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Review

O-ORGANOMETAL HYDROXYLAMINES AND OXIMES

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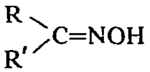
CONTENTS

I. Introduction 145
II. Preparative methods 145
  A. From organometal halides 146
  B. From organometal hydrides 147
  C. From organometal oxides, hydroxides and alkoxides 148
  D. From organometal amides 152
  E. From alkylmetals 152
  F. Miscellaneous reactions 153
III. Properties 153
  A. Thermal stability 153
  B. Hydrolysis 154
  C. Reaction with hydrogen chloride 155
  D. Reaction with acyl halides 155
  E. Alcoholysis reactions 155
  F. Hydrogenation 155
  G. Reactions with organometal halides 155
  H. Insertion reactions 156
  I. Structural studies 156
References 168

I. INTRODUCTION

Compounds considered to be within the scope of this review are those obtained by the replacement of hydroxyl hydrogen of hydroxylamines, RR′NOH and oximes,  $\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}NOH$ by an organometal moiety of a non-transition element. The alkoxy metal analogues are few and have been included only for comparison. An attempt has been made to provide comprehensive literature coverage up to January 1972.

II. PREPARATIVE METHODS

The replacement of hydrogen of the N–OH group in hydroxylamines and oximes by an organometal moiety can be carried out from a number of starting materials, *e.g.*, organometal halides, oxides, hydrides and amides. The preparative methods, therefore, may conveniently be discussed under the heading of starting materials.

A. From organometal halides

The reaction of organometal halides with hydroxylamines or oximes is a convenient and generally useful method for preparing these derivatives. The reaction is usually facilitated by the presence of a suitable hydrogen halide acceptor such as pyridine, triethylamine or an excess of the starting material (oxime or hydroxylamine) itself.

O-Methylsilyl derivatives of hydroxylamine have been obtained in 70–80% yield by the reaction of methylchlorosilanes with excess *N,N*-diethylhydroxylamine in heptane[1-3]:

$$\mathrm{Me_{4-\mathit{n}}SiCl_{\mathit{n}} + 2\mathit{n}Et_2NOH \rightarrow Me_{4-\mathit{n}}Si(ONEt_2)_{\mathit{n}} + \mathit{n}Et_2NOH{\cdot}HCl} \qquad (1)$$

However, $\mathrm{Si(ONEt_2)_4}$ and $\mathrm{MeSiCl(ONEt_2)_2}$ could be obtained only in 40–45% yield by this procedure.

O-Trimethylsilyl-substituted alkylhydroxylamines, $\mathrm{Me_3SiONRR'}$ ($\mathrm{R = H, R' = Me}$; $\mathrm{R = R' = Et}$; $\mathrm{R = Me, R' = SiMe_3}$), were also prepared by a similar reaction using triethylamine as HCl acceptor[4]:

$$\mathrm{Me_3SiCl + HONRR' + Et_3N \rightarrow Me_3SiONRR' + Et_3N{\cdot}HCl} \qquad (2)$$

Reactions of trialkylchlorosilanes with unsubstituted hydroxylamine have been studied in detail by Wannagat and coworkers[4-7]. Mono-, bis-, and tris(trimethylsilyl)-substituted hydroxylamines were obtained by the following methods[7]:

$$\mathrm{R_3SiCl + 2HONH_2 \rightarrow R_3SiONH_2 + H_3NOHCl} \qquad (3)$$
(R = Me, Et and Ph)

$$\mathrm{Me_3SiONH_2 + Me_3SiCl + Et_3N \rightarrow Me_3SiONHSiMe_3 + Et_3NHCl} \qquad (4)$$

$$\mathrm{Me_3SiONHSiMe_3 + BuLi \rightarrow Me_3SiON(Li)SiMe_3 + BuH}$$
$$\mathrm{Me_3SiON(Li)SiMe_3 + Me_3SiCl \rightarrow Me_3SiON(SiMe_3)_2 + LiCl} \qquad (5)$$

Although no pure compound was obtained from the reaction of boron trichloride with hydroxylamine hydrochloride, there was surprisingly some evidence for the formation of β-trichloro-*N*-trihydroxy borazine, $\mathrm{(ClB{-}NOH)_3}$[8].

Reactions of trialkylchlorosilanes with a variety of aldoximes and ketoximes in the presence of pyridine have been carried out by Voronkov and coworkers[9-11]. *O*-Trialkylsilyl furaldoxime[12] and *O*-trimethylsilyl(germyl)cyclohexanone oxime[13,14] were also prepared by the above method using triethylamine as HCl acceptor:

$$\mathrm{R_3MCl + HON{=}CR'R'' + C_5H_5N\ (or\ Et_3N) \rightarrow R_3MON{=}CR'R'' + C_5H_5N{\cdot}HCl\ (or\ Et_3NHCl)} \qquad (6)$$

Singh, Rai and Mehrotra demonstrated the versatility of this reaction by synthesizing a large variety of mono-, di-, tri-, and tetra-oximato derivatives of silicon[15,16] and germanium[17] using pyridine or triethylamine:

$$R_{4-n}MCl_n + n\mathrm{HON{=}CR'R''} + n\mathrm{C_5H_5N}\ (\text{or } \mathrm{Et_3N}) \xrightarrow[\text{or PhH}]{\mathrm{Et_2O}} R_{4-n}M(\mathrm{ON{=}CR'R''})_n + n\mathrm{C_5H_5N{\cdot}HCl}\ (\text{or } \mathrm{Et_3N{\cdot}HCl}) \qquad (7)$$

Reactions of $AsCl_3$[18], $RAsCl_2$[19] and R_2AsCl[20,21] with various oximes have been studied by Kamai and coworkers[18-21] in ether in the presence of triethylamine or pyridine:

$$R_{3-n}AsCl_n + n\mathrm{HON{=}CR'R''} + n\mathrm{C_5H_5N}\ (\text{or } \mathrm{Et_3N}) \rightarrow R_{3-n}As(\mathrm{ON{=}CR'R''})_n + n\mathrm{C_5H_5N{\cdot}HCl}\ (\text{or } \mathrm{Et_3N{\cdot}HCl}) \qquad (8)$$

For experimental convenience, ammonia has also been successfully used as HCl acceptor for the synthesis of mono-, di- and tetra-oximates of germanium[17,22]:

$$R_{4-n}GeCl_n + n\mathrm{HON{=}CR'R''} + n\mathrm{NH_3} \rightarrow R_{4-n}Ge(\mathrm{ON{=}CR'R''})_n + n\mathrm{NH_4Cl} \qquad (9)$$

Sodium or lithium salts of oximes react with organometal halides readily. The interaction between sodium acetoximate and trimethylchlorosilane[15], triethylchlorosilane[23] and dimethyldichlorosilane[15] in petroleum ether gave the corresponding silicon acetoximates in good yields. Trialkyltin oximates[13,24], dialkyltin dioximates[25], alkyltin trioximates[25] and diphenylarsenic cyclohexanone oximate[14] have been similarly prepared:

$$R_{x-n}MCl_n + n\mathrm{Na(Li)ON{=}CR'R''} \rightarrow R_{x-n}M(\mathrm{ON{=}CR'R''})_n + n\mathrm{NaCl}\ (\text{or } \mathrm{LiCl}) \qquad (10)$$

O-Trimethylsilylbis(trifluoromethyl)hydroxylamine[26] has also been reported recently by an analogous route:

$$\mathrm{Me_3SiCl + NaON(CF_3)_2 \rightarrow Me_3SiON(CF_3)_2 + NaCl} \qquad (11)$$

$Hg[ON(CF_3)_2]_2$ has been found to be a potential reagent for the synthesis of the corresponding boron, silicon, germanium, phosphorus, arsenic, antimony and bismuth compounds[27-30]:

$$MCl_n + \frac{n}{2}Hg[ON(CF_3)_2]_2 \rightarrow M[ON(CF_3)_2]_n \qquad (12)$$

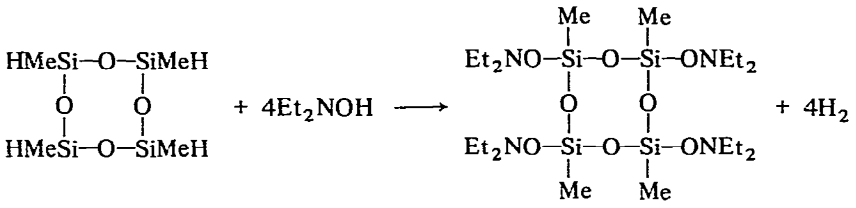
B. From organometal hydrides

Hydroxylamine and *N,N*-dialkylhydroxylamines have been shown to catalyse the reactions of silicon hydrides with alcohols and carboxylic acids[31], indicating the formation of some intermediates between amines and silanes.

