined by thermochemical (heats of complex formation) and infrared spectral measurements (*114, 150*).

V. Isothiocyanates

A. PREPARATION

Physical properties such as molecular refractions, boiling points, and infrared, Raman, and microwave spectra indicate that the organometallic thiocyanates of Group IIIB and IVB elements have the iso (M—N=C=S) structure. These compounds are therefore named isothiocyanates, even when reference is made to publications in which the normal ($M{-}S{-}C{\equiv}N$) structure was originally postulated. (See Table IV.)

Four general types of reaction (Eqs. 115–118) are available for the preparation of isothiocyanates of Groups IIIB and IVB:

$$2MH + (SCN)_2 \rightarrow 2MNCS + H_2 \qquad (115)$$

$$MX + M'NCS \rightarrow MNCS + M'X \qquad (116)$$

$$MOH + HNCS \rightarrow MNCS + H_2O \qquad (117)$$

$$MNC + S \rightarrow MNCS \qquad (118)$$

Scheme (115) is illustrated by Eq. (119) ($M{=}Li$ or Na), using tetrahydrofuran or ether at somewhat below room temperature (*107*, *108*):

$$MBH_4 + \frac{n}{2}(SCN)_2 \rightarrow MBH_{4-n}(NCS)_n + \frac{n}{2}H_2 \qquad (119)$$

With sodium borohydride the number of hydrogens displaced by —NCS groups never exceeds three. Lithium tetraisothiocyanatoborate was not isolated, owing to its instability, but from the ether solution an insoluble complex, $[LiB(NCS)_4{\cdot}2C_4H_8O_2]$, could be precipitated. Lithium aluminum hydride and thiocyanogen in ether behaved similarly, to afford a solvated complex of $LiAl(NCS)_4$, which decomposed at ~50° (*108*).

Modifications of scheme (115) are shown in Eqs. (120) and (121) (*1*):

$$H_3BOR_2 + NH_4CNS \xrightarrow[R_2O]{-80^\circ} R_2O + NH_4BH_3NCS \xrightarrow{0^\circ} H_3NBH_2NCS + H_2 \qquad (120)$$

$$B_2H_6 + 2NaCNS \xrightarrow{C_4H_8O_2} 2NaBH_3NCS{\cdot}2C_4H_8O_2 \qquad (121)$$

Apart from $B(NCS)_3$, the first isothiocyanatoboranes to be prepared were obtained by route (116), from halo- (Cl, Br) boranes and Ag, Na, or Pb salts of thiocyanic acid (*112–115*, *150*). With the silver salts high yields were realized by using nonpolar solvents such as benzene, but with sodium or lead thiocyanates it was necessary to use a polar medium.

The preparation of triisothiocyanatoborane, originally reported (*46*) in 1906, was carried out according to route (116), from tribromoborane and silver thiocyanate in benzene solution. The product was described as an unstable crystalline solid. However, more recently triisothiocyanatoborane was obtained as a distillable liquid (38%, according to Eq. 122), from trichloroborane and potassium or sodium thiocyanate, in sulfur dioxide at −30° (*170*):

$$BCl_3 + 3NaCNS \rightarrow B(NCS)_3 + 3NaCl \qquad (122)$$

Using similar reaction conditions, a number of 4-coordinate isothiocyanatoboranes have been synthesized, as shown in Eq. (123) ($R = CH_3$, C_6H_5, or $C_6H_5CH_2$) (*170*):

$$RCN{\cdot}BCl_3 + 3NaCNS \rightarrow RCN{\cdot}B(NCS)_3 + 3NaCl \tag{123}$$

These isothiocyanatoboranes were also obtained by the addition of the nitriles to triisothiocyanatoborane, and analogous procedures afforded pyridine- and triethylamine-triisothiocyanatoboranes. The latter compounds could not be prepared from the appropriate BCl_3 complexes, as these failed to react with sodium thiocyanate, using sulfur dioxide as solvent at −30°. On the other hand, py·BCl_3 (unlike $Me_3N{\cdot}BCl_3$) and AgNCS in benzene gave the Base·$B(NCS)_3$ product (*114*, *150*).

B-Triisothiocyanatoborazine (*40*, *93*), *P*-hexamethyl-*B*-isothiocyanatoborophane (*191*), and tetra-*B*-isothiocyanatotetra-*N*-*t*-butylborazocine $(Bu^tNBNCS)_4$ (*184*, *185a*) have been synthesized [see Eqs. (124–126)]:

$$(ClBNH)_3 + 3KCNS \xrightarrow{MeCN} (SCNBNH)_3 + 3KCl \tag{124}$$

$$Me_6P_3B_3H_5I + KCNS \xrightarrow{Me_2NCOH} Me_6P_3B_3H_5NCS + KI \tag{125}$$

$$(ClBNBu^t)_4 + 4KCNS \xrightarrow{Me_2CO} (SCNBNBu^t)_4 + 4KCl \tag{126}$$

2-Isothiocyanato-1,3,2-dioxaborinane $[(CH_2)_3O_2BNCS]$ (*68*), 2-isothiocyanato-1,3,2-dioxaborolane $[(CH_2)_2O_2BNCS]$ (*69*), and butoxyisothiocyanatophenylborane $[PhB(OBu^n)NCS]$ (*122*) were obtained from the interaction of silver thiocyanate and the corresponding chlorides. A hexaisothiocyanatoaluminate has been made by the procedure of Eq. (127) (*158*):

$$AlCl_3 + 6KCNS \xrightarrow{CH_3CN} 3KCl + K_3[Al(NCS)_6]{\cdot}CH_3CN \xrightarrow{140°} K_3[Al(NCS)_6] \tag{127}$$

