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Silicon, germanium and tin arsines.

John W. Anderson

*University of Windsor*

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SILICON, GERMANIUM AND TIN ARSINES

BY

John W. Anderson

A Dissertation

Submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario
1971
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Kellah
Jim Conner
Edwin J. Burnside
Robert C. Rumpf
John E. Dick
ABSTRACT

A number of silicon, germanium and tin arsines have been prepared by various methods.

Primary arsines such as \( R_3MA\; M = Si, Ge; R = H, Me \) and \( R_2Si(AsH_2)_2 \) were prepared from \( LiAl(AsH_2)_4 \) and the appropriate halide. Similarly \( R_3MA2 \) were prepared from \( LiAl(AsHMe)_3H \) or \( LiAl(AsMe_2)_3H \). The reaction of excess trisilylarsine with \( LiAlH_4 \) gave a disilylarsinoaluminate which was used to prepare \( (SiH_3)_2AsR \) (R = H, Me, Me_3Si).

The tertiary arsines \( R_3MA\; M = Si, Ge; R = H, Me \) were prepared from \( LiAsR_j \) and \( LiAsHR \) (m = Si, Ge; R = H, Me; R' = Me, Ph). The reaction of \( Me_3MAs \) with a lithium alkyl gave \( LiAs(MMe_3)_2 \) which was used to prepare \( (Me_3M)_2AsR \) (M = Ge, Sn; R = H, Me and M = Si; R = H, Me, SiH_3).

\( Me_3MAs \) was prepared from \( Me_3MCl \) and \( AsH_3 \) in the presence of triethylamine (M = Ge, Sn).

The reaction of an arsine with a germanium or tin amine was used to prepare \( (Me_3Ge)_nAsR_{3-n} \) and \( (Me_3Sn)_2AsR \) (R = Me, Ph; n = 1-3).

The exchange reaction between a silyl arsine and a germanium or tin halide was used to prepare \( (R_3M)_nAsR'_{3-n} \), \( Me_2Ge(AsMe_2)_2 \), \( MeGe(AsMe_2)_3 \) and \( Me_2Ge(AsH_2)_2 \) (R' = Me, Ph; n = 1-3; M = Ge; R = Me, H and M = Sn; R = Me).

Primary arsines are best prepared from \( LiAl(AsH_2)_4 \) and secondary arsines by acidification of lithium disilylarsinoaluminates or disilylarsenides. Tertiary arsines are best prepared from lithium arsenides

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or by exchange reactions (for germanium and tin).

Chlorine cleaved the M-As bond to give the two chlorides (M = Si, Ge, Sn) and Chloroboranes cleaved the M-As bond to give the group IV chloride and arsinoboranes. The reaction of AsCl₃ with (MH₃)₃As gave the cyclic arsines (MH₃As)₅ Germanium and tin amines reacted with group IV arsines to give the mixed arsines Me₃Ge(Me₃Sn)AsR (R = Me₃Ge, Me, Ph), (Me₃Si)₂AsMe₃ (M = Ge, Sn) and Me₂M[As(GeMe₃)₂]₂ (M = Ge, Sn).

The vibrational spectra of trimethyliodogermane and trimethyl-fluorogermane were assigned.
ACKNOWLEDGEMENTS

The investigations described in this work were carried out in the chemical laboratories of the University of Southampton, England and the University of Windsor, Ontario, Canada between 1968 and 1971 under the supervision of Dr. J.E. Drake.

The author would like to express his gratitude to his supervisor for his unfailing help, encouragement and boundless enthusiasm, to his parents and wife for their encouragement and to Drs. C. Riddle and J. Davis and Messrs. G. Barker and R. Hemmings for valuable discussions and gifts of chemicals.

The author would also like to acknowledge the Science Research Council for the award of a maintenance grant, the University of Windsor library for its persistent efforts to hinder this investigation and members of the technical staff for valuable assistance.
To the many dedicated chemists across the world pushing forward the frontiers of science
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INTRODUCTION

The considerable interest in group IV chemistry over the last decade has furnished several reviews which describe the previous advances in the subject field. Four reviews deal with group V derivatives of silicon, germanium and tin in some detail. At the start of this investigation very little had been published concerning the arsenic derivatives of group IV.

The first silicon arsines were prepared from iodosilane and arsenic giving low yields of trisilylarsine and some silyliodo-arsines. The reaction of alkali metal derivatives of group IV with arsenic chlorides was used to prepare some silicon and tin arsines but this method usually gave poor yields. More satisfactory yields were achieved from the reaction of alkali metal arsenides with group IV halides, with the exception of As-H containing arsines. The reaction of arsinopotassium with trimethylfluorosilane gave mainly tris(trimethylsilyl)arsine with a little bis(trimethylsilyl)arsine and with bromosilane gave only trisilylarsine. Arsines containing an As-H bond were prepared in low yields by alloy hydrolysis and by silent electric discharge. Finally some tin arsines were prepared by the action of an arsine on a tin amine.