Diphenylsilane reacts with *N,N*-diethylhydroxylamine to give $Ph_2Si(ONEt_2)_2$. Siloxanes containing Si-H bonds, *e.g.*, $(Me_2SiH)_2O$ and $[(Me_3SiO)SiHMe]_2$ also react similarly[3]:

$$>\!Si\text{-}H + HONEt_2 \rightarrow\ >\!Si\text{-}ONEt_2 + H_2 \qquad (13)$$

Pande and Ridenour[2] obtained a cyclic siloxane containing the *N,N*-diethylaminoxy group on silicon by the following reaction:



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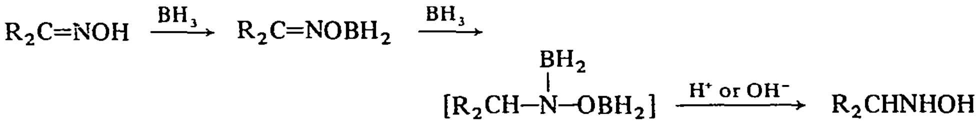
A variety of trialkylsilyl oximates have been synthesized (in 80-90% yields) by refluxing trialkylsilane with oximes[12] in presence of $ZnCl_2$[23,32]:

$$R_3SiH + HON{=}CR'R'' \rightarrow R_3SiON{=}CR'R'' + H_2 \qquad (15)$$

Parry and coworkers[33,34] have studied the reactions of diborane with hydroxylamine and various alkyl-substituted hydroxylamines; addition compounds were obtained which eliminated hydrogen on heating. In ether, oximes are reduced by diborane to hydroxylamines, presumably via the intermediate $R_2C{=}NOBH_2$[35]:



$$R_2C{=}NOH \xrightarrow{BH_3} R_2C{=}NOBH_2 \xrightarrow{BH_3} [R_2CH\text{-}\overset{\displaystyle BH_2}{\overset{|}{N}}\text{-}OBH_2] \xrightarrow{H^+ \text{ or } OH^-} R_2CHNHOH$$

Compounds of the type $M[ON(CF_3)_2]_n$ (M = Si, Ge and As) are formed along with $(CF_3)_2NOH$ during the reaction of the mercury analogue, $Hg[ON(CF_3)_2]_2$ with compounds containing M-H bonds[27,29].

$$M\text{-}H + Hg[ON(CF_3)_2]_2 \rightarrow M[ON(CF_3)_2] + Hg + (CF_3)_2NOH \qquad (16)$$

C. *From organometal oxides, hydroxides and alkoxides*

The sodium salt of *N,N*-bis(trifluoromethyl)hydroxylamine[26] and of potassium 2-pyridine aldoximate[36], are obtained by the reaction of the free hydroxylamine and oxime respectively with metal hydroxides:

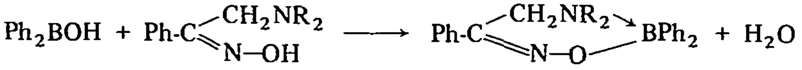
$$>\!N\text{-}OH + MOH \longrightarrow\ >\!N\text{-}OM + H_2O \qquad (17)$$

Sodium ethoxide on reaction with acetoxime precipitated $NaON{=}CMe_2$[37]:

$$Me_2C{=}NOH + NaOEt \rightarrow NaON{=}CMe_2 + EtOH \qquad (18)$$

Boronic and borinic acids form 1/1 complexes with hydroxylamine[38]. Reactions of dibutylborinic acid with hydroxylamine and *N*-substituted hydroxylamine[39,40] and of diphenylborinic acid with *Z* and *E* oximes of tertiary *N*-phenacylamines[41] gave corresponding products:

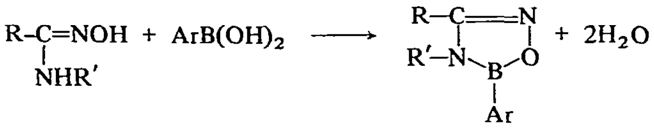
$$R_2BOH + HONR'R'' \rightarrow R_2BONR'R'' + H_2O \qquad (19)$$



(20)

However, only *Z* derivatives could be characterised in the latter reactions[41].

A variety of amidoximes have been shown to react with arylboronic acids giving cyclic products[42,43]:



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Reactions of ethyl, isopropyl and butyl borates with *N*,*N*-diethylhydroxylamine have been studied by Sharma, Gupta and Mehrotra[44,45]. The reactions are slow in refluxing benzene. The bis and tris derivatives are obtained as yellow monomeric sublimable solids:

$$B(OR)_3 + nHONEt_2 \rightarrow (RO)_{3-n}B(ONEt_2)_n + nROH \qquad (22)$$

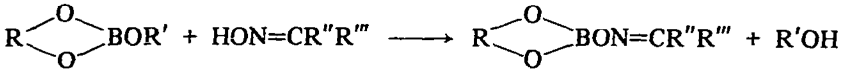
The reactions in equimolar ratio appeared to give mainly the bis product, indicating that the mono products are probably unstable and disproportionate to yield the bis products.

Singh and Mehrotra[46] investigated the reactions of a variety of oximes with ethyl and isopropyl borates in refluxing benzene:

$$B(OR)_3 + nHON{=}CR'R'' \rightarrow B(OR)_{3-n}(ON{=}CR'R'')_n + nROH \qquad (23)$$

It was observed that these reactions are sterically controlled. Thus the removal of the first alkoxy group is facile after which the reaction becomes quite slow. With slow and efficient fractionation of the alcohol (ethanol or isopropanol)-benzene azeotrope, the reaction could be pushed to completion with acetoxime and methyl ethyl ketoxime. However, with diethyl ketoxime the final product was only the bis derivative, $(RO)B(ON{=}CEt_2)_2$. All the unsymmetrical mono and bis derivatives disproportionated during attempted distillation. Such disproportionations are quite common in alkoxyboron chemistry[47].

In view of the high stability of unsymmetrical cyclic borates[48], Singh *et al.*[46] studied the reactions of various oximes with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane. Reactions are slow, requiring 10–20 hours for completion even with continuous azeotrope removal; distillable products are finally obtained: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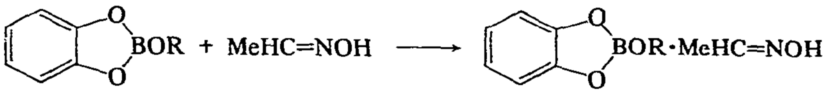
Exothermic reactions with the formation of white crystalline 1/1 adducts[46] were observed when 2-alkoxy-1,3,2-benzodioxaboroles were mixed with aldoximes (*e.g.*, acetaldoxime):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The electrophilic nature of boron in aryloxy derivatives is well established. Steric factors are important in the above complex formation reactions. Thus 2-isopropoxy-1,3,2-benzodioxaborole does not appear to form a stable adduct with butyraldoxime[46].

Reactions of aluminium isopropoxide with oximes[49] and diethylhydroxylamine[44,45] are much faster than those of alkyl borates. Two isopropoxy groups are easily replaced; replacement of the third is slower. These observations are in line with those for alcoholysis[50,51] and transesterification[52] reactions of aluminium isopropoxide:

$$\mathrm{Al(OPr\text{-}i)_3} + n\mathrm{HON}< \longrightarrow \mathrm{(Pr\text{-}i\text{-}O)_{3-n}Al(ON<)_n} + n\mathrm{Pr\text{-}i\text{-}OH} \qquad (26)$$

Reactions of bis(tributylgermanium) oxide and dibutylgermanium oxide with a number of ketoximes have been investigated recently. These reactions are sluggish but could be completed in 4–8 hours in the presence of *p*-toluene sulphonic acid as catalyst; water formed in the reaction was removed azeotropically[17]:

$$\mathrm{(Bu_3Ge)_2O + 2HON{=}CRR' \rightarrow 2Bu_3GeON{=}CRR' + H_2O} \qquad (27)$$

$$\mathrm{Bu_2GeO + 2HON{=}CRR' \rightarrow Bu_2Ge(ON{=}CRR')_2 + H_2O} \qquad (28)$$

The reaction of bis(triorganotin) oxide with oximes[13,14,24,53–58] is much easier and no catalyst is needed. A variety of triorganotin oximates have thus been prepared by removing the water formed azeotropically:

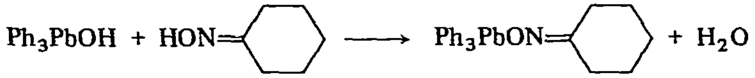
$$\mathrm{(R_3Sn)_2O + 2HON{=}CR'R'' \rightarrow 2R_3SnON{=}CR'R'' + H_2O} \qquad (29)$$

Triorganotin hydroxides have been used similarly for the synthesis of oxime[13,14] and hydroxylamine[59] derivatives:

$$\mathrm{R_3SnOH + HON}< \longrightarrow \mathrm{R_3SnON}< + \mathrm{H_2O} \qquad (30)$$

The reaction has been extended to prepare oximates of arsenic[21] and lead[14]:

$$\mathrm{(Et_2As)_2O + 2HON{=}C(Me)Pr \rightarrow 2Et_2AsON{=}C(Me)Pr + H_2O} \qquad (31)$$



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(33)

Reactions of alkoxy derivatives of Group IVB metals with hydroxylamine and oximes have been studied in detail during the last few years. It has been observed that the reactions of alkoxysilanes with *N,N*-diethylhydroxylamine are very slow[2]. During a study of interactions between tetraethoxysilane and dimethyldiethoxysilane with acetoxime and methyl ethyl ketoxime, Singh, Rai and Mehrotra[15] made similar observations and found that these reactions can be catalysed by a small amount of sodium. Thus the reaction of dimethyldiethoxysilane could be pushed to completion in 18-20 hours in the presence of sodium by slowly fractionating out the ethanol-benzene azeotrope:

$$Me_2Si(OEt)_2 + 2HON{=}CRR' \rightarrow Me_2Si(ON{=}CRR')_2 + 2EtOH \qquad (34)$$

However, with tetraethoxysilane and acetoxime, the tris derivative is the final product:

$$Si(OEt)_4 + 4HON{=}CMe_2 \rightarrow (EtO)Si(ON{=}CMe_2)_3 + 3EtOH + Me_2C{=}NOH \qquad (35)$$

This may be due to steric hindrance as silicon tetraacetoximate could be prepared from silicon tetrachloride.