The only other isothiocyanates of Group IIIB elements at present known are diethylisothiocyanatothallium (Eq. 128) (*84*), diisothiocyanatophenylthallium (Eq. 129) (*44*), and indium(III) isothiocyanate (obtained from $Ba(CNS)_2/In_2(SO_4)_3$ in aqueous solution and removal of the insoluble $BaSO_4$) (*141a*).

$$Et_2TlBr + AgNCS \rightarrow Et_2TlNCS + AgBr \tag{128}$$

$$PhTlCl_2 + 2KCNS \rightarrow PhTl(NCS)_2 + 2KCl \tag{129}$$

For the preparation of silicon and germanium isothiocyanates, all four general methods have been used extensively.

Interaction of cyclohexyl- (*23*) or *n*-heptyl- (*26*) silane, or di-*n*-butylgermane (*24*) and silver or mercury thiocyanate, in the presence of solvent, gave the corresponding isothiocyanates, as shown in Eqs. (130–132); from the second and third reactions, isothiocyanic acid, a mixture of organosilanes and germanes, and some starting materials were also isolated:

$$2C_6H_{11}SiH_3 + 2AgNCS \xrightarrow{CCl_4} 2C_6H_{11}SiH_2NCS + 2Ag + H_2 \tag{130}$$

$$2n\text{-}C_7H_{15}SiH_3 + Hg(NCS)_2 \xrightarrow{CCl_4} 2n\text{-}C_7H_{15}SiH_2NCS + Hg + H_2 \tag{131}$$

$$2(n\text{-}C_4H_9)_2GeH_2 + Hg(NCS)_2 \rightarrow 2(n\text{-}C_4H_9)_2GeHNCS + Hg + H_2 \tag{132}$$

Treatment of organogermanium or organosilicon halides (Cl, Br, or I), with a variety of salts of thiocyanic acid in the vapor phase, or in solvents such as benzene, carbon tetrachloride, hexane, acetonitrile, nitromethane, or water, resulted in high yields of germanium or silicon isothiocyanates (*15, 23, 26, 134, 152, 153, 171*). Examples are shown in Eqs. (133–137):

$$C_6H_{11}SiCl_3 + 3AgNCS \rightarrow C_6H_{11}Si(NCS)_3 + 3AgCl \tag{133}$$

$$n\text{-}C_7H_{15}SiCl_3 + 3AgNCS \xrightarrow{CCl_4} n\text{-}C_7H_{15}Si(NCS)_3 + 3AgCl \tag{134}$$

$$GeBr_4 + 4AgNCS \xrightarrow{C_6H_5{\cdot}C_3H_7} Ge(NCS)_4 + 4AgBr \tag{135}$$

$$(CH_3)_2GeCl_2 + 2KCNS \xrightarrow{H_2O} (CH_3)_2Ge(NCS)_2 + 2KCl \tag{136}$$

$$H_3GeBr + AgNCS \rightarrow H_3GeNCS + AgBr \tag{137}$$

A vapor phase reaction, passing silyl iodide over silver thiocyanate, has been used for the preparation of silyl isothiocyanate (*130*). Fused alkali metal salts have been employed as reaction media, as shown in Eq. (138) (*179*):

$$R_{4-n}SiCl_n + nKCNS \rightarrow R_{4-n}Si(NCS)_n + nKCl \tag{138}$$

The interaction of organotin halides and metal thiocyanates has provided routes to tin derivatives, under the conditions of Eqs. (139–142). Triphenyllead isothiocyanate has similarly been obtained from Ph_3PbI/AgNCS (*173*) or Ph_3PbCl/KCNS/EtOH (*63*), and triethyllead isothiocyanate from Et_3PbCl/KCNS/EtOH (*95*).

$$Et_3SnI + AgNCS \xrightarrow{C_6H_6} Et_3SnNCS + AgI \tag{139}$$

$$Me_2SnCl_2 + 2NaCNS \xrightarrow{Me_2CO} Me_2Sn(NCS)_2 + 2NaCl \tag{140}$$

$$Bu^n{}_3SnCl + KCNS\ (\text{or } NH_4CNS) \xrightarrow[(49)]{\text{ROH; reflux}} Bu^n{}_3SnNCS + KCl \tag{141}$$

$$Bu^n{}_3SnCl + AgNCS \xrightarrow[(49)]{180^\circ;\ 4\text{ hr}} Bu^n{}_3SnNCS\ (15\%) + AgCl \tag{142}$$

For the preparation according to Eq. (140), liquid sulfur dioxide or acetonitrile has been suggested as a more suitable solvent, as they are less reactive than acetone toward the chlorides used as starting materials (*93*). These media dissolve appreciable amounts of ammonium and potassium thiocyanates, while the chlorides are only sparingly soluble.