The arsines prepared prior to 1968 and the methods used are shown in table 1.
<table>
<thead>
<tr>
<th>Arsine</th>
<th>Preparative Method</th>
<th>Reference</th>
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<td>SiH₃AsH₂</td>
<td>S.E.D. of SiH₄ + AsH₃</td>
<td>5</td>
</tr>
<tr>
<td>SiH₃AsI₂</td>
<td>SiH₃I + As</td>
<td>6</td>
</tr>
<tr>
<td>(SiH₃)₂AsI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SiH₃)₃As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₃SiAsPh₂</td>
<td>Ph₃SiX + LiAsPh₂</td>
<td>7</td>
</tr>
<tr>
<td>Ph₃SiAsMe₂</td>
<td>Ph₃SiLi + Me₂AsCl</td>
<td>8</td>
</tr>
<tr>
<td>Ph₃SiAsEt₂</td>
<td>Ph₃SiLi + Et₂AsCl</td>
<td>8</td>
</tr>
<tr>
<td>(Ph₃Si)₂AsMe</td>
<td>Ph₃SiLi + MeAsCl₂</td>
<td>8</td>
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<td>Me₃SiAsMe₂</td>
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<tr>
<td>(SiH₃)₃As</td>
<td>SiH₃Br + KAsH₂</td>
<td>10</td>
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<tr>
<td>(Me₃Si)₂AsH</td>
<td>Me₃SiF + KAsH₂</td>
<td>11</td>
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<tr>
<td>(Me₃Si)₃As</td>
<td></td>
<td></td>
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<tr>
<td>GeH₃AsH₂</td>
<td>S.E.D. of AsH₃</td>
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<td></td>
<td>Ca₂Ge/C₃As₂ hydrolysis</td>
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<tr>
<td>Ph₃GeAsPh₂</td>
<td>Ph₃Ge X + KAsPh₂</td>
<td>13</td>
</tr>
<tr>
<td>(Me₃Ge)₃As</td>
<td>Me₃Ge X + Na₃As</td>
<td>14</td>
</tr>
<tr>
<td>Me₃SnAsPh₂</td>
<td>Me₃SnNMe₂ + Ph₂AsH</td>
<td>15</td>
</tr>
<tr>
<td>Et₃SnAsPh₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pr₃SnAsPh₂</td>
<td>R₃Sn X + NaAsPh₂</td>
<td>16</td>
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TABLE 1 (contd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>( \text{Ph}_3\text{SnAsPh}_2 )</td>
<td>( \text{Ph}_3\text{SnLi} + \text{Ph}<em>n\text{AsCl}</em>{3-n} )</td>
<td>17</td>
</tr>
<tr>
<td>( (\text{Ph}_3\text{Sn})_2\text{AsPh} )</td>
<td>( (\text{Ph}_3\text{Sn})_3\text{As} )</td>
<td>17</td>
</tr>
<tr>
<td>( \text{Ph}_2\text{Sn(AsPh}_2)_2 )</td>
<td>( \text{Ph}<em>n\text{SnX}</em>{4-n} + \text{NaAsPh}_2 )</td>
<td>17</td>
</tr>
<tr>
<td>( \text{Sn(AsPh}_2)_3 )</td>
<td>( (\text{Me}_3\text{Sn})_3\text{As} )</td>
<td>18</td>
</tr>
<tr>
<td>( \text{Sn(AsPh}_2)_4 )</td>
<td>( \text{Me}_3\text{SnNMe}_2 + \text{AsH}_3 )</td>
<td></td>
</tr>
</tbody>
</table>

In particular there was a need for a suitable method for the synthesis of As-H containing arsines. Interest in the compounds centres on the reactivity of the M-As bond \((M = \text{Si, Ge, Sn})\), the effect of differing substituents on the donor abilities of the arsine and the possibility of As \(\rightarrow M\) pπ \(\rightarrow d\pi\) bonding. This investigation describes the synthesis of a large number of group IV arsines suitable for such studies. Both previously established and new methods have been used.
CHAPTER I

Techniques and Starting Materials

Standard vacuum line techniques were used as most of the compounds prepared were air-unstable and many were poisonous, pyrophoric or explosive. These techniques have been described in several texts. 19-22

The Vacuum Line

The main vacuum line was constructed of pyrex glass and consisted of a set of four U-traps with 4 mm. greased stopcocks connected at each side to a manifold also fitted with 4 mm. greased stopcocks. The manifold was connected by 6 mm. greased stopcocks to a top manifold leading to the pumping system. A similar system utilising greaseless stopcocks (Springham, Viton A diaphragm) for handling the higher hydrides was attached to the other side of the rack. All the manifolds were equipped with S19 Quickfit ball and socket joints at take-off points.

The pumping system consisted of a rotary pump, a mercury diffusion pump and two liquid nitrogen backing traps. The exhaust gases from the pump were fed into a fume chamber.

The pressure was monitored by mercury manometers on each manifold and for pressures less than 1 torr by a Pirani gauge attached to the top manifold.

The Ozoniser Discharge System

This consisted of an automatic toepler pump in series with a discharge tube, a U-trap and a surge bulb. The discharge tube consisted of two 20 cm. long concentric tubes ca. 2 mm. apart. The live lead from the high tension transformer was placed in the centre tube. Acetone,
containing a little hydrochloric acid to improve conductivity was used as a contact. The discharge tube stood in a dewar containing dry ice/acetone or ice/water with a little hydrochloric acid into which the earth lead was immersed. The pressure in the system was monitored with a mercury manometer.

Typically the discharge was filled to a pressure of 20 cms and operated at 12 kv for 1-2 hours. The U-trap was then immersed in liquid nitrogen and hydrogen pumped out through four U-traps also immersed in liquid nitrogen on the main vacuum line. The condensible products were then distilled out and separated.

Reactions and Separations

Reactions were carried out in round-bottomed flasks or three-necked flasks equipped with dropping funnels. For small scale reactions that did not require a solvent a glass finger or a n.m.r. tube was used.

Two types of n.m.r. tube were used. One was a normal 5 mm o.d. tube, the other was pulled out from an MS19 joint to about 2 mm o.d.

Products were separated by trap to trap distillation or by a fractionating column. The slush baths used and their temperatures are tabulated on the following page.
TABLE 1.1

Slush Baths

<table>
<thead>
<tr>
<th>Bath</th>
<th>Temperature °C</th>
<th>Bath</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice Water</td>
<td>0</td>
<td>dry-ice acetone</td>
<td>-78.5</td>
</tr>
<tr>
<td>Ice-NaCl Solution</td>
<td>0 to -20</td>
<td>ethylacetate</td>
<td>-83.6</td>
</tr>
<tr>
<td>t-amyl alcohol</td>
<td>-12</td>
<td>toluene</td>
<td>-95</td>
</tr>
<tr>
<td>diethylcarbonate</td>
<td>-15</td>
<td>carbon disulphide</td>
<td>-111.6</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>-22.9</td>
<td>methylcyclohexane</td>
<td>-126.3</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>-45.2</td>
<td>n-pentane</td>
<td>-131.5</td>
</tr>
<tr>
<td>diacetone alcohol</td>
<td>-55</td>
<td>iso-pentane</td>
<td>-160.5</td>
</tr>
<tr>
<td>chloroform</td>
<td>-63.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Characterisations and Spectroscopy

a) Infrared spectra were recorded on Beckman IR 10 and IR 12 and Perkin-Elmer 337 spectrometers. Gas cells of 5 and 10 cm path lengths with KBr plates were used. Liquids were recorded as smears between KBr or CsI plates or were condensed into a low temperature cell and allowed to melt.

b) Raman spectra were recorded on a Spectra Physics 700 (Helium/neon excitation) spectrometer as liquids in sealed pyrex tubes (2 mm. o.d.)

c) $^1$H n.m.r. spectra were recorded on Jeol C-60 HL and Varian A60 spectrometers in sealed tubes (2 mm. or 5 mm. o.d.).

d) Mass spectra were recorded on Metropolitan Vickers MS2 and AEI MS10c2 spectrometers with ionising potentials of 70 eV.