In contrast to tetraethoxysilane, germanium tetraethoxide reacts readily with acetoxime giving the tetraacetoximate:

$$Ge(OEt)_4 + 4HON{=}CMe_2 \rightarrow Ge(ON{=}CMe_2)_4 + 4EtOH \qquad (36)$$

Reactions of butylgermanium ethoxides required a catalyst (*p*-toluene sulphonic acid)[17]:

$$Bu_{4-n}Ge(OEt)_n + nHON{=}CRR' \rightarrow Bu_{4-n}Ge(ON{=}CRR')_n + nEtOH \qquad (37)$$

Reactions of alkyltin alkoxides with oximes are much easier than with silicon or germanium and the method has been employed by a number of workers to prepare organotin oximates[13,14,53,58,60], *e.g.*:

$$R_{4-n}Sn(OR')_n + nHON{<} \longrightarrow R_{4-n}Sn(ON{<})_n + nR'OH \qquad (38)$$

Sharmá[45], studied the reactions of dialkyltin dialkoxides with *N,N*-diethylhydroxylamine and isolated mono- and bis-hydroxylamine compounds:

$$R_2Sn(OR')_2 + nEt_2NOH \rightarrow R_2Sn(OR')_{2-n}(ONEt_2)_n + nR'OH \qquad (39)$$

An oximate derivative of antimony[14] has been obtained by a similar method:

$$Ph_3Sb(OR)_2 + 2MeCH{=}NOH \rightarrow Ph_3Sb(ON{=}CHMe)_2 + 2ROH \qquad (40)$$

D. From organometal amides

Organometal amides react readily with alcohols to give organometal alkoxides[61] Similarly *N,N*-diethylhydroxylamine derivatives of boron were readily obtained from aminoboranes[62]:

$$\mathrm{R}_{3\text{-}n}\mathrm{B(NMe_2)}_n + n\mathrm{HONEt_2} \rightarrow \mathrm{R}_{3\text{-}n}\mathrm{B(ONEt_2)}_n + n\mathrm{Me_2NH} \qquad (41)$$

Unsymmetrical derivatives of the type $\mathrm{(Me_2N)_2B(ONEt_2)}$ and $\mathrm{(Me_2N)B(ONEt_2)_2}$ could not be isolated due to their easy disproportionation into symmetrical derivatives.

Silylamines, $\mathrm{R_3SiNH_2}$ (R = alkyl or phenyl) and $\mathrm{Me_3SiNEt_2}$ have been shown to react with hydroxylamine hydrochloride[63] and hydroxylammonium sulphate[64] respectively to yield $\mathrm{R_3SiONH_2}$ and *N,N,O*-tris(trimethylsilyl)hydroxylamine:

$$\mathrm{R_3SiNR'R''} + \mathrm{HO{-}N}\!< \; \rightarrow \mathrm{R_3SiON}\!< \; + \mathrm{HNR'R''} \qquad (42)$$

The method has been used in preparing *O*-trialkylsilyl and *O*-trimethylstannyl derivatives of oximes from bis(trimethylsilyl)amine[23,32], triethylsilylamine[23], trimethylsilyl[15,16] and trimethylstannyl[13] diethylamines:

$$\mathrm{(Me_3Si)_2NH} + 2\mathrm{HON{=}CRR'} \rightarrow 2\mathrm{Me_3SiON{=}CRR'} + \mathrm{NH_3} \qquad (43)$$

$$\mathrm{R_3MNR'R''} + \mathrm{HON{=}CR'''R''''} \rightarrow \mathrm{R_3MON{=}CR'''R''''} + \mathrm{R'R''NH} \qquad (44)$$

E. From alkylmetals

A polar metal–carbon bond in alkylmetals can be readily cleaved by oximes with the liberation of alkanes and the formation of metal oximates. A vigorous exothermic reaction was observed in mixing acetoxime with methyllithium in diethyl ether, and lithium acetoximate[65] was simultaneously precipitated as an insoluble, infusible polymer. Similarly lithium cyclohexanone oximate[13] was obtained from butyllithium and cyclohexanone oxime:

$$\mathrm{RLi} + \mathrm{HON{=}CR'R''} \rightarrow \mathrm{LiON{=}CR'R''} + \mathrm{RH} \qquad (45)$$

Reactions of diethylzinc[66], dimethylzinc[67] and dimethylberyllium[68] with acetoxime as well as that of diphenylzinc[69] with *N,N*-diethylhydroxylamine and benzaldoxime and of diethylzinc[69] with acetophenoneoxime have been studied and depending on the ratio of reactants, mono or bis derivatives have been obtained:

$$\mathrm{R_2M} + n\mathrm{HON}\!< \; \rightarrow \mathrm{R}_{2\text{-}n}\mathrm{M(ON}\!<)_n + n\mathrm{RH} \qquad (46)$$

Wade *et al.* studied the reactions of acetoxime[65] and pyridine-2-carbaldehyde oxime[70] with trimethyl-boron, -aluminium, -gallium, -indium and -thallium and isolated dimethylmetal oximates:

$$\mathrm{Me_3M} + \mathrm{HON}\!< \; \rightarrow \mathrm{Me_2MON}\!< \; + \mathrm{MeH} \qquad (47)$$

F. Miscellaneous reactions

The reactions of bis(trifluoromethyl)nitroxide radical with tris(trifluoromethyl)phosphine and -arsine have been studied by Ang and Ho[71]. The phosphines are converted into P^V derivatives:

$$(CF_3)_3P + 2(CF_3)_2NO^{\bullet} \rightarrow (CF_3)_3P[ON(CF_3)_2]_2 \tag{48}$$

$$(CF_3)_2PCl + 2(CF_3)_2NO^{\bullet} \rightarrow (CF_3)_2PCl[ON(CF_3)_2]_2 \tag{49}$$

The reaction with tris(trifluoromethyl)arsine[71] takes a different course and stepwise substitution of the alkyl group occurs:

$$(CF_3)_3As \xrightarrow[\text{Room temp.}]{(CF_3)_2NO^{\bullet}} (CF_3)_2AsON(CF_3)_2 \xrightarrow{(CF_3)_2NO^{\bullet}}$$

$$(CF_3)As[ON(CF_3)_2]_2 \xrightarrow[70^{\circ}C]{(CF_3)_2NO^{\bullet}} As[ON(CF_3)_2]_3 \tag{5}$$

Bis(trifluoromethyl)nitroxide reacts slowly at room temperature with tin, lead[72], arsenic[73], selenium and tellurium[74] to provide crystalline derivatives:

$$M + n(CF_3)_2NO^{\bullet} \rightarrow M[ON(CF_3)_2]_n \tag{51}$$
$$(M = Pb, Sn; n = 2; M = As; n = 3; M = Se, Te; n = 4)$$

The nitroxide radical reacts with organometal hydrides of silicon, phosphorus and arsenic giving the corresponding nitroxides[73]:

$$M\text{-}H + (CF_3)_2NO^{\bullet} \rightarrow M[ON(CF_3)_2] \tag{52}$$

Tin nitrosodicyanomethanides[75] have been obtained by the following reactions:

$$R_3SnCl + AgC(NO)(CN)_2 \rightarrow R_3SnON{=}C(CN)_2 + AgCl \tag{53}$$

$$R_2SnCl_2 + 2AgC(NO)(CN)_2 \rightarrow R_2\,Sn[ON{=}C(CN)_2]_2 + 2AgCl \tag{54}$$

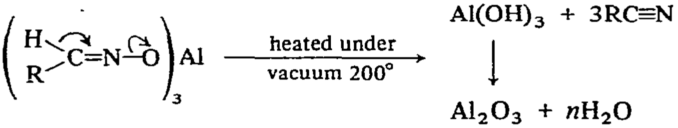
III. PROPERTIES

The main emphasis in the field of hydroxylamine and oxime derivatives of metals has been on the preparative side. Only a few reactions of these compounds have been studied and the results indicate that these behave like simple metal alkoxides towards other reagents.

A. Thermal stability

No systematic study of the thermal stability of these metal derivatives has been undertaken. However, it appears that most of the derivatives of boron, silicon, germanium and tin are volatile and can be distilled unchanged. In cases where there is increased polymerisation, the compounds are either infusible insoluble solids or viscous liquids which decompose on heating. Thus derivatives of the type $R_2Sn(OR')(ONEt_2)$ and $R_2Sn(ONEt_2)_2$[45] are generally infusible and insoluble solids. Only the dibutyltin derivatives could be volatilised and the yields were very poor.