Organic derivatives of silicon, germanium, and tin often interchange isothiocyanate, isocyanate, halogen, and other groups at the boiling point of the mixture, when the most volatile component can be distilled out as it forms. For the triethylsilyl compounds, conversion may be affected in the following direction (*14, 17, 27*) (for example, as shown in Eqs. 143, 144), $\equiv SiNHPh \rightarrow \equiv SiNCS \rightarrow \equiv SiI \rightarrow \equiv SiNCO \rightarrow \equiv SiBr \rightarrow \equiv SiCl$.

$$Me_2Si(NHPh)_2 + Ph_2Si(NCS)_2 \xrightarrow{(19)} Me_2Si(NCS)_2 + Ph_2Si(NHPh)_2 \qquad (143)$$

$$2Me_3SiNCS + (Et_3Sn)_2O \xrightarrow{(20)} 2Et_3SnNCS + (Me_3Si)_2O \qquad (144)$$

However, these reactions are not of great value for the synthesis of isothiocyanates, since the starting materials are usually prepared from the halides, and these may be converted directly to the isothiocyanates by use of metal salts.

"Conversion series" for boron (*115*), silicon (*25, 57*), germanium (*15, 25, 171*), and tin (*28*) have been proposed. Using dry silver salts, with or without an inert solvent such as benzene, carbon tetrachloride, or toluene, any compound on the left may be converted to one on the right within a series. For silicon, germanium, and tin these "conversion series" are (for boron, see Section IV):

$$R_3SiI \rightarrow (R_3Si)_2S \rightarrow R_3SiBr \rightarrow R_3SiCN \rightarrow R_3SiCl \rightarrow R_3SiNCS \rightarrow R_3SiNCO \rightarrow (R_3Si)_2O \rightarrow R_3SiF$$

$$R_3GeI \rightarrow (R_3Ge)_2S \rightarrow R_3GeBr \rightarrow R_3GeCN \rightarrow (R_3GeNCS \text{ and } R_3GeCl) \rightarrow R_3GeNCO \rightarrow [(R_3Ge)_2O \text{ and } R_3GeOCOR] \rightarrow R_3GeF$$

$$Et_3SnSMe = (Et_3Sn)_2S \rightarrow Et_3SnI \rightarrow Et_3SnBr \rightarrow Et_3SnCN \rightarrow Et_3SnNCS \rightarrow Et_3SnCl \rightarrow (Et_3Sn)_2O \rightarrow Et_3SnNCO \rightarrow Et_3SnOCOMe \rightarrow Et_3SnF$$

Anomalies have been noted, and sometimes are ascribed to steric factors (*10*). Examples are shown in Eqs. (145–148):

$$Si(NCS)_4 + 4AgNCO \rightarrow \text{no reaction} \qquad (145)$$

$$Et_3SiNCS + AgNCO \rightarrow Et_3SiNCO + AgNCS \qquad (146)$$

$$Me_3SiNCS + AgNCO \rightarrow Me_3SiNCO + AgNCS \qquad (147)$$

$$Me_2Si(NCS)_2 + 2AgNCO \rightarrow Me_2Si(NCO)_2 + 2AgNCS \qquad (148)$$

Thiocyanic acid has been shown to react readily with organometallic oxides or hydroxides, to give isothiocyanates in high yields. Examples are shown in Eqs. (149–152):

$$(R_2GeO)_3 + 6HNCS \xrightarrow{(24)} 3R_2Ge(NCS)_2 + 2H_2O \qquad (149)$$

$$(Et_3Ge)_2O + 2HNCS \xrightarrow{(15)} 2Et_3GeNCS + H_2O \qquad (150)$$

$$Pr^i{}_3GeOH + HNCS \xrightarrow{(18)} Pr^n{}_3GeNCS + H_2O \qquad (151)$$

$$(Et_3Sn)_2O + 2HNCS \xrightarrow{(28)} 2Et_3SnNCS + H_2O \qquad (152)$$

Trimethyl- and triphenyl-cyanosilanes (*133*), dimethylphenylcyanosilane (*125*), trimethylcyano-germane and -stannane (*162*), and tri-*n*-butylcyanostannane (*49*) added sulfur readily, to afford the corresponding isothiocyanates, as shown in Eq. (153) (see also Section III):

$$MCN + S \rightarrow MNCS \qquad (153)$$

Thiourea has proved a possible starting material for isothiocyanates, as shown in Eqs. (154–156):

$$Ph_3SiCl + (NH_2)_2CS \xrightarrow{(81)} Ph_3SiNCS + NH_4Cl \tag{154}$$

$$Bu^n{}_3SnCl + (NH_2)_2CS \xrightarrow{(49)} Bu^n{}_3SnNCS \text{ (16\% in 2 hr at 170°)} \tag{155}$$

$$(Bu^n{}_3Sn)_2O + (NH_2)_2CS \xrightarrow{(49)} Bu^n{}_3SnNCS \text{ (15\%)} \tag{156}$$