Compounds were characterised by spectroscopy and by molecular weight determinations and by chemical analysis. Molecular weights were
determined in the vapour phase for volatile compounds and cryoscopically in benzene or ebullioscopically in dimethyl ether for involatile compounds using standard methods. The arsines were analysed by reaction with a hydrogen halide (usually the bromide). This quantitatively cleaved the M-As bonds to form the parent arsine and the appropriate halide, both of which are easily identified.

\[ \text{M-As} + \text{HX} \rightarrow \text{MX} + \text{HAs} \quad \text{M = Si, Ge, Sn} \]

Analysis for Si-H was accomplished by running an excess of five per cent sodium hydroxide from a dropping funnel onto the sample and measuring the amount of hydrogen evolved.

**Starting Materials**

The following compounds were prepared as starting materials. Other starting materials and solvents were obtained commercially. Their purity was checked spectroscopically and on occasion by a molecular weight determination.

**ARSINE, AsH₃**, prepared as described below.

Sodium (7.5 g) was cut into small pieces under oil, dried and placed in a crucible. An excess of finely powdered arsenic (~15 g) was then placed around the sodium and the crucible placed on an insulating layer of asbestos fibre in a glass vessel fitted with a dropping funnel and attached to the vacuum line. The system was flushed with nitrogen and evacuated twice then filled with nitrogen to a pressure of 10 cm. The bottom of the reaction vessel was warmed gently until alloy formation
took place. (At this stage a black and red cloud rises up the vessel and it is advisable to check that the reaction vessel has not cracked). After the vessel had cooled the system was evacuated and distilled water (ca 10 ml) dripped onto the alloy evolving arsine which was purified by distillation through a trap at -110°. IR NMR

Arsine was also prepared by the borohydride reduction of sodium arsenate.

BROMOGERMANE, GeH<sub>3</sub>Br, prepared by the action of bromine on germane. IR NMR

BROMOSILANE, SiH<sub>3</sub>Br, prepared by the hydrogen bromide cleavage of phenylsilane which was prepared by the lithium tetrahydroaluminate reduction of phenyltrichlorosilane. IR NMR

CHLOROGERMANE, GeH<sub>3</sub>Cl, prepared as described below.

Thionyl chloride (Fisher) was purified by passage through a series of U-traps maintained at 0°, to trap out less volatile impurities; -78°, to hold the thionyl chloride; and -196°, to trap hydrogen chloride and sulfur dioxide. The thionyl chloride showed no spurious peaks in its i.r. spectrum. The most likely impurity, sulfur dioxide, has a very strong band at 1360 cm<sup>-1</sup>, whereas the S-O stretch in thionyl chloride is at 1251 cm<sup>-1</sup>. When the thionyl chloride is not from a freshly-opened bottle, an initial purification may be necessary.

Typically, thionyl chloride (4.0 moles) and then germane (4.0 moles) were condensed at -196° into a thick-walled tube (approx. 5 mm o.diam. and 3 mm i.diam.) with a tapered end. The tube was then sealed just above the level of the frozen germane giving approx. 8 cm of sealed-tube containing
the reactants. The tube was left for 22 hours at room temperature in a fume hood (in case it breaks under pressure). The reaction was usually complete after 20 hours and there was evidence from \(^1\)H n.m.r. spectra that after 30 hours some of the monochlorogermane decomposed. The reaction vessel was recooled to \(-196^\circ\) and then opened on the vacuum line by breaking the tapered end in the barrel of a heavy stop-cock. The products were separated using U-traps at -78, -95, and -196\(^\circ\). Purified monochlorogermane (3.5 mmoles) was retained in the -95\(^\circ\) trap, its mass spectrum only had peaks attributable to GeH\(^+\)_n and GeClH\(^+\)_n (n = 0, 1, 2, 3). IR \(^{28}\) NMR \(^{29}\)

**Diborane,** B\(_2\)H\(_6\), prepared \(^{33}\) by dropping sodium borohydride onto 96 percent sulphuric acid. IR \(^{34}\)

**DibromoGermane,** GeH\(_2\)Br\(_2\), prepared \(^{27}\) by the action of bromine on germane. IR \(^{35}\) NMR \(^{29}\)

**DibromoSilane,** SiH\(_2\)Br\(_2\), prepared \(^{36}\) by the action of boron tribromide on silane. IR \(^{37}\) NMR \(^{32}\)

**Digermane,** Ge\(_2\)H\(_6\), prepared \(^{38}\) by the ozoniser discharge of germane. IR \(^{39}\) NMR \(^{38}\)

**Digermyl Bromide,** Ge\(_2\)H\(_5\)Br, prepared \(^{40}\) by passing digermane over heated silver bromide. IR \(^{41}\) NMR \(^{42}\)

**Dimethylarsine,** Me\(_2\)AsH, prepared by the action of methyl iodide on potassium methylarsenide. Methyarsine was admitted over a stirred slurry of finely powdered potassium hydroxide in dimethylsulphoxide. When absorption was complete methyl iodide was added in small portions until the solution was decolourised. An almost identical procedure for methylphosphine is described.
in detail elsewhere\textsuperscript{43}

\textbf{DIPHENYLARSINE}, $\text{Ph}_2\text{AsH}$, prepared\textsuperscript{44} by the cleavage of triphenylarsine with potassium. IR\textsuperscript{45}

\textbf{DISILANE}, $\text{Si}_2\text{H}_6$, prepared\textsuperscript{46} by the ozoniser discharge of silane. IR\textsuperscript{47} NMR\textsuperscript{48}

\textbf{DISILANYL BROMIDE}, $\text{Si}_2\text{H}_3\text{Br}$, prepared\textsuperscript{49} by the action of $\text{Br}_3\text{Br}$ on disilane. IR\textsuperscript{49} NMR\textsuperscript{49}

\textbf{HYDROGEN IODIDE}, HI, commercial hydriodic acid was "pumped on" through a -196\textdegree\, trap and the HI collected was purified by distillation at -78\textdegree\, and stored at -78\textdegree.