N,N-Diethylhydroxylamine derivatives of aluminium[44,45] are viscous liquids which decomposed on heating. Similarly aldoxime derivatives of aluminium[22,49] are white, glassy, infusible solids, which appear to resist wetting. These are stable up to 100° but decompose with explosive violence at bath temperature of about 200° on attempted vacuum distillation at 0.2 mm; the volatile product formed during decomposition appears to be a nitrile (characterised by the presence of a medium intensity band at 2252 cm^{-1}) and the residue corresponds to $Al_2O_3{\cdot}O{\cdot}5H_2O$. The decomposition, therefore, appears to take the following course:



Aluminium ketoximates[22,49] also tend to decompose when heated under reduced pressure, but apparently not explosively.

The unsymmetrical derivatives of boron[46], *e.g.*, $(RO)_{3-n}B(ONEt_2)_n$, $(RO)_{3-n}B(ON{=}CR'R'')_n$ and $(R_2N)_{3-n}B(ONEt_2)_n$ disproportionate on heating into the symmetrical products.

B. Hydrolysis

The organometal hydroxylamines are generally moisture sensitive and are readily hydrolysed. The silicon derivatives are rather more stable towards hydrolysis, particularly in neutral medium. However, the Si–O bond cleavage is strongly catalysed by acids. Triethylsilicon acetoximate[11] as well as other oximates[9] were partially hydrolysed by 5% hydrochloric acid in 7 hours, yielding hexaethyldisiloxane, the parent oxime and a nitrogeneous tar. On the other hand, the trimethylsilicon acetoximate as well as trimethylsilicon cyclopentanone oximate are completely hydrolysed by 5% hydrochloric acid in an hour[22].

Although no detailed study has been made, the ease of hydrolysis of the compounds of the type, $Me_nSi(ON{=}CR'R'')_{4-n}$, appears to increase in the following order[22]: $Me_3SiON{=}CR'R'' < Me_2Si(ON{=}CR'R'')_2 < MeSi(ON{=}CR'R'')_3 < Si(ON{=}CR'R'')_4$.

There is a report that hydrolysis of organosilicon aldoximates by water, aq. KOH or HCl gave the original aldehyde, NH_2OH and silanols or disiloxanes[10]. Boron[46], silicon[15,16], germanium[17] and tin[13,58] oximates are also readily hydrolysed by water to give the parent oxime quantitatively.

C. Reaction with hydrogen chloride

The tri-n-butyltin derivative of cyclohexanone oxime reacted exothermally with hydrogen chloride gas[13] forming tributyltin chloride:

$$Bu_3SnON{=}C_6H_{10} + HCl \rightarrow Bu_3SnCl + HON{=}C_6H_{10}$$

Similarly, $As[ON(CF_3)_2]_3$ with HCl gives arsenic trichloride and hydroxylamine[29].

D. Reaction with acyl halides

Organosilicon[22,23], -germanium[17], -tin[58] and -arsenic[19] oximates react with acyl (and benzoyl) halides forming *O*-acyl (and *O*-benzoyl) oximes and organometal halides:

$$Me_3SiON{=}CMe_2 + C_6H_5COCl \rightarrow Me_3SiCl + Me_2C{=}NO\cdot COC_6H_5$$

$$EtAs(ON{=}CMeEt)_2 + 2CH_3COCl \rightarrow EtAsCl_2 + 2MeEtC{=}NO\cdot COCH_3$$

E. Alcoholysis reactions

Organoarsenic oximates react with alcohols[19] and ethylene glycol[21] under appropriate conditions:

$$PrAs(ON{=}CMePr)_2 + 2C_6H_{13}OH \xrightarrow[130^\circ]{CO_2,\ 2\ h} PrAs(OC_6H_{13})_2 + 2MePrC{=}NOH$$

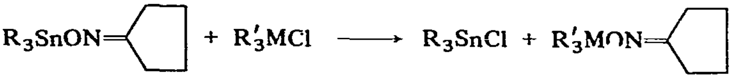
$$2Bu_2AsON{=}CMeEt + (HOCH_2)_2 \xrightarrow[17\ mm]{1\ h,\ 80^\circ} (Bu_2AsOCH_2)_2 + 2\ MeEtC{=}NOH$$

F. Hydrogenation

Attempts have been made to study the hydrogenation of the C=N bond in trialkylsilicon oximates. Reduction of the compound $Me_3SiON{=}CMePh$ afforded a mixture of hexamethyldisiloxane and an amine $PhCH(Me)NH_2$[11]. Hydrogenation of $Me_3SiON{=}CHPr$, over Pt-black in ethanol gave Me_3SiOH, $(Me_3Si)_2O$, $BuNH_2$, Bu_2NH and Bu_3N[10].

G. Reactions with organometal halides

Triorganotin oximates undergo exothermic reactions with organogermanium and -silicon chlorides with cleavage of the Sn–O bond. The reactions of tributyltin-cyclohexanone oximate and trialkyltin-cyclopentanone oximates have been studied,[13,15–17] *e.g.*:



H. Insertion reactions

Insertion reactions of organotin alkoxides[76] have been studied in great detail. Trialkyltin oximates also react with unsaturated substrates, although less readily than organotin alkoxides. Reactions of trialkyltin cyclohexanone oximate[13] with CCl_3CHO, CBr_3CHO, PhNCO, MeNCO, EtNCO and PhNCS and of trialkyltin cyclopentanone oximate[58] with PhNCO have been studied. The acceptor strength of multiply bonded reagents appears to decrease in the following order[13]: $X_3CCHO > PhNCO > RNCO > PhNCS$.

$$R_3SnON{=}C_6H_{10} + A{=}B \rightarrow R_3SnABON{=}C_6H_{10}$$

Trialkylgermanium oximates are less reactive and appear to react only with the strongest acceptor, *i.e.*, chloral. The silicon derivatives do not appear to show this type of reaction at all[13].

I. Structural studies

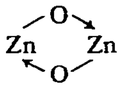
Structural studies on organometal hydroxylamines and oximes are limited to only a few derivatives and the conclusions derived are mostly tentative. As would be evident from the following description, much more systematic investigations are required to throw light on the nature of bonding causing association and to determine the stereochemical details.

Lithium oximates, $LiON{=}CMe_2$[65] and $LiON{=}C_6H_{10}$[13] are presumably polymeric and exhibit in their IR spectra, ν(CN) lower than in the parent ligand; this has been ascribed to the presence of Li-O-N → Li bridges.

Hexameric zinc derivative of diethylhydroxylamine, $PhZnONEt_2$ in its PMR spectra showed methylene protons shifted to low field in comparison to the hydroxylamine, indicating a lower electron density on nitrogen; this has been interpreted to arise probably from the involvement of nitrogen in the coordination process[69].

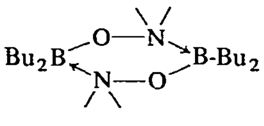
Alkylzinc[67] and alkylberyllium[68] oximates exist as tetrameric species. PMR spectra of $MeZnON{=}CMe_2$ in aromatic solvents showed non-equivalence of isopropylidene protons, $N{=}CMe_2$ appearing as doublets of equal intensity; this is consistent with the known geometry of acetoxime itself as reported by Lustig[77] and Hatton and Richards[78]. A preliminary X-ray observation[79] showed the zinc compound as possessing cage-like structure involving 5- and 6-membered Zn-O-N rings with common coordination numbers for zinc, 4; nitrogen and oxygen, 3.

On the basis of the similarity in PMR spectra, a similar structure has been proposed for $EtZnON{=}CMePh$[69] and $MeBeON{=}CMe_2$[68]. In all these oximates of zinc and beryllium, the observance of low ν(CN) (in comparison to the parent oxime) has also been regarded as additional evidence for the involvement of nitrogen in coordination association.

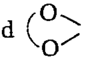
Interestingly phenylzinc benzaldoximate, $PhZnON{=}CHPh$ has been found to be highly associated[69]. Because of no change in ν(CN) in the IR spectrum of the oximate,  bridges are considered to be responsible for the polymerisation. This significant increase in polymerisation as well as change in the mode of association on replacing merely the Me group by H, is not easily understood.

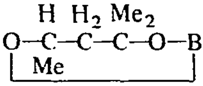
The presence of a strong coordinate bond in these beryllium and zinc complexes is also revealed by their unreactivity towards strong donors like dimethylaminopyridine.

Products of the type Bu_2BONHR[39] (R = H and Bu) have been reported to be dimeric in acetonitrile. On the basis of the presence of only one pair of NH stretching vibrations in the range 3300–3200 cm^{-1} in the IR spectra which is characteristic of 4-coordinate nitrogen, a six-membered BONBON ring has been postulated to be present:



A similar structure has been proposed for a number of other dimeric hydroxylamine complexes, $RR'BONH_2$ (R = R' = Ph; R = Ph, R' = 2-thienyl and R = R' = 2-thienyl)[40]. With sterically bulkier hydroxylamines like Bu_2NOH, the product, Bu_2BONBu_2 is monomeric. Similarly, a few derivatives of ethyl, isopropyl and butyl borates with diethylhydroxylamine, Et_2NOH are also found to be monomeric[39]. A shift of ν(NO) and ν(BO) towards higher values has been regarded as an indication of delocalization of the type $B \frown \ddot{\underset{..}{O}} \frown \ddot{N}<$[44].