Silyl isothiocyanate was obtained from the interaction of disilylcyanamide and silver thiocyanate, as shown in Eq. (157) (*59*):

$$(H_3Si)_2NCN + 2AgNCS \rightarrow 2H_3SiNCS + Ag_2NCN \tag{157}$$

Miscellaneous methods for preparing isothiocyanates are illustrated in Eqs. (158–162). There was no reaction between isocyanatoboranes with either mercury(II) or phosphorus(V) sulfide (*115*):

$$PhB(NR_2)_2 + PhB(NCS)_2 \xrightarrow{(97)} 2PhB(NR_2)NCS \tag{158}$$

$$Et_3GeOSO_2R + KCNS \xrightarrow{(25)} Et_3GeNCS + RSO_3K \tag{159}$$

$$(Bu^n{}_3Sn)_2O + KCNS \xrightarrow{(49)} Bu^n{}_3SnNCS \text{ (60\% in } \tfrac{1}{2} \text{ hr at 80° in 2 } M \text{ HCl)} \tag{160}$$

$$Ph_2Pb(OCOMe)_2 + 2NH_4CNS \xrightarrow{(143)} Ph_2Pb(NCS)_2 + 2MeCOOH + 2NH_3 \tag{161}$$

$$Pb(OCOMe)_4 + 4HNCS \xrightarrow{(106)} Pb(NCS)_4 + 4MeCOOH \tag{162}$$

B. STRUCTURES

Isothiocyanatoboranes are monomeric in benzene solutions and, unlike corresponding >BNCO derivatives (see Section IV), show little tendency for polymerization (*112–115*, *150*). On the other hand, the difference in boiling point between the isothiocyanatoboranes and corresponding chloroboranes (~100° at 760 mm, per group) is far greater than between the isothiocyanates and chlorides of silicon or phosphorus (~65° at 760 mm per group) (*115*). This must be due to enhanced molecular association for the boron compounds, probably due to increased polarization of the —N=C=S group, as a result of conjugation with boron.

The molar refractivities of isothiocyanatoboranes, obtained from refractive indices and liquid densities, agree well with values calculated on a >B—N=C=S model, but not with >B—S—C≡N (*115*). A detailed comparison of the electronic (NCS chromophore) and infrared spectra of isothiocyanatoboranes with those of organic thiocyanates and isothiocyanates points also to the >B—N=C=S structure (*112*, *114*, *150*). The preference for the former may be related to B—N π-bonding (*114*, *150*).

The infrared spectra of many isothiocyanato-boranes (*69, 93, 107, 112, 114, 150, 170*), -silanes (*40b, 62, 92, 93, 169*), -germanes (*172*), and -stannanes (*93*) have been recorded, and full assignments for some compounds proposed [e.g., the series Me_3MNCS (M = Si, Ge, Sn, or Pb) (*180c*)].

All the spectra showed strong absorption in the regions 2080–1940 cm^{-1} and 1070–920 cm^{-1}, and these bands are associated with the asymmetrical and symmetrical stretching vibration of the $—N{=}C{=}S$ group. In $>$BNCS derivatives these fall within the narrower ranges of 2089 ± 31 and 995 ± 30 cm^{-1} (*112, 114, 150*). Vibrational spectra for $Si(NCS)_4$ indicate T_d symmetry with linearity of the $Si—N{=}C{=}S$ chain (*40b*).

Linearity of the $>Si—N{=}C{=}S$ chain was established in isothiocyanatosilane, from microwave (*101, 102*) and infrared (*62*) spectra. From the microwave spectrum, C_{3v} symmetry of the molecule was deduced and the following structural parameters were determined:

$$\begin{aligned} \text{Si—N} &= 1.714 \pm 0.010\ \text{Å} \\ \text{N—C} &= 1.211 \pm 0.010\ \text{Å} \\ \text{Si—H} &= 1.489 \pm 0.010\ \text{Å} \\ \text{H—Si—H} &= 111°22' \pm 10' \\ \text{C—S} &= 1.560\ \text{Å (assumed)} \end{aligned}$$

On the other hand, an electron-diffraction study of Me_3SiNCS shows a substantial deviation from linearity (*106b*); the molecular parameters are: r_g(C—H) = 1.09 ± 0.02, r_g-(C—S) = 1.56 ± 0.01, r_g-(N—C) = 1.18 ± 0.01, r_g(Si—N) = 1.78 ± 0.02, r_g(C—Si) = 1.87 ± 0.01A, and $<$(Si—N—C) = $154 \pm 2°$.

The linearity of the $\equiv$SiNCS skeleton in H_3SiNCS may be a consequence of $p_\pi—d_\pi$ bonding. Consequently, a short Si—N bond distance is to be expected, and the value of 1.714 Å is significantly lower than the calculated value of 1.87 Å obtained by adding Pauling single-bond radii. The N—C bond distance of 1.211 Å is very similar to that found in HNCS (*54*) and CH_3NCS (*30*).

The C_{3v} symmetry of silyl isothiocyanate has been confirmed by a study of infrared and Raman spectra of this compound and its deuterated analog (*62*). Similar spectroscopic work on derivatives of silicon (*58, 70*) and tin (*49*) likewise points to the iso structure. The proton resonance in H_3SiNCS was very close to that for H_3SiNCO and $H_3SiNCNSiH_3$, but about 0.7 p.p.m. to lower field from the H_3Si resonance found in H_3SiCN and $H_3SiC{\equiv}CH$. This offers independent support for Si—N bonding (*58*).