\textbf{HYDROGEN SELENIDE}, $\text{H}_2\text{Se}$, prepared in a similar apparatus to arsine. The alloy was prepared by plunging a strip of burning magnesium into a finely powdered mixture of aluminium and selenium and hydrolysed with distilled water.

\textbf{HYDROGEN SULPHIDE}, $\text{H}_2\text{S}$, prepared as hydrogen selenide using sulphur in place of selenium.

\textbf{LITHIUM TETRA-ARSINOALUMINATE}, $\text{LiAl}(\text{AsH}_2)_4$, prepared by a method similar to the analogous phosphinoaluminate.\textsuperscript{50} Lithium tetrahydroaluminate (ca 2 mmoles) in 10 mls of dry diglyme and arsine (ca 10 mmoles) were held together at room temperature. Every 3 hours the vessel was cooled to -196\textdegree, $\text{H}_2$ pumped away and the arsine atmosphere renewed. The colour of the solution turned to yellow to green to brown. Usually no further reaction occurred after two days by which time approximately 8 mmoles of hydrogen had been evolved and approximately 8 mmoles of arsine consumed.
The residual Al-H content of typical solutions was determined by hydrolysis. Three such experiments gave values of 3, 6 and 4 percent.

**Lithium Tetrahydroaluminate**, LiAlH$_4$, Alfa, was purified by recrystallisation from diethyl ether and stored under nitrogen.

**Methylarsine**, MeAsH$_2$, prepared$^{51}$ by the zinc/hydrochloric acid reduction of sodium methylarsenate. IR$^{52}$.

Methylarsine was also prepared by the reaction of LiAl(AsH$_2$)$_4$ with methyl iodide under similar conditions to those used in the preparation of silyl and germyl arsines (Chapter 3).

**Methylbromogerlane**, MeGeH$_2$Br, prepared$^{53}$ by the action of boron tribromide on methylgermane. IR$^{53}$ NMR$^{53}$

**Methylbromosilane**, MeSiH$_2$Br, prepared$^{49}$ by the action of boron tribromide on methylsilane. IR$^{54}$ NMR$^{55}$

**Methylgermane**, MeGeH$_3$, prepared$^{56}$ by the action of methyl iodide on potassium germyl in hexamethylphosphoramide on monoglyme. IR$^{57}$ NMR$^{58}$

**Methylsilane**, CH$_3$SiH$_3$, prepared by lithium tetrahydroaluminate reduction of methyl trichlorosilane. IR$^{59}$ NMR$^{55}$

**Phenylarsine**, PhAsH$_2$, prepared by the lithium tetrahydroaluminate reduction of phenyl dichloroarsine IR$^{45}$.

**Trimethylgermyldimethylamine**, Me$_3$GeNMe$_2$, and other dimethylamino germanes, prepared$^{60}$ from lithium dimethylamide and a halogermane or as described below.

A solution of lithium tetradimethylaminoaluminate (4.0 mmoles) in
10 ml of diglyme prepared by the reaction of dimethylamine with lithium tetrahydroaluminate. 15.0 mmoles of trimethylbromogermane was condensed in and the mixture allowed to warm to 0° and shaken occasionally. After 30 minutes trimethylgermyldimethylamine (13.6 mmoles) was recovered.

Using similar procedures bis(dimethylamino) dimethylgermane and tris(dimethylamino) methylgermane were prepared in yields of 75 and 69 percent respectively. IR \textsuperscript{62} NMR \textsuperscript{62}

TRIMETHYlstanyldimethylamine, Me\textsubscript{3}SnNMe\textsubscript{2}, and other dialkylamino stannanes, prepared \textsuperscript{63} from a lithium dialkylamide and a halostannane or by the dimethylaminoaluminate method as used for the dimethylaminoger mananes. The aluminate method gave Me\textsubscript{3}SnNMe\textsubscript{2}, Me\textsubscript{2}Sn(NMe\textsubscript{2})\textsubscript{2} and MeSn(NMe\textsubscript{2})\textsubscript{3} in yields of 82 percent 72 percent and 74 percent respectively. IR \textsuperscript{62} NMR \textsuperscript{62}

TRISILYLARsINE, (SiH\textsubscript{3})\textsubscript{3}As, prepared \textsuperscript{64} from potassium arsenide and bromosilane. IR \textsuperscript{65} NMR \textsuperscript{66}

TRIS(TRIMETHYLSILYL)ARsINE, (Me\textsubscript{3}Si)\textsubscript{3}As, prepared \textsuperscript{11} from potassium arsenide and trimethylchlorosilane. IR \textsuperscript{67} NMR \textsuperscript{67}
CHAPTER 2

The Vibrational Spectra of Trimethyliodogermane and Trimethylfluorogermane

The vibrational spectra of trimethylsilyl and trimethylstannyl derivatives have been studied extensively and have been the subject of two reviews. In addition the assignments of the trimethylsilyl and trimethylstannyl halides have been confirmed by normal coordinate analyses. In contrast, only the spectra of trimethylchlorogermane had been reported before the commencement of this study. The number of bands found in the low frequency region was notably less than the number of skeletal fundamentals and this was explained by assuming an accidental degeneracy of some of the fundamentals. Recently the spectra of trimethylchlorogermane was reinvestigated and those of trimethylbromogermane reported. This chapter describes the vibrational spectra of trimethyliodogermane and trimethylfluorogermane. The assignments are supported by a normal coordinate analysis and were used to interpret the more complex spectra of the methylated germyl arsines.