Boron oximates[46] of the type $B(OR)_{3-n}(ON{=}CR'R'')_n$ and  B-ON=CR'R'' are mostly monomeric, except tris-acetoximate $B(ON{=}CMe_2)_3$, and the compound

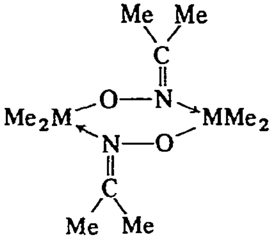


$$\underset{\text{Me}}{\text{O}}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\text{Me}_2}{\text{C}}-\text{O}-\text{B}-\text{ON{=}CHMe}$$

which indicated degrees of association of the order ~1.5 in boiling benzene and which might be dimeric in the solid state although no experimental evidence has been adduced. Steric reasons appear to be responsible for this association. Structures involving 6-membered BONBON rings have been postulated for the tris-acetoximes on the basis of IR data; two ν(CN) stretchings, one considerably lower than in the oxime itself, are observed. In glycosyloxy oximate, as expected only one ν(CN) is observed in the lower range[46].

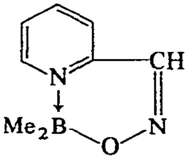
Singh, Rai and Mehrotra[49] reported that oximates derived from aluminium alkoxides are invariably polymeric. The solubility of these decreased after they were isolated from the solvent; this may be due to the increased polymerisation. Similar observations have been made for the products derived from diethylhydroxylamine[44]. IR data have been reported, but not much structural information can be derived from it.

Dimethylmetal acetoximates of aluminium, gallium, indium and thallium, $Me_2MON{=}CMe_2$[65] exist as dimers in gas, solution and the crystal, whereas the boron analogue, $Me_2BON{=}CMe_2$ tends to dissociate in solution ($n \simeq 1.4$). On the basis of a progressive decrease of ν(CN) in the infrared spectra in nujol mull of all these derivatives with increase in molecular weight (in comparison to acetoxime itself), a possible MONMON six-membered ring structure has been suggested:

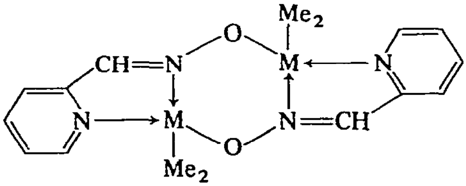


The formation of such rings finds some support from mass spectral data. ^{11}B NMR spectra of the boron analogue are also consistent with the presence of tri- and tetra-covalent boron in equilibrium. Moreover, the boron complex in the vapour state did not show any change in $\nu(CN)$ stretching (in comparison to acetoxime) indicating its monomeric nature in the vapour phase. PMR spectra of these compounds in aromatic solvents expectedly show a doublet due to the methyl protons of the $Me_2C{=}N$ moiety as observed for the acetoxime itself[77,78].

Pyridine-2-carbaldehyde oxime derivatives of the type $Me_2MON{=}CHR$ (M = B, Ga, In and Tl) have been investigated by Pattison and Wade[70]. Cryoscopic determination of their association indicated the boron compound to be monomeric, the gallium analogue partly associated ($n \simeq 1.5$), and $Me_2MON{=}CHR$ (M = Al, In and Tl) dimeric. The downfield shift of methylmetal signals in all the cases in comparison to those in corresponding acetoximates has been taken as evidence for higher coordination numbers of all the elements in their derivatives. For the monomeric boron compound, the involvement of an anti-oxime configuration in the structure seems to be most probable:

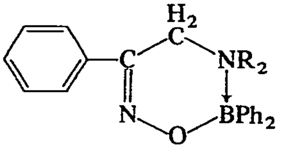


For other derivatives, the structure:



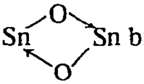
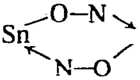
finds supports from PMR spectra wherein the aldehydic proton appears in the range appropriate for the *cis*-isomer of the ligand. The presence of an MONMON ring in which the oximate residue is attached through oxygen to one metal atom and through both the nitrogen atoms to the other metal atom of the dimer has been supported by IR spectra, showing a progressive decrease in the pyridine ν(CN) and oxime ν(CN) stretchings with increase of molecular weight. The anomalous position of oxime ν(CN) in the boron compound is consistent with the absence of any direct link between oxime nitrogen and boron[70].

Z-(ω-Aminoacetophenone oximate)-diphenylboron[41]

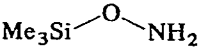


has been found to be monomeric by mass spectroscopy. Like the pyridine aldoximate of dimethylboron, a cyclic structure having no direct link between oxime nitrogen and boron has been established by IR and PMR spectra.

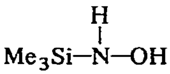
Silicon[15,16] and germanium[17] oximates are monomeric. Two types of peaks assignable to ν(CN) have been observed in dimethyl- and dibutylgermanium oximates and this has been tentatively ascribed to the different environment of the oxime residue in the compounds. The lowering of ν(CN) by 20-50 cm^{-1} in the oximates of silicon, germanium and tin has been ascribed to arise from a mass effect[13]. On the basis of the IR spectral difference between trimethyltin acetoximate and cyclohexanone oximate in the range 600-300 cm^{-1}, Harrison and Zuckerman[13] concluded that the formed compound tended to associate, unlike the former compound and other higher alkyl- or aryltin analogues. The quadrupole splitting data in the Mössbauer spectra also indicated a higher coordination number for tin in trimethyltin cyclohexanone oximate.

Mass spectral fragments of trimethyltin cyclohexanone oximate[13] gave evidence for the dimeric units having cyclic  bridges rather than the  ring. The tendency for oligomerisation in this derivative in contrast to the acetoximate is not yet understood although the steric requirement is more for the former.

Mono(trimethylsilyl)hydroxylamine, for which the following three structures are possible, was previously assigned the amine-oxide structure (III)

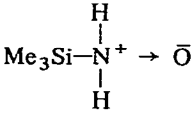


(I)



$$\mathrm{Me_3Si{-}\overset{\displaystyle H}{\overset{|}{N}}{-}OH}$$

(II)



$$\mathrm{Me_3Si{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{N}}}}{}^{+} \rightarrow \bar{O}}$$

(III)

However, later studies of the dipole moment indicated that the compound is in fact the *O*-trimethylsilyl derivative (I). Structural evidence for the bis- and tris(trimethylsilyl) derivatives has come from PMR[4-7] and vibrational spectra[4-7,64].

Some preliminary observations on the PMR spectra of organosilicon oximates by Singh, Rai and Mehrotra[15] can be summarised as follows. In the series $Me_{4-n}Si(ON{=}CEt_2)_n$ (n = 1-3), deshielding of the Si-Me protons seems to increase slightly with the successive introduction of oximate groups suggesting probably that in these silicon compounds, deshielding by the electronegative oximato group and by steric factors is more than sufficient to compensate the shielding brought about by π bonding (provided it exists).

In compounds Me_3SiX, Si–Me proton shielding seems to decrease in the order X = $Et_2C{=}NO > MeEtC{=}NO > MePrC{=}NO > Me\text{-}i\text{-}PrC{=}NO$. In dimethylsilicon aldoximates, *syn/anti* isomer ratios (estimated from signal intensities) increase relative to the parent oxime[22]. A similar increase in the *syn* ratio has been observed by PMR spectra of dimethylgermanium aldoximates, $Me_2Ge(ON{=}CHR)_2$[17,22] (R = Me and Pr). Splitting of the signal of isopropylidene protons into a doublet has also been observed in the PMR spectra of $Me_2Ge(ON{=}CMe_2)_2$ in aromatic solvent as described earlier.

Diorganotin diethylhydroxylamines[45], of the type $Bu_2Sn(OR)(ONEt_2)$ (R = Et and i-Pr) are reported to possess an average molecular association ~3.0 in boiling benzene. Their IR spectra (4000–400 cm^{-1}) have been analysed and possible assignments have been made. The association of these derivatives is thought to be more likely through the SnONSnON ring in view of the monomeric nature of dibutyltin dialkoxides[80].

The presence of the Sn–O–N bond has been established in compounds of the type $R_{4-n}Sn[ON{=}C(CN)_2]_n$[75] ($n$ = 1 and 2) by IR spectra.