Further evidence for the iso structure ($M—N{=}C{=}S$) in the isothiocyanatosilanes is obtained from molecular refractions and boiling points (*7, 9, 76*).

C. PROPERTIES

The isothiocyanates of Groups IIIB and IVB vary in stability from the unstable (at 0°) isothiocyanatomethylsilane (MeH_2SiNCS) (*111*), through isothiocyanatogermane, stable at room temperature but decomposing completely when heated for 20 hours at 50° into germanes and thiocyanic acid [$n H_3GeNCS \rightarrow (GeH_2)_n + n HNCS$] (*171*), to methyltriisothiocyanatosilane, which can be distilled at 267° with no decomposition (*190*). The presence of M—H bonds in either silicon or germanium isothiocyanates reduces the stability of these compounds. Tri-*n*-butylisothiocyanatostannane withstood prolonged heating *in vacuo* at 180° (*49*). Tetraisothiocyanatolead readily disproportionates to produce thiocyanogen and lead(II) isothiocyanate (*106*).

From reaction of boron isothiocyanate and aniline a solid, containing no boron, was isolated (*46*), which on treatment with boiling water was converted to phenylthiocarbamide. It was therefore concluded that the original compound had the thiocyanate structure. However, the evidence is ambiguous, as $B(NCS)_3$ would also be expected to yield $B(NHPh)_3$.

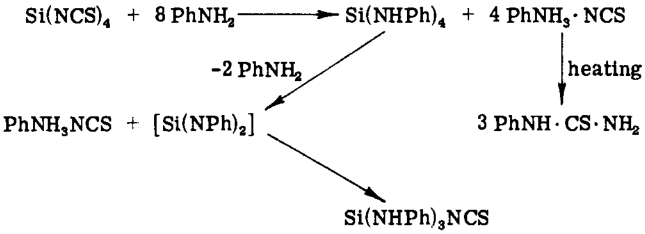
Triisothiocyanatoborane and nitriles or tertiary amines formed 1:1 complexes at low temperature (*170*). The acceptor properties $\left(>\mathrm{BBr} > \;>\mathrm{BCl} > \;>\mathrm{BNCS} > \;>\mathrm{BNCO} > \;>\mathrm{BF}\right)$ of related boranes toward EtOAc and C_5H_5N have been examined (*114*, *150*). Pyridine, quinoline, and isoquinoline formed 2:1 complexes with $Si(NCS)_4$ (*159*, *160*); from conductivity and infrared spectral data these were formulated as $[Si(NCS)_2(Base)_2](SCN)_2$. $Bu^n{}_2Sn(NCS)_2$ formed a 1:1 complex with 2,2′-dipyridyl (*2*), and similar complexes of the methyl, ethyl, and *n*-propyl homologs have been prepared (*190a*). The anions $[MeSn(NCS)_5]^{2-}$, $[Me_2Sn(NCS)_4]^{2-}$, and $[Me_3Sn(NCS)_2]^-$ are known (*41a*).

Silicon isothiocyanates are readily hydrolyzed to silanols, and the case of hydrolysis is dependent upon the nature of other substituents and the number of isothiocyanate groups directly attached to silicon (*57*, *133*).

The reactions of isothiocyanatoboranes with alcohols or amines invariably lead to substitution products (see also Section IV) (e.g., Eq. 163) (*113–115*, *150*):

$$(Et_2N)_2BNCS + 2Et_2NH \xrightarrow{(114)} B(NEt_2)_3 + [Et_2NH_2]^+[NCS]^- \qquad (163)$$

Tetraisothiocyanatosilane and aniline, when kept for 10 days at room temperature, gave tetraanilinosilane and anilinium thiocyanate, which on heating gave *N*-phenylthiourea. The anilinosilane lost two molecules of aniline, to give a diimide, which added one molecule of aniline thiocyanate (*152*). These reactions are illustrated in scheme (164).



(164)

Isothiocyanatosilanes and isothiocyanatogermanes reacted with alcohols according to Eq. (165) (*9*, *133*):

$$R_{4-n}M(NCS)_n + 2nROH \rightarrow R_{4-n}M(OR)_n + nH_2NCOOR \qquad (165)$$

Phenyllithium with triphenylisothiocyanatosilane gave, after hydrolysis, triphenysilanol and thiobenzamide; tetraphenylsilane was also isolated (*81*). The reaction sequence (166) was proposed:

$$\begin{tikzcd} Ph_3SiNCS + PhLi \arrow[r] & Ph_3SiN{=}CPhSLi \arrow[d, "H_2O"] \\ Ph_3SiOH + PhCSNH_2 & Ph_3SiN{=}CPhSH \arrow[l] \end{tikzcd} \qquad (166)$$

Isothiocyanatoboranes reacted with mercury(II) oxide according to Eq. (167) (*114*, *150*), and with organic isocyanates to give addition products (Eqs. 168–170) (*100b*). In the addition reactions they resemble chloroboranes (*111a*), and it is interesting that Ph > NCS is migratory aptitude.

$$2\,{>}BNCS + HgO \rightarrow {>}B{-}O{-}B{<} + Hg(NCS)_2 \qquad (167)$$

$$o\text{-}C_6H_4O_2BNCS + PhNCO \rightarrow o\text{-}C_6H_4O_2BNPhCONCS \qquad (168)$$

$$PhB(NCS)_2 + 2PhNCO \rightarrow SCNB(NPhCONCS)(NPhCOPh) \qquad (169)$$

$$Ph_2BNCS + 2PhNCO \rightarrow PhB(NPhCONCS)(NPhCOPh) \qquad (170)$$

Diisothiocyanatophenylthallium, when refluxed in water, gave isothiocyanatobenzene, and, with potassium iodide, iodobenzene (*44*).