Experimental

1) Preparation of Trimethyliodogermane

Trimethylchlorogermane (2.0 mmoles) and hydrogen iodide (3.1 mmoles) were held together in a 100 ml reaction vessel for one hour. The products were separated on the fractionating column yielding hydrogen chloride (2.0 mmoles); hydrogen iodide (1.1 mmoles) and trimethyliodogermane (1.9 mmoles). The purity of the trimethyliodogermane was established by
its \(^1\)H n.m.r. spectrum which showed only the expected singlet. The infrared and Raman spectra are shown in figures 2.1 and 2.2 and frequency listings are given in Table 2.1.

2) Preparation of trimethylfluorogermane

Trimethylbromogermane (1.0 mmol) was repeatedly passed through a column of lead (II) fluoride (4 in. x \(\frac{1}{2}\) in.) packed loosely on glass wool. After ten passes a \(^1\)H n.m.r. spectrum of the products showed only the doublet expected for trimethylfluorogermane. The infrared and Raman spectra are shown in figures 2.3-2.5 and frequency listings are given in Table 2.2.

**Discussion**

The spectra were assigned on the basis of \(C_{3v}\) symmetry. There are twenty four fundamentals of which eight are \(a_1\) type, four \(a_2\)-type and twelve are \(e\)-type. The \(a_1\) and \(e\) modes are infrared and Raman active and the \(a_2\) are inactive in both. The \(a_1\) Raman bands should be polarised.

**The C-H Stretching Vibrations** \((\nu_1, \nu_9, \nu_{13,} \nu_{14,} \nu_2\) and \(\nu_{15}\))

The bands at 2990 cm\(^{-1}\) in the iodide and 3009 cm\(^{-1}\) in the fluoride are attributed to the asymmetric C-H stretching vibrations \(\nu_1, \nu_{13}\) and \(\nu_{14}\) and the bands at 2913 cm\(^{-1}\) in the iodide and 2932 cm\(^{-1}\) in the fluoride are assigned to \(\nu_2\) and \(\nu_{15}\), the symmetric C-H stretching vibrations.

**The CH\(^3\)-Deformation Vibrations** \((\nu_3, \nu_{10,} \nu_{16,} \nu_{17,} \nu_4\) and \(\nu_{18}\))

The bands at 1410 and 1250 cm\(^{-1}\) in the iodide and 1420 and 1265 cm\(^{-1}\) in the fluoride are attributed to the asymmetric deformations, \(\nu_3, \nu_{16}\), and \(\nu_{17}\), and the symmetric deformations, \(\nu_4\) and \(\nu_{18}\), respectively.
<table>
<thead>
<tr>
<th>IR (gas)</th>
<th>IR (liq.)</th>
<th>Raman (liq.)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3820, 3760</td>
<td></td>
<td></td>
<td>$\nu_2 + \nu_{19} = 3753$</td>
</tr>
<tr>
<td>3690, vw</td>
<td></td>
<td></td>
<td>$\nu_2 + \nu_{15} = 3678$</td>
</tr>
<tr>
<td>2990 w</td>
<td>2995 s</td>
<td>2995 dp</td>
<td>$\nu_1 \nu_9 \nu_{13} \nu_{14}$</td>
</tr>
<tr>
<td>2910 w</td>
<td>2913 s</td>
<td>2913 p</td>
<td>$\nu_2 \nu_{15}$</td>
</tr>
<tr>
<td>2795, 2480</td>
<td></td>
<td></td>
<td>$2\nu_{16} = 2830, 2\nu_4 = 2490$</td>
</tr>
<tr>
<td>2090, 1870 w</td>
<td></td>
<td></td>
<td>$\nu_2 \nu_{19} = 2073$</td>
</tr>
<tr>
<td>1815</td>
<td></td>
<td></td>
<td>$\nu_4 + \nu_{21} = 1870, \nu_4 + \nu_6 = 182$</td>
</tr>
<tr>
<td>1410 vw</td>
<td>1415 s</td>
<td>1410 dp</td>
<td>$\nu_3 \nu_{10} \nu_{16} \nu_{17}$</td>
</tr>
<tr>
<td>1245 w</td>
<td>1245 s</td>
<td>1250 p</td>
<td>$\nu_4 \nu_{18}$</td>
</tr>
<tr>
<td>830 m</td>
<td>840 br.s.</td>
<td>832 dp</td>
<td>$\nu_5 \nu_{19}$</td>
</tr>
<tr>
<td>730 m</td>
<td>765 s</td>
<td>n.o.</td>
<td>$\nu_{20} \nu_{11}$</td>
</tr>
<tr>
<td>617 w</td>
<td>625 s</td>
<td>623 dp</td>
<td>$\nu_{21}$</td>
</tr>
<tr>
<td>570 w</td>
<td>580 s</td>
<td>578 p</td>
<td>$\nu_6$</td>
</tr>
<tr>
<td></td>
<td>228 s</td>
<td>224 p</td>
<td>$\nu_7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>179 p</td>
<td>$\nu_8 \nu_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>132 dp</td>
<td>$\nu_{23}$</td>
</tr>
</tbody>
</table>

$\nu_1 - \nu_8$ are $a_1$; $\nu_9 - \nu_{12}$ are $a_2$; $\nu_{13} - \nu_{24}$ are $e$. 