A number of trialkyltin hydroxylamines, $R_3SnONR'R''$[59], characterised by IR, PMR and Mössbauer spectra, have been found to be monomeric. In *N*-benzoylhydroxylamine derivatives, lowering in ν(C=O) in the order of ~75 cm^{-1} (in comparison to the parent hydroxylamine) has been taken as an evidence for five-coordinate tin with the probable structure:

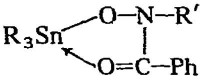
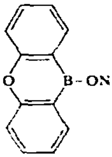


TABLE I

O-ORGANOMETAL HYDROXYLAMINES

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
$NaON(CF_3)_2$	17				26
$PhZnONEt_2$	46	(168–169)			69
Bu_2BONH_2	19	(130 (dec.))			39
$Bu_2BONHBu$	19	(92–94)			39
Bu_2BONBu_2	19	78/2.5			39
$(2\text{-}C_4H_3S)_2BONH_2$	19	(200)			40
$Ph(2\text{-}C_4H_3S)BONH_2$	19	(190)			40
Ph_2BONH_2	19	(214–216)			40
	19	(285)			40
$B[ON(CF_3)_2]_3$	12				27,28,30
$B(ONEt_2)_3$	22	subl. 100/0.5			44
$Al(ONEt_2)_3$	26				44,45
Me_3SiONH_2	3	99.6/737	0.8572	1.4051	5
	2	54.5/127	0.857	1.4047	7
$Me_3SiONHMe$	2	92/753	0.824	1.3958	4
$Me_3SiON(CF_3)_2$	11				26
	52				73

(continued)

TABLE 1 (*continued*)

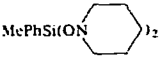
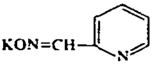
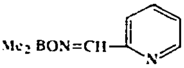
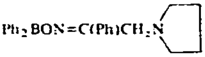
Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
$Me_2Si(Cl)ON(CF_3)_2$	52				73
$Me_3SiONH(SiMe_3)$	4	79.5/97	0.827	1.4122	7
$Me_3SiONMe(SiMe_3)$	2	85/97	0.819	1.4163	4
$Me_3SiON(SiMe_3)_2$	5	128.5/97	0.859	1.4353	7
	42	39–40/11		1.4150	64
$Me(AcO)_2SiONEt_2$	1	46/0.4			1
$[MeSi(OSiMe_3)(ONEt_2)]_2O$	13			1.4160	3
$[Me(Et_2NO)SiO]_4$	14				2
$[Me_2Si(ONEt_2)]_2O$	13	88–89/2.5		1.4220	3
$[Me_2(Et_2NO)Si]_2C_6H_4$-*p*	13				3
$Me_3SiONEt_2$	2	35/15	0.816	1.4092	4
	1	44/23			2
	1	84			1
Et_3SiONH_2	3	53/7	0.8876	1.4392	5
Ph_3SiONH_2	3	(57–59)			5
$Me_2Si(ONEt_2)_2$	1	34/0.05			1,2
	1	84–85/9		1.4261	3
$MeHSi(ONEt_2)_2$	1	36/0.25			1
	1	36/0.2			2
$MeSiCl(ONEt_2)_2$	1	36/0.07			2
$C_5H_{11}SiH(ONEt_2)_2$	13	74–78/0.2		1.4356	3
$CH_2{=}CHSiMe(ONEt_2)_2$	1	54/0.025			1
	1	54/0.02			2
	13				3
$Ph_2Si(ONEt_2)_2$	13	140–150/0.05		1.5250	3
$MeSi(ONEt_2)_3$	1	76/0.025			1
	1	76/0.05			2
$Si(ONEt_2)_4$	1	95/0.045			1
	1	95/0.05			2
	1			1.4400	3
$Si[ON(CF_3)_2]_4$	12,16				27,28,29,30
$Ge[ON(CF_3)_2]_4$	12,16				27,28,29,30
$Me_3SnONEt_2$	30	30–32/0.02			59
$Me_3SnONHCOPh$	30	(255 (dec.))			59
$Me_3SnONPhCOPh$	30	(120–122)			59
$Pr_3SnONHCOPh$	30	(200 (dec.))			59
$Pr_3SnONPhCOPh$	30				59
$Ph_3SnONPhCOPh$	30	(115.5–116.5)			59
$Me_2Sn(OPr\text{-}i)(ONEt_2)$	39				45
$Me_2Sn(ONEt_2)_2$	39				45
$Et_2Sn(OPr\text{-}i)(ONEt_2)$	39				45
$Et_2Sn(ONEt_2)_2$	39				45
$Bu_2Sn(OEt)(ONEt_2)$	39				45
$Bu_2Sn(OPr\text{-}i)(ONEt_2)$	39				45
$Bu_2Sn(ONEt_2)_2$	39				45
$Sn[ON(CF_3)_2]_2$	51				72
$Pb[ON(CF_3)_2]_2$	51				72
$(CF_3)_3P[ON(CF_3)_2]_2$	48				71
$(CF_3)_2PCl[ON(CF_3)_2]_2$	49				71
$(CF_3)_2P[ON(CF_3)_2]_3$	52				73
$P[ON(CF_3)_2]_5$	12				27,28
$(CF_3)_2AsON(CF_3)_2$	52				73
$As[ON(CF_3)_2]_3$	50				71
	12,16	(30)			29,30
	51				73
$Sb[ON(CF_3)_2]_3$	12				29
$Bi[ON(CF_3)_2]_3$	12				27,30
$Se[ON(CF_3)_2]_4$	51				74
$Te[ON(CF_3)_2]_4$	51				74

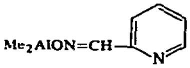
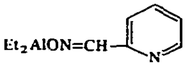
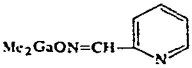
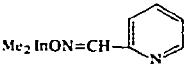
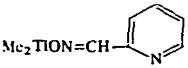
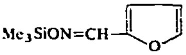
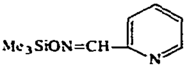
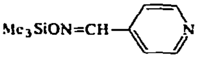
TABLE 2

O-ORGANOMETAL OXIMES

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
$LiON{=}CMe_2$	45				65
$LiON{=}C_6H_{10}$	45	(250 (dec.))			13
$NaON{=}CMe_2$	18				37
	17				36
$MeBeON{=}CMe_2$	46	(180–230 (dec.))			68
$Be[ON{=}CMe_2]_2$	46	(190–193 (dec.))			68
$MeZnON{=}CMe_2$	46				67
$EtZnON{=}CMe_2$	46				66
$EtZnON{=}CMePh$	46	(130–132)			69
$PhZnON{=}CHPh$	46	(115–140)			69
$Zn[ON{=}CMe_2]_2$	46				66
$Me_2BON{=}CMe_2$	47	(91–92)			65
	47	(132)			70
$Ph_2BON{=}C(Ph)CH_2NMe_2$	20	(180–182)			41
	20	(174)			41
	20	(158)			41
	20	(147–148)			41
$Pr\underline{BON{=}C(4\text{-}C_5H_4N)N}H$	21				42
$Ph\underline{BON{=}C(4\text{-}C_5H_4N)N}H$	21	(211–213)			42
$Ph\underline{BON{=}C(Ph)N}H$	21	(161–163)			43
$Ph\underline{BON{=}C(Ph)N}Ph$	21	(235–237)			43
$Ph\underline{BON{=}C(COOEt)N}Ph$	21	(106–107)			43
$Ph\underline{BON{=}C(COOEt)N}CH_2COOEt$	21	(69–71)			43
$p\text{-}MeC_6H_4\underline{BON{=}C(p\text{-}NH_2SO_2C_6H_4)N}H$	21				42
$2,4\text{-}Me_2C_6H_3\underline{BON{=}C(4\text{-}C_5H_4N)N}H$	21				42
$1,3,5\text{-}Me_3C_6H_2\underline{BON{=}C(4\text{-}C_5H_4N)N}H$	21	(159–160)			42
$1\text{-}C_{10}H_7\underline{BON{=}C(4\text{-}C_5H_4N)N}H$	21	(200–202)			42
$1\text{-}C_{10}H_7\underline{BON{=}C(3\text{-}C_5H_4N)N}H$	21	(198–200)			42
$1\text{-}C_{10}H_7\underline{BON{=}C(p\text{-}ClC_6H_4)N}H$	21	(148–150)			42
$2\text{-}C_{10}H_7\underline{BON{=}C(m\text{-}MeC_6H_4)N}H$	21				42
$2\text{-}C_{10}H_7\underline{BON{=}C(p\text{-}MeOC_6H_4)N}H$	21				42
$B(ON{=}CMe_2)_3$	23	120–122/0.85			46
$B(ON{=}CMeEt)_3$	23	128–130/0.75			46
$Me_2AlON{=}CMe_2$	47	(71.5)			65
$Me_2AlON{=}CHPh$	47				70

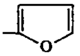
(continued)

TABLE 2 (*continued*)

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
	47	(115)			70
	47				70
$Al(ON{=}CHMe)_3$	26				49
$Al(ON{=}CHEt)_3$	26				49
$Al(ON{=}CHPr)_3$	26				49
$Al(ON{=}CMe_2)_3$	26				49
$Al(ON{=}CMeEt)_3$	26				49
$Me_2GaON{=}CMe_2$	47	(90–91)			65
	47	(35)			70
$Me_2InON{=}CMe_2$	47	(57)			65
	47	(164)			70
$Me_2TlON{=}CMe_2$	47	(124)			65
	47	(139)			70
$Me_3SiON{=}CHMe$	6	28–30/39	0.8333	1.4030	10
$Me_3SiON{=}CHEt$	6	40/28	0.8321	1.4102	10
$Me_3SiON{=}CHPr$	6	39–41/10	0.8336	1.4160	10
$Me_3SiON{=}CHPr\text{-}i$	6	41.5–42/16	0.8256	1.4109	10
$Me_3SiON{=}CHPh$	6	87.5–88/5	0.9657	1.5114	11
	6	74/10	0.9976	1.4849	12
	7	69/0.8		1.5000	15
	7	69–71/0.6		1.5450	15
$Me_3SiON{=}CH{-}C_6H_4{-}OH\text{-}o$	6	110–111/4	1.0174	1.5200	11
$Me_3SiON{=}CHC_6H_4{-}OSiMe_3\text{-}o$	6	128–128.8/4	0.9621	1.4950	11
$Me_3SiON{=}CMe_2$	6	120–120.5/776	0.8318	1.4112	11
	10	120–121/760		1.4112	15
	43	121/757	0.8283	1.4100	23
$Me_3SiON{=}CMeEt$	7,44	132–133/760		1.4115	15
$Me_3SiON{=}CMePr$	7,44	153–154/760		1.4165	15
$Me_3SiON{=}CMePr\text{-}i$	7,44	143–145/760		1.4115	15
$Me_3SiON{=}CMeBu\text{-}i$	7	157–159/760 55/7.5		1.4128	15
$Me_3SiON{=}CMePh$	6	93–94/4	0.9607	1.5073	11
$Me_3SiON{=}CEt_2$	7,44	143/760		1.4100	15
	43	86/100	0.8308	1.4170	23
$Me_3SiON{=}CEtBu$	7	68/8		1.4200	15
$Me_3SiON{=}CBu\text{-}i_2$	6	70/4	0.8295	1.4267	11
$Me_3SiON{=}\underbrace{C(CH_2)_3CH_2}$	7,44	64/7.5		1.4465	15