Various other reactions of isothiocyanates of silicon are illustrated in Eqs. (171–175):

$$Et_2Si(NCS)_2 + PhPCl_2 \xrightarrow{(80)} Et_2SiCl_2 + PhP(NCS)_2 \qquad (171)$$

$$Pr^nSi(NCS)_3 + 3PhCOCl \xrightarrow{(19)} Pr^nSiCl_3 + 3PhCONCS \qquad (172)$$

$$2Me_3SiNCS + S_2Cl_2 \xrightarrow{(19)} 2Me_3SiCl + 2(SNCS) \qquad (173)$$

$$2Me_3SiNCS + (Me_3Si)_2NNa \xrightarrow{(193)} Me_3SiNCNSiMe_3 + (Me_3Si)_2S + NaCNS \qquad (174)$$

$$R_nSi(NCS)_{4-n} + n(CH_2)_2O \xrightarrow{(67)} R_nSi(OCH_2CH_2NCS)_{4-n} \qquad (175)$$

TABLE IV
DATA ON ISOTHIOCYANATES*

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties^a
$B(NCS)_3$	—	92/0.1	—	—	—	—	(*46, 170*)	B (*170*)
$(CH_2)_2O_2BNCS$	—	—	—	—	—	—	(*69*)	B
$(CH_2)_3O_2BNCS$	—	58–60/0.01	—	—	—	—	(*68, 69*)	B (*69*)
$PhB(OBu^n)NCS$	—	94–100/0.6	—	—	—	—	(*122*)	B
$PhB(NMe_2)NCS$	—	—	—	—	—	—	(*114*)	B, C
$PhB(NR_2)NCS$	—	—	—	—	—	—	(*97*)	—
$(Bu^nO)_2BNCS$	—	64.5–65/0.25	1.4449	20	0.9488	20	(*112, 115, 150*)	A (*112*), B (*150*)
$(Me_2N)_2BNCS$	—	50/0.4	1.5231	20	0.9941	20	(*112, 115, 150*)	B (*150*)
$(Et_2N)_2BNCS$	—	65/0.1	1.5032	20	0.943	20	(*115, 150*)	B (*150*)
o-$C_6H_4O_2BNCS$	—	84/0.7	1.6048	20	1.2814	20	(*112, 115, 150*)	A (*112*), B (*150*)
Ph_2BNCS	—	114–116/0.02	1.6714	20	1.119	20	(*115, 150*)	B (*150*)
$(HNBNCS)_3$	154	—	—	—	—	—	(*40, 93, 112, 113, 150*)	A (*112*), B (*93, 150*)
$(MeNBNCS)_3$	202–204	—	—	—	—	—	(*113, 150*)	A (*150*), B (*150*)
$(EtNBNCS)_3$	87–88	130/0.01	—	—	—	—	(*113, 150*)	A (*150*), B (*150*)
$(Pr^nNBNCS)_3$	121	—	—	—	—	—	(*113, 150*)	B (*150*)
$(Bu^sNBNCS)_3$	54	—	—	—	—	—	(*113, 150*)	B (*150*)
$(PhNBNCS)_3$	212–214	—	—	—	—	—	(*113, 150*)	B (*150*)
$(Bu^tNBNCS)_4$	291–295 (decomp.)	—	—	—	—	—	(*184, 185, 185a*)	B (*184, 185a*)
$Me_6P_3B_3H_3(NCS)_3$	63–64	—	—	—	—	—	(*191*)	B
$B(NCS)_3 \cdot C_5H_5N$	118–120	—	—	—	—	—	(*170*)	B
$B(NCS)_3 \cdot Et_3N$	102–104	—	—	—	—	—	(*170*)	B
$B(NCS)_3 \cdot CH_3CN$	137 (decomp.)	—	—	—	—	—	(*170*)	B
$B(NCS)_3 \cdot PhCN$	105 (decomp.)	—	—	—	—	—	(*170*)	B
$B(NCS)_3 \cdot PhCH_2CN$	95–96 (decomp.)	—	—	—	—	—	(*170*)	B
$PhB(NCS)_2 \cdot C_5H_5N$	153–155	—	—	—	—	—	(*150*)	B