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FIGURE 2.1 The Infrared Spectrum of Trimethylgermane
FIGURE 2.2 The Raman Spectrum of Trimethyliodogermaine
TABLE 2.2
The Vibrational Spectra of \((\text{CH}_3)_2\text{GeF}\)

<table>
<thead>
<tr>
<th>IR (gas)</th>
<th>Raman (liquid)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3760 w</td>
<td></td>
<td>(v_{2} + v_{19} = 3768)</td>
</tr>
<tr>
<td>3009 s</td>
<td>2990 dp</td>
<td>(v_{1} + v_{13} + v_{14})</td>
</tr>
<tr>
<td>2932 m</td>
<td>2917 p</td>
<td>(v_{2}, v_{15})</td>
</tr>
<tr>
<td>2830</td>
<td></td>
<td>(2v_{16} = 2840)</td>
</tr>
<tr>
<td>2490</td>
<td></td>
<td>(2v_{4} = 2530)</td>
</tr>
<tr>
<td>2151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2116 w</td>
<td></td>
<td>(v_{2} - v_{19} = 2096)</td>
</tr>
<tr>
<td>1880</td>
<td></td>
<td>(v_{4} + v_{6} = 1895)</td>
</tr>
<tr>
<td>1835</td>
<td></td>
<td>(v_{4} + v_{21} = 1845)</td>
</tr>
<tr>
<td>1420 w</td>
<td></td>
<td>(v_{3} + v_{10} + v_{16} + v_{17})</td>
</tr>
<tr>
<td>1265 s</td>
<td>1255 p</td>
<td>(v_{4} + v_{18})</td>
</tr>
<tr>
<td>836 s</td>
<td></td>
<td>(v_{5} + v_{19})</td>
</tr>
<tr>
<td>760 s</td>
<td></td>
<td>(v_{20} + v_{11})</td>
</tr>
<tr>
<td>662 s</td>
<td></td>
<td>(v_{7})</td>
</tr>
<tr>
<td>630 s</td>
<td>629 dp</td>
<td>(v_{21})</td>
</tr>
<tr>
<td>580 w</td>
<td>578 p</td>
<td>(v_{6})</td>
</tr>
<tr>
<td></td>
<td>230 dp</td>
<td>(v_{22})</td>
</tr>
<tr>
<td></td>
<td>195 p</td>
<td>(v_{8})</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>(v_{23})</td>
</tr>
</tbody>
</table>

\(v_{1} - v_{8}\) are \(a_i\); \(v_{9} - v_{12}\) are \(a_2\); \(v_{13} - v_{24}\) are \(e\)

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FIGURE 2.3 The Infrared Spectrum of Trimethylfluorogermane (4000-1600 cm$^{-1}$)
FIGURE 2.4 The Infrared Spectrum of Trimethylfluorogermane (1500-400 cm\(^{-1}\))
The CH₃ Rocking Modes \( v_{11}, v_{19}, v_{20} \)

The symmetric rocking modes, \( v_5 \) and \( v_{19} \) are assigned to the broad band at 840 cm\(^{-1}\) in the infrared spectrum of the iodide and to the band at 836 cm\(^{-1}\) for the fluoride, and likewise the bands at 730 cm\(^{-1}\) for the iodide and 760 cm\(^{-1}\) for the fluoride are attributed to \( v_{20} \). These bands were too weak to be detected in the Raman spectra. In the recent study of trimethylchlorogermane\(^7\) the methyl rocking modes also remained undetected in the Raman spectrum.

The Skeletal Stretches \( v_6, v_{21}, v_7 \)

The Ge-C asymmetric stretches, \( v_{21} \), are assigned to the strong bands in the infrared at 617 cm\(^{-1}\) for the iodide and 630 cm\(^{-1}\) in the fluoride. The corresponding Raman bands are depolarised. The symmetric stretches, \( v_6 \), are assigned to the weaker infrared bands and strong polarised Raman bands at 570 cm\(^{-1}\) for the iodide and 580 cm\(^{-1}\) for the fluoride. The Ge-I stretch \( v_7 \), is assigned to the very intense polarised Raman band at 244 cm\(^{-1}\). The Ge-F stretch is assigned to the band at 662 cm\(^{-1}\) in the infrared. Although this should appear as a polarised band in the Raman spectrum no such band was detected in this region. However fluorides are very poor Raman scatterers and it may prove possible to locate this band using a more powerful laser.

The Skeletal Deformations \( v_8, v_{22}, v_{23} \)

These appear below 250 cm\(^{-1}\) in the Raman spectra (figures 2 and 3). The symmetric deformations, \( v_8 \), should be polarised whereas the asymmetric deformations, \( v_{22} \) and the GeC₃ rocking mode \( v_{23} \) should be depolarised. \( v_8 \) is assigned to the shoulder at 195 cm\(^{-1}\) for the fluoride and to the polarised band at 176 in the iodide. \( v_{22} \) is assigned to the bands at
230 cm\(^{-1}\) in fluoride and 179 cm\(^{-1}\) in the iodide and \(v_{23}\) at 185 cm\(^{-1}\) for the fluoride and 132 cm\(^{-1}\) for the iodide.

The torsional modes were not observed.
CHAPTER 3

The Preparation of Silicon, Germanium and Tin

Primary Arsines Using LiAl(AsH$_2$)$_4$

There are relatively few primary arsines among the group IV arsines known. The methods used to synthesise primary arsines usually gave a mixture of products with a poor yield of the desired arsine. Ozoniser discharge of mixtures of hydrides such as SiH$_4$/AsH$_3$, GeH$_4$/AsH$_3$ and MeSiH$_3$/AsH$_3$ has been used to prepare silyl, germyl and methylsilyl-arsines. The method requires special equipment and gives large quantities of diarsine, disilanes or digermanes, higher hydrides and solids. The hydrolysis of mixtures of arsenide and germanide alloys has given traces of germyl arsine, GeH$_3$AsH$_2$. The reaction of arsinopotassium with MH$_3$Br gives mainly (MH$_3$)$_3$As (M = Si, Ge) but some silyl and germyl arsine can be obtained under specific conditions. Disilanyl arsine has been obtained from an exchange reaction between silylarsine and chlorodisilane and trimethylsilylarsine from the action of water on tris(trimethylsilyl) arsine.