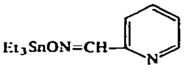
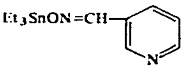
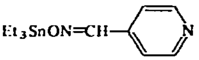
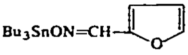
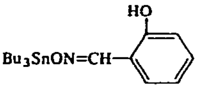
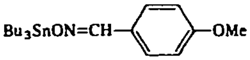
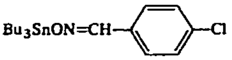
(*continued*)

TABLE 2 (*continued*)

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
$Me_3SiON=\underline{C(CH_2)_4CH_2}$	6	35/0.5, 120/8			13,14
$Et_3SiON=CHMe$	6	62–63/13	0.8614	1.4316	10
$Et_3SiON=CHEt$	6	86/20	0.8562	1.4340	10
$Et_3SiON=CHPr$	6	91.5–93/12	0.8554	1.4375	10
$Et_3SiON=CHPr\text{-}i$	6	95/20	0.8468	1.4825	10
$Et_3SiON=CH$— 	6,15	91–92/3	0.9881	1.4920	12
$Et_3SiON=CMe_2$	6	40–41/1	0.8555	1.4340	11
	10,15,44	91/30	0.8584	1.4339	23
$Et_3SiON=CMeEt$	15,44	97/25	0.8308	1.4362	23
$Et_3SiON=CMePr$	15	107/25	0.8519	1.4370	23
$Et_3SiON=CMePr\text{-}i$	15	107/25	0.8407	1.4349	23
$Et_3SiON=CMePh$	15	105/1	0.9420	1.5060	23
$Et_3SiON=CEt_2$	15,44	113/30	0.8470	1.4369	23
$Et_3SiON=CPh_2$	15	154/1	0.9990	1.5485	23
$Et_3SiON=\underline{C(CH_2)_3CH_2}$	15	86/0.5	0.9114	1.4620	23
$Et_3SiON=\underline{C(CH_2)_4CH_2}$	15	100/1.5	0.9096	1.4660	23
$Pr_3SiON=CMe_2$	15	118/28	0.8450	1.4393	23
$Ph_3SiON=CMe_2$	15	(91–92)			23
$Me_2Si(ON=CHMe)_2$	7	67–70/8		1.4245	15
$Me_2Si(ON=CHPr)_2$	7	97.5–98.5/4.5		1.4335	15
$Me_2Si(ON=CMe_2)_2$	7,10,34	73–74/4		1.4275	15
$Me_2Si(ON=CMeEt)_2$	7,34	89/4		1.4280	15
$Me_2Si(ON=CMePr)_2$	7	92.5–94.5/2		1.4350	15
$Me_2Si(ON=CMePr\text{-}i)_2$	7	106/5		1.4320	15
$Me_2Si(ON=CMeBu\text{-}i)_2$	7	104/3		1.4350	15
$Me_2Si(ON=CEt_2)_2$	7	97/4		1.4285	15
$Me_2Si(ON=CEtBu)_2$	7	144–145/6.5		1.4385	15
$MeSi(ON=CMe_2)_3$	7	106.5/1.6		1.4508	15
$MeSi(ON=CMeEt)_3$	7	111–112/1		1.4480	15
$MeSi(ON=CMePr)_3$	7	124–125/0.4		1.4490	15
$MeSi(ON=CMePr\text{-}i)_3$	7	109.5–111.5/0.6		1.4435	15
$MeSi(ON=CMeBu\text{-}i)_3$	7	127–129/0.5		1.4450	15
$MeSi(ON=CEt_2)_3$	7	125/1		1.4460	15
$CH_2=CHSi(ON=CMe_2)_3$	6	100.5/0.5		1.4675	16
$CH_2=CHSi(ON=CMePr)_3$	6	138–140/0.3		1.4590	16
$CH_2=CHSi(ON=CMePr\text{-}i)_3$	6	126/0.2		1.4552	16
$EtSi(ON=CMe_2)_3$	7	83.5–84.5/0.4		1.4515	16
$EtSi(ON=CMeEt)_3$	7	96.5/0.4		1.4510	16
$EtSi(ON=CMePr)_3$	7	131–132/0.3		1.4535	16
$EtSi(ON=CMePr\text{-}i)_3$	7	121–122/0.3		1.4500	16
$EtSi(ON=CMeBu\text{-}i)_3$	7	132–134/0.4		1.4485	16
$EtSi(ON=CEt_2)_3$	7	130–131/0.4		1.4500	16
$EtSi(ON=CEtBu)_3$	7	142–144/0.3		1.4525	16
$Si(ON=CMe_2)_4$	7	128/0.5			15
$Si(ON=CMeEt)_4$	7	141.5–143.5/0.6			15
$Me_3GeON=\underline{C(CH_2)_4CH_2}$	6	48/0.1			13,14
$Bu_3GeON=CHMe$	7	82–83/0.4		1.4570	17
$Bu_3GeON=CHPr$	7	106–107/0.4		1.4560	17
$Bu_3GeON=CHPh$	7	147–149/0.5		1.5090	17
$Bu_3GeON=CMe_2$	7,9, 27,37	106/0.6		1.4555	17,22
$Bu_3GeON=CMeEt$	7,9 27,37	92–93/0.3		1.4550	17,22
$Bu_3GeON=CMePr$	7	95–97/0.3		1.4568	17
$Bu_3GeON=CMePr\text{-}i$	7	110–111/0.9		1.4558	17
$Bu_3GeON=CMeBu\text{-}i$	7	97–98/0.3		1.4562	17
$Bu_3GeON=CMeAm$	7	117–118/0.2		1.4553	17
$Bu_3GeON=CMePh$	7	140/0.5		1.5053	17
$Bu_3GeON=CEt_2$	7	108/0.8		1.4556	17
$Bu_3GeON=CEtBu$	7	104–107/0.3		1.4569	17
$Bu_3GeON=\underline{C(CH_2)_3CH_2}$	7,9 27,37	103–104/0.3		1.4725	17,22
$Bu_3GeON=\underline{C(CH_2)_4CH_2}$	7,9 27,37	110–111/0.3		1.4755	17,22

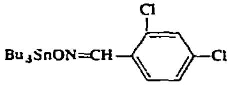
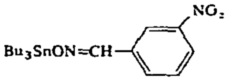
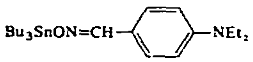
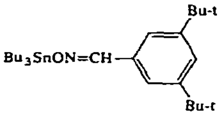
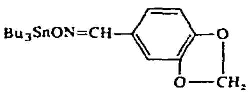
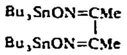
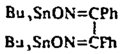
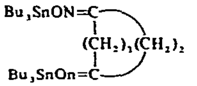
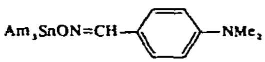
(*continued*)

TABLE 2 (*continued*)