$PhB(NCS)_2 \cdot EtOAc$	46–48	—	—	—	—	—	(*150*)	B
$BrB(NCS)_2$	—	80/0.15	—	—	1.3721	20	(*112, 115, 150*)	B (*150*)
Br_2BNCS	—	40/5	—	—	—	—	(*100a*)	B
$NaBH(NCS)_3$	—	—	—	—	—	—	(*107, 108*)	B (*107, 108*)
$K_3[Al(SCN)_6]$	—	—	—	—	—	—	(*158*)	—
$In(NCS)_3$	—	—	—	—	—	—	(*141a*)	—
Me_2TlNCS	—	—	—	—	—	—	(*94b*)	C
Et_2TlNCS	—	—	—	—	—	—	(*84, 94b*)	C (*94b*)
$PhTl(NCS)_2$	—	—	—	—	—	—	(*44*)	—
H_3SiNCS	−51.8	84/760	—	—	—	—	(*58, 59, 62, 70, 101, 102, 126*)	B (*62, 70*), C (*58*), G (*102*), H (*62*)
D_3SiNCS	—	—	—	—	—	—	(*62*)	B, H
$MeSiH_2NCS$	—	—	—	—	—	—	(*111*)	—
Me_3SiNCS	−32.8	143.1/760	1.4820	20	0.931	20	(*51, 70, 76, 89, 92, 93, 106b, 169, 179, 180c, 190*)	B (*70, 89, 93, 169, 180c*), I (*106b*)
Et_3SiNCS	—	210.5/760	1.4944	20	0.934	20	(*9, 70, 190*)	B (*70*)
$Pr^n{}_3SiNCS$	—	—	—	—	—	—	(*70*)	B
$PhMe_2SiNCS$	—	252–254/760	1.5556	30	1.0384	30	(*128*)	—
n-HeptylSiH_2NCS	—	235/760 (decomp.); 75–77/1	1.4939	20	0.921	20	(*26*)	—
CyclohexylSiH_2NCS	—	231/760; 91–91.8/1	1.5336	20	1.018	20	(*23*)	—
Ph_3SiNCS	76 ± 1	396/760	—	—	—	—	(*7, 70, 81*)	B (*70*)
$Me_2SiHNCS$	—	—	—	—	—	—	(*102*)	—
Cl_3SiNCS	−75	129.5/760	1.5091	20	1.461	24	(*4, 92*)	—
$(MeO)_3SiNCS$	—	170.5/760	1.4426	20	1.134	20	(*5*)	—
$(EtO)_3SiNCS)$	—	205.8/760	1.4431	20	1.036	20	(*10*)	—

TABLE IV (*Continued*)

Compound	M.P. (°C)	B.P. (°C)/mm	n_D	°C	d_4	°C	Reference	Other properties[a]
$Me_2Si(NCS)_2$	18	217.3/760; 55/0.08	1.5677	20	1.142	20	(*10, 57, 76, 92, 93, 169, 179, 190*)	B (*93, 169*)
$Et_2Si(NCS)_2$	—	245.5/760	1.5540	20	1.089	20	(*9, 190*)	—
$Ph_2Si(NCS)_2$	46	376/760	—	—	—	—	(*7*)	—
$MeSi(NCS)_3$	72	267.5/760	—	—	1.304	—	(*57, 76, 93, 169, 179, 190*)	B (*169*)
$EtSi(NCS)_3$	—	276/760	1.6195	20	1.264	20	(*9*)	—
$Pr^nSi(NCS)_3$	—	289.5/760	1.6014	20	1.2248	20	(*11, 19*)	—
$Bu^nSi(NCS)_3$	−0.5	300.6/760	1.5928	20	1.189	20	(*10*)	—
n-Heptyl$Si(NCS)_3$	—	347/760; 174/1	1.5739	20	1.129	20	(*26*)	—
Cyclohexyl$Si(NCS)_3$	—	348/760; 172–173/1	1.6179	20	1.231	20	(*23*)	—
$PhSi(NCS)_3$	52	339.6/760	—	—	—	—	(*7, 190*) —	—
$PhCH_2Si(NCS)_3$	36	348.9/760	—	—	1.28	20	(*10, 190*)	—
$CH_2{=}CH{-}CH_2Si(NCS)_3$	—	126–128/2.5	1.6140	26	—	—	(*83*)	B
$CH_2{=}CH{-}Si(NCS)_3$	—	134–138/3	1.6350	26	—	—	(*83*)	B
p-$MeC_6H_4Si(NCS)_3$	—	182–185/3.5	1.6490	26	—	—	(*83*)	B
$[(SCN)_3Si]_2O$	120–121	—	—	—	—	—	(*76*)	—
$Si(NCS)_4$	146	313/760	—	—	1.41	20	(*6, 40b, 92, 93, 134, 152, 169, 179, 190*)	A (*40b*), B (*40b, 93, 169*)
$Si(NCS)_4{\cdot}2C_5H_5N$	—	—	—	—	—	—	(*159, 160*)	B (*159, 160*)
$Si(NCS)_4{\cdot}2$ quinoline	—	—	—	—	—	—	(*159, 160*)	B (*159, 160*)
$Si(NCS)_4{\cdot}2$ isoquinoline	—	—	—	—	—	—	(*159, 160*)	B (*159, 160*)
H_3GeNCS	18.6 ± 0.3	150/760 (extr.)	—	—	—	—	(*171*)	D, F
Me_3GeNCS	—	—	—	—	—	—	(*162, 172, 180c*)	B (*172, 180c*)
Et_3GeNCS	−46	252/760; 113–114/8	1.517	20	1.184	20	(*15, 25*)	—