At the start of this investigation lithium tetraphosphinoaluminate had been found to be a useful phosphinating agent for the preparation of alkyl and germyl phosphines and varying success was claimed for silyl phosphines. A similar compound, lithium tetra-arsinoaluminate LiAl(AsH$_2$)$_4$, had been prepared but its reactions had not been investigated. This chapter describes the preparation of primary arsines using LiAl(AsH$_2$)$_4$.
Experimental

Table 1 lists the reagents and reaction conditions. In each case the halide was condensed onto the LiAl(AsH₂)₄ solution at -196° and the mixture was allowed to warm until the solvent melted. The appropriate slush bath was placed around the reaction vessel and the mixture was stirred or shaken vigorously. The initial brown colour of the solution gradually turned to green then to yellow. When this colour started to darken the products were immediately pumped out of the reaction vessel and separated. Table 1 lists the products. The silanes, germanes, and arsines were characterised by their ¹H n.m.r. spectra and by their i.r. spectra: trimethylsilane,⁸⁴ trimethylgermane,⁵⁷ dimethylgermane,⁵⁷ 1,2-dimethyldigermane,⁸⁵ methylgermane,⁵⁷ methyilsilane,⁹⁷ disilane,⁴⁷ digermane,⁹⁷ silylarsine,⁸⁶ germylarsine,⁸⁷ disilanylarsine,⁸¹ and trimethylsilylarsine.⁸⁸ I.R. and ¹H n.m.r. spectra of the new compounds are given (Tables 2 and 3). It was found that longer reaction times led to reduced yields. In a similar set of experiments using a 1:1 mole ratio of halide to LiAl(AsH₂)₄, similar yields were obtained.

The reaction of dibromosilane, dibromogermane, dimethyldibromosilane and trimethylbromostannane with the stoichiometric amount of LiAl(AsH₂)₄ did not give any of the expected arsines, the only products were traces of the corresponding hydrides and arsine. Bis(arsino)silane, SiH₂(AsH₂)₂; bis(arsino)dimethysilane, Me₂Si(AsH₂)₂ and trimethylstannylarsine, Me₃SnAsH₂, were prepared in yields of 10, 14 and 9 percent using an excess of LiAl(AsH₂)₄.
TABLE 3.1

Syntheses of the arsines

<table>
<thead>
<tr>
<th>Halide RBr</th>
<th>LiAl(AsH₂)₄ (mmole)</th>
<th>RAsH₂ (mmole)</th>
<th>%</th>
<th>AsH₃ (mmole)</th>
<th>RH (mmole)</th>
<th>Other Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) SiH₃Br</td>
<td>11.18</td>
<td>3.20</td>
<td>7.80</td>
<td>70</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>2) GeH₃Br</td>
<td>9.77</td>
<td>2.63</td>
<td>6.33</td>
<td>65</td>
<td>1.8</td>
<td>0.5 Ge₂H₆(0.6)</td>
</tr>
<tr>
<td>3) Si₂H₅Br</td>
<td>7.21</td>
<td>1.91</td>
<td>4.26</td>
<td>59</td>
<td>1.9</td>
<td>SiH₄(0.1)</td>
</tr>
<tr>
<td>4) Ge₂H₅Br</td>
<td>5.21</td>
<td>1.54</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
<td>2.6 GeH₄(3.1)</td>
</tr>
<tr>
<td>5) CH₃SiH₂Br</td>
<td>10.00</td>
<td>2.60</td>
<td>5.72</td>
<td>57</td>
<td>2.6</td>
<td>0.8</td>
</tr>
<tr>
<td>6) CH₃GeH₂Br</td>
<td>6.61</td>
<td>2.12</td>
<td>3.18</td>
<td>48</td>
<td>3.1</td>
<td>(CH₃GeH₂)₂(0.16)</td>
</tr>
<tr>
<td>7) (CH₃)₂SiBr</td>
<td>14.95</td>
<td>4.00</td>
<td>11.48</td>
<td>77</td>
<td>2.72</td>
<td>1.32</td>
</tr>
<tr>
<td>8) (CH₃)₃GeBr</td>
<td>12.10</td>
<td>3.51</td>
<td>8.20</td>
<td>68</td>
<td>1.90</td>
<td>(CH₃)₂GeH₂(1.10)</td>
</tr>
</tbody>
</table>

In reactions 1, 2, 3, 5 diglyme was used as the solvent and in 4, 6, 7, 8 triglyme was used.

Reaction times were 20 mins. for 1, 2, 3; 15 mins. for 4; 25 mins. for 5, 6, 7, 8.

Reaction temperatures were -45° for 1, 2, 3; -23° for 4, 5, 6; 0° for 7, 8.
<table>
<thead>
<tr>
<th></th>
<th>MeSiH₂·AsH₂</th>
<th>MeGeH₂·AsH₂</th>
<th>Me₃Ge·AsH₂</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2978m</td>
<td>2985w</td>
<td>2970s</td>
<td></td>
<td>Me asym. str.</td>
</tr>
<tr>
<td>2920w</td>
<td></td>
<td>2910s</td>
<td></td>
<td>Me sym. str.</td>
</tr>
<tr>
<td>2676w</td>
<td></td>
<td></td>
<td></td>
<td>SiH str.</td>
</tr>
<tr>
<td>2160s</td>
<td>2068s</td>
<td></td>
<td></td>
<td>GeH str.</td>
</tr>
<tr>
<td>2102s</td>
<td>2080s</td>
<td>2085s</td>
<td></td>
<td>AsH str.</td>
</tr>
<tr>
<td>1410w</td>
<td>1415vw</td>
<td>1412w</td>
<td></td>
<td>Me asym. def.</td>
</tr>
<tr>
<td>1368w</td>
<td></td>
<td></td>
<td></td>
<td>Me sym. def.</td>
</tr>
<tr>
<td>1258m</td>
<td>1250w</td>
<td>1239m</td>
<td></td>
<td>(Si-O impurity)</td>
</tr>
<tr>
<td>1086w</td>
<td></td>
<td></td>
<td></td>
<td>SiH₂ def.</td>
</tr>
<tr>
<td>948s</td>
<td>905m</td>
<td>954m</td>
<td></td>
<td>AsH₂ def.</td>
</tr>
<tr>
<td>938sh</td>
<td>888s</td>
<td></td>
<td></td>
<td>SiH₂ def.</td>
</tr>
<tr>
<td>920s</td>
<td>870s</td>
<td></td>
<td></td>
<td>GeH₂ def.</td>
</tr>
<tr>
<td>892s</td>
<td>838s</td>
<td>828vs</td>
<td></td>
<td>Me rock</td>
</tr>
<tr>
<td>748m</td>
<td>831sh</td>
<td>756m</td>
<td></td>
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<tr>
<td>682m</td>
<td>640w</td>
<td></td>
<td></td>
<td>Si-C str.</td>
</tr>
<tr>
<td></td>
<td>589w</td>
<td>601s</td>
<td></td>
<td>Ge-C str.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>572m</td>
<td>AsH₂ wag</td>
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<tr>
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<td>566m</td>
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<td>554m</td>
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<td></td>
<td></td>
<td>SiH₂ rock</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>402w</td>
<td></td>
<td></td>
<td></td>
<td>GeH₂ rock</td>
</tr>
</tbody>
</table>
TABLE 3.3