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
$Me_2Ge(ON{=}CHMe)_2$	7	60–62/0.8		1.4620	17
$Me_2Ge(ON{=}CHPr)_2$	7	113–115/6		1.4570	17
$Me_2Ge(ON{=}CMe_2)_2$	7	60/0.6		1.4625	17
$Me_2Ge(ON{=}CMeEt)_2$	7	82–84/1.5		1.4590	17
$Me_2Ge(ON{=}CMePr)_2$	7	90/0.7		1.4580	17
$Me_2Ge(ON{=}CEt_2)_2$	7	81–82/0.5		1.4560	17
$Bu_2Ge(ON{=}CHMe)_2$	7	93–94/0.5		1.4675	17
$Bu_2Ge(ON{=}CHPr)_2$	7	137/1.5		1.4635	17
$Bu_2Ge(ON{=}CMe_2)_2$	7,28,37	101–102/0.6		1.4610	17
$Bu_2Ge(ON{=}CMeEt)_2$	7	111–113/0.5		1.4620	17
$Bu_2Ge(ON{=}CMePr)_2$	7	129–132/0.8		1.4588	17
$Bu_2Ge(ON{=}CMePr\text{-}i)_2$	7	128–131/1.0		1.4550	17
$Bu_2Ge(ON{=}CEt_2)_2$	7	122–125/0.8		1.4575	17
$Bu_2Ge(ON{=}CEtBu)_2$	7	150–152/0.6			17
$Ge(ON{=}CMe_2)_4$	7,9,36	152–154/0.6			17,22
$Me_3SnON{=}CMe_2$	30	58/0.01			13,14
$Me_3SnON{=}C(CH_2)_4CH_2$	10,30	58–59/0.02			13,14
	38			1.5618	53
	38			1.5860	53
	38			1.6068	53
$Et_3SnON{=}CHC_6H_4\text{-}NEt_2\text{-}p$	38			1.5875	53
$Et_3SnON{=}C(CH_2)_3CH_2$	29	89/0.7		1.5052	58
$Et_3SnON{=}C(CH_2)_4CH_2$	29	74–76.5/0.01			13
$Pr_3SnON{=}CHPh$	29	140–141/0.3		1.5388	58
$Pr_3SnON{=}CMe_2$	29	84/0.7		1.4750	58
$Pr_3SnON{=}CMeEt$	29	92–94.5/0.8		1.4758	58
$Pr_3SnON{=}CMePr$	29	98–100/0.7		1.4752	58
$Pr_3SnON{=}CMePr\text{-}i$	29	98/0.9		1.4740	58
$Pr_3SnON{=}CMeBu\text{-}i$	29	98–100/0.6		1.4720	58
$Pr_3SnON{=}CMePh$	29	146/0.7		1.5322	58
$Pr_3SnON{=}CMe(CH_2)_3NEt_2$	38			1.4804	53
$Pr_3SnON{=}CEt_2$	29	94–96/0.7		1.4725	58
$Pr_3SnON{=}CEtBu$	29	110–111/0.7		1.4722	58
$Pr_3SnON{=}C(CH_2)_3CH_2$	29	116–117/0.4			58
$Pr_3SnON{=}C(CH_2)_4CH_2$	10	85/0.02			13
$Bu_3SnON{=}CH_2$	10	75–76/0.006		1.4837	24,54,55
	29	113–115/0.001		1.5325	57
$Bu_3SnON{=}CHPh$	29			1.5150	57
	29			1.5698	57
	29			1.5325	57
	29			1.5378	57

(*continued*)

TABLE 2 (*continued*)

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	d_4^t	n_D^t	References
	29			1.5457	57
	29			1.5426	57
	38			1.5573	53
	29			1.5270	57
	29			1.5468	56
$Bu_3SnON{=}CHR$ ($RCHO$ = 2-ethylhexenal)	29			1.4936	56
$Bu_3SnON{=}CMe_2$	10	79/0.01			25
	29			1.4751	56
	29	83-85/0.005		1.4768	24,54,55
$Bu_3SnON{=}CMeEt$	29			1.4728	56
$Bu_3SnON{=}CMeBu\text{-}i$	29			1.6896	56
$Bu_3SnON{=}CMePh$	29			1.5239	56
$Bu_3SnON{=}CMeCHMeCH_2NMe_2$	38			1.4778	53
$Bu_3SnON{=}CPh_2$	29			1.5518	56
	29	215/0.25		1.5553	24,54,55
$Bu_3SnON{=}\underbrace{C(CH_2)_3CH_2}$	29,38	140-143/1		1.4876	58
$Bu_3SnON{=}\underbrace{C(CH_2)_4CH_2}$	29,38	120/0.02			13
	29			1.4896	56
	29			1.5065	54
$Bu_3SnON{=}C(CN)_2$	53				75
 $\begin{array}{l}Bu_3SnON{=}CMe\\ \qquad\quad\;\; \vert\\ Bu_3SnON{=}CMe\end{array}$	29			1.5050	24,54,55
 $\begin{array}{l}Bu_3SnON{=}CPh\\ \qquad\quad\;\; \vert\\ Bu_3SnON{=}CPh\end{array}$	29			1.5382	24,54,55
	29			1.5065	24,55
	38			1.5478	53
$(C_6H_{13})_3SnON{=}CMe_2$	29	118/0.005		1.4750	24,54,55
$(C_6H_{13})_3SnON{=}CPh_2$	29	192-193/0.01		1.5388	24,54,55
$(C_{12}H_{25})_3SnON{=}CMe_2$	29	(45-49)			24,54,55
$(C_{12}H_{25})_3SnON{=}CPh_2$	29	(133-137)			24,54,55
$Ph_3SnON{=}CMe_2$	29	(110-115)			56

(*continued*)

TABLE 2 (*continued*)

Compounds	Methods of preparation (Eqn. numbers)	B.p. (°/mm) (M.p.)	$d_4{}^t$	n_D^t	References
$\mathrm{Ph_3SnON{=}\underbrace{C(CH_2)_4CH_2}}$	30				13
$\mathrm{Ph_3SnON{=}C(CN)_2}$	53				75
$\mathrm{Et_2Sn[ON{=}CMe(CH_2)_3NEt_2]_2}$	38			1.4910	53
$\mathrm{Bu_2Sn(ON{=}CHPr)_2}$	38				60
$\mathrm{Bu_2Sn(ON{=}CHPh)_2}$	10				25
$\mathrm{Bu_2Sn(ON{=}CMe_2)_2}$	10	100/0.08			25
$\mathrm{Bu_2Sn[ON{=}CMe(CH_2)_3NEt_2]_2}$	38			1.4902.	53
$\mathrm{Bu_2Sn[ON{=}C(CN)_2]_2}$	54				75
$\mathrm{Ph_2Sn[ON{=}C(CN)_2]_2}$	54				75
$\mathrm{BuSn(ON{=}CMe_2)_3}$	10				25
$\mathrm{Ph_3PbON{=}\underbrace{C(CH_2)_4CH_2}}$	32,33	(179–181)			14
$\mathrm{Et_2AsON{=}CMe_2}$	8	70/10	1.1447	1.4847	20
$\mathrm{Et_2AsON{=}CMeEt}$	8	91/5	1.1233	1.4839	20
$\mathrm{Et_2AsON{=}CMePr}$	8,31	106–107/17	1.0885	1.4810	21
$\mathrm{Et_2AsON{=}CMeBu}$	8	113/11	1.0795	1.4814	20
$\mathrm{Et_2AsON{=}CPr_2}$	8	112/8	1.0656	1.4788	20
$\mathrm{Pr_2AsON{=}CMe_2}$	8	92/8	1.0901	1.4810	20
	8	120–122/20	1.1601	1.4610	18
$\mathrm{Pr_2AsON{=}CMeEt}$	8	109/13	1.0747	1.4800	20
$\mathrm{Pr_2AsON{=}CMePr}$	8,30	128–130/14	1.0626	1.4796	21
$\mathrm{Pr_2AsON{=}CMeBu}$	8	140/13	1.0426	1.4779	20
$\mathrm{Pr_2AsON{=}CPr_2}$	8	129/5	1.0275	1.4763	20
$\mathrm{Bu_2AsON{=}CMe_2}$	8	130–132/17	1.0591	1.4796	21
$\mathrm{Bu_2AsON{=}CMeEt}$	8	126/12	1.0404	1.4780	21
$\mathrm{Bu_2AsON{=}CMePr}$	8	149–150/17	1.0268	1.4760	21
$\mathrm{Bu_2AsON{=}CMeBu}$	8	160/13	1.0155	1.4759	21
$\mathrm{Bu_2AsON{=}CPr_2}$	8	148–150/8	1.0051	1.4754	21
$\mathrm{Ph_2AsON{=}\underbrace{C(CH_2)_4CH_2}}$	10				14
$\mathrm{PrAs(OBu)ON{=}CMe_2}$	8	122–124/19	1.1305	1.4739	18
$\mathrm{EtAs(ON{=}CMe_2)_2}$	8	86–87/3	1.2040	1.4940	18
$\mathrm{EtAs(ON{=}CMeEt)_2}$	8	128–129/8	1.1520	1.4905	19
$\mathrm{EtAs(ON{=}CMePr)_2}$	8	155–156/11	1.1080	1.4861	19
$\mathrm{EtAs(ON{=}CMeBu)_2}$	8	162–163/8	1.0781	1.4819	19
$\mathrm{EtAs(ON{=}CPr_2)_2}$	8	175–177/12	1.0483	1.4784	19
$\mathrm{PrAs(ON{=}CMe_2)_2}$	8	116/6	1.1833	1.4934	18
$\mathrm{PrAs(ON{=}CMeEt)_2}$	8	151–152/17	1.1298	1.4878	19
$\mathrm{PrAs(ON{=}CMePr)_2}$	8	175–177/20	1.0865	1.4826	19
$\mathrm{PrAs(ON{=}CMeBu)_2}$	8	178–179/13	1.0653	1.4810	19
$\mathrm{PrAs(ON{=}CPr_2)_2}$	8	180–181/12	1.0293	1.4730	19
$\mathrm{BuAs(ON{=}CMe_2)_2}$	8	110/4	1.1530	1.4900	18
$\mathrm{BuAs(ON{=}CMeEt)_2}$	8	156–158/14	1.1167	1.4872	19
$\mathrm{BuAs(ON{=}CMePr)_2}$	8	172–173/15	1.0773	1.4825	19
$\mathrm{BuAs(ON{=}CMeBu)_2}$	8	189–190/13	1.0541	1.4782	19
$\mathrm{BuAs(ON{=}CPr_2)_2}$	8	187–189/10	1.0180	1.4772	19
$\mathrm{PhAs(ON{=}CMe_2)_2}$	8	142/4	1.2735	1.5556	18
$\mathrm{As(ON{=}CMe_2)_3}$	8	148/7	1.2471	1.5016	18
$\mathrm{Ph_3Sb(ON{=}CHMe)_2}$	40	(88–90)			14

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