$\mathrm{Pr^{n}_{3}GeNCS}$	−56	287/760; 143–144/9	1.5063	20	1.105	20	*(15)*		—
$\mathrm{Pr^{i}_{3}GeNCS}$	18	277/760	1.512	20	1.112	20	*(18, 25)*		—
$\mathrm{Bu^{n}_{3}GeNCS}$	—	319/760; 135–136/2	1.5039	20	1.071	20	*(15)*		—
$\mathrm{Bu^{n}_{2}GeHNCS}$	—	96–98/1	1.5097	20	1.123	20	*(24)*		—
$\mathrm{Me_2Ge(NCS)_2}$	45.5–47	266–268/760	—	—	—	—	*(153)*		—
$\mathrm{Et_2Ge(NCS)_2}$	16	298/760; 113–116/1	—	—	1.356	20	*(15)*		—
$\mathrm{Pr^{i}_{2}Ge(NCS)_2}$	—	296/760; 105–107/1	1.558	20	1.234	20	*(25)*		—
$\mathrm{Bu^{n}_{2}Ge(NCS)_2}$	—	337/760; 140–141/1	1.5501	20	1.210	20	*(24)*		—
$\mathrm{EtGe(NCS)_3}$	—	—	—	—	—	—	*(12)*		—
$\mathrm{Ge(NCS)_4}$	—	—	—	—	—	—	*(15, 93)*	B *(93)*	
$\mathrm{Me_3SnNCS}$	108.5	—	—	—	—	—	*(162, 180c)*	B	—
$\mathrm{Et_3SnNCS}$	33	130/1	1.5825	20	—	—	*(20, 28, 41)*		—
$\mathrm{Bu^{n}_{3}SnNCS}$	—	160–162/0.8	1.543	20	1.2350	20	*(49)*	B	
$\mathrm{Ph_3SnNCS}$	172–173	—	—	—	—	—	*(173)*		—
$\mathrm{Me_2Sn(NCS)_2}$	198.6–199.4	—	—	—	—	—	*(163)*		—
$\mathrm{Et_2Sn(NCS)_2}$	—	—	—	—	—	—	*(41)*		—
$\mathrm{Bu^{n}_{2}Sn(NCS)_2}$	144–145	—	—	—	—	—	*(93, 163, 190a)*	B *(93)*	
$\mathrm{(CH_2{=\!=}CH)_2Sn(NCS)_2}$	163.5–165	—	—	—	—	—	*(164)*		—
$\mathrm{Sn(NCS)_4}$	—	—	—	—	—	—	*(93)*	B *(93)*	
$\mathrm{Bu^{n}_{2}Sn(NCS)_2\cdot 2,2'}$-bipyridine	152.5/153	—	—	—	—	—	*(2)*		—
$\mathrm{Me_3PbNCS}$	145 decomp.	—	—	—	—	—	*(180c)*	B	
$\mathrm{Et_3PbNCS}$	35	—	—	—	—	—	*(95, 116a)*		—
$\mathrm{Ph_3PbNCS}$	—	—	—	—	—	—	*(63, 173)*	B *(63)*	
$\mathrm{Ph_2Pb(NCS)_2}$	—	—	—	—	—	—	*(116a, 143)*		—

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[a] See Table I for symbols used.

* See data added in proof, p. 184.

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Data Added in Proof

TABLE I (*Continued*)
DATA ON AZIDES

Compound	M.P. (°C)	B.P. (°C)/mm	Reference	Other properties
$Si(N_3)_4$	—	—	(*201*)	—
Et_3SiN_3[a]	—	104/95	(*202a*)	B
$Bu^n_3SiN_3$[b]	—	88/0.01	(*202a*)	B
$(Me_2N)_3SiN_3$[c]	—	76/11	(*202a*)	B
$(MeO)_3SiN_3$[d]	—	18/4	(*202a*)	B
F_3SiN_3	—	—	(*202a*)	B
$(1,3,5\text{-}Me_3C_6H_2)_2SiMeN_3$	65–68	—	(*202a*)	B
$(1,3,5\text{-}Me_3C_6H_2)_2Si(NPPh_3)N_3$	189	—	(*202a*)	B
$(1,3,5\text{-}Me_3C_6H_2Si(N_3)_2$	87.5	—	(*202a*)	B
$Me_2Ge(N_3)_2$	−14	43.5/2	(*155, 157*)	—

[a] $n_D = 1.4424$, 20°C. [b] $n_D = 1.4522$, 22°C. [c] $n_D = 1.4494$, 20°C. [d] $n_D = 1.3969$, 26°C.

TABLE IV (*Continued*)
DATA ON ISOTHIOCYANATES

Compound	M.P. (°C)	Reference
$Bu^n_2Sn(NCS)_2.2,2'$-bipyridine	152.5/153	(*2*)
$Pr^n_2Sn(NCS)_2$	135–136	(*190a*)
$Et_2Sn[OSn(OH)Et_2]NCS$	170–176 decomp.	(*190a*)
$(Et_2SnNCS)_2O$	178–179	(*190a*)
$Me_2Sn(OC_9H_6N)NCS$	123–124	(*190a*)
$Pr^n_2Sn(OC_9H_6N)NCS$	144	(*190b*)
Et_2PnNCS	35	(*95, 116a*)
Ph_3PbNCS	—	(*63, 173a*), B (*63*)
$Ph_2Pb(NCS)_2$	—	(*116a, 143*)