N.M.R. Parameters of Group IV Primary Arsines

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{a}$AsH</th>
<th>$^{a}$MH</th>
<th>$^{a}$CH</th>
<th>$^{b}$HAsMH</th>
<th>$^{b}$HMCH</th>
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</thead>
<tbody>
<tr>
<td>SiH$_3$AsH$_2$</td>
<td>0.78</td>
<td>3.67</td>
<td>---</td>
<td>5.1</td>
<td>---</td>
</tr>
<tr>
<td>MeSiH$_2$AsH$_2$</td>
<td>0.84</td>
<td>4.12</td>
<td>0.43</td>
<td>4.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Me$_3$SiAsH$_2$</td>
<td>0.69</td>
<td>---</td>
<td>0.33</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>GeH$_3$AsH$_2$</td>
<td>1.02</td>
<td>3.57</td>
<td>---</td>
<td>4.8</td>
<td>---</td>
</tr>
<tr>
<td>MeGeH$_2$AsH$_2$</td>
<td>1.00</td>
<td>3.81</td>
<td>0.41</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Me$_3$GeAsH$_2$</td>
<td>0.81</td>
<td>---</td>
<td>0.33</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Me$_3$SnAsH$_2$</td>
<td>1.1</td>
<td>---</td>
<td>0.31</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>SiH$_3$SiH$_2$AsH$_2$</td>
<td>0.95</td>
<td>3.60</td>
<td>---</td>
<td>5.0</td>
<td>---</td>
</tr>
<tr>
<td>SiH$_2$(AsH$_2$)$_2$</td>
<td>0.88</td>
<td>5.07</td>
<td>---</td>
<td>4.9</td>
<td>---</td>
</tr>
<tr>
<td>Me$_2$Si(AsH$_2$)$_2$</td>
<td>0.93</td>
<td>---</td>
<td>0.61</td>
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<td>---</td>
</tr>
</tbody>
</table>

(a) Ref. 98   (b) Ref. 67   (c) Ref. 81   (d) $^{a}$SiH$_3$ 3.45

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Typically, trimethylbromostannane (ca 10 mmoles) was condensed onto a monoglyme solution of LiAl(AsH₂)₄ (12.5 mmoles) and the mixture held at -45º for ca. 10 minutes. Separation of the products by trap-to-trap distillation gave trimethylstannylarsine (0.9 mmole) in a trap at 0º while the solvent, arsine and a mixture of methylstannanes passed through into a -196º trap.

The new compounds were identified by their infrared and ¹H n.m.r. spectra (tables 2 and 3) molecular weight determinations and by reaction with a hydrogen halide. Table 4 lists the found and calculated molecular weights, the amount of compound taken for analysis and the amounts of group IV halide and arsine produced on reaction with HX. The compounds were treated with a 15% excess of hydrogen halide for 30 minutes at room temperature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MeSiH₂AsH₂</td>
<td>121</td>
<td>123</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>MeGeH₂AsH₂</td>
<td>163</td>
<td>166</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Me₃GeAsH₂</td>
<td>191</td>
<td>195</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Me₃SnAsH₂</td>
<td>238</td>
<td>241</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Me₂Si(AsH₂)₂</td>
<td>204</td>
<td>214</td>
<td>0.5</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>H₂Si(AsH₂)₂</td>
<td>178</td>
<td>184</td>
<td>0.4</td>
<td>0.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>
In a series of experiments 4 mmols of silylarsine was left at -45° for 30 minutes in contact with diglyme solutions of 1 mmole of a) LiAlH₄, b) AlBr₃ c) LiBr d) LiBr/AlBr₃ e) LiAl(AsH₃)₄ and with diglyme itself (table 5). The volatile products were taken off and the residual solutions treated with anhydrous hydrogen bromide.

The residual solids from a silylarsine preparation were treated with HCl at -95° in dimethyl ether for 4 hours. The products were small quantities of di- and tri-chlorosilanes and arsine.
<table>
<thead>
<tr>
<th>Reactant</th>
<th>SiH$_3$AsH$_2$</th>
<th>AsH$_3$</th>
<th>SiH$_4$</th>
<th>Di- and trisilylarsines</th>
<th>Others</th>
<th>Products from HBr treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH$_4$</td>
<td>trace</td>
<td>trace</td>
<td>3.6</td>
<td>trace</td>
<td>trace H$_2$</td>
<td>0.2 mmoles H$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>trace SiH$_3$Br</td>
<td>3.7 mmoles AsH$_3$</td>
</tr>
<tr>
<td>AlBr$_3$</td>
<td>---</td>
<td>2.0</td>
<td>1.1</td>
<td>trace</td>
<td>trace SiH$_3$Br</td>
<td>Mixture of SiH$_4$-Br$_n$ and arsine</td>
</tr>
<tr>
<td>LiBr</td>
<td>3.9</td>
<td>trace</td>
<td>trace</td>
<td>---</td>
<td>---</td>
<td>Mixture of SiH$_4$-Br$_n$ and arsine</td>
</tr>
<tr>
<td>LiBr/AlBr$_3$</td>
<td>2.4</td>
<td>0.3</td>
<td>0.2</td>
<td>trace</td>
<td>---</td>
<td>Mixture of SiH$_4$-Br$_n$ and arsine</td>
</tr>
<tr>
<td>LiAl(AsH$_2$)$_4$</td>
<td>2.6</td>
<td>2.0</td>
<td>trace</td>
<td>---</td>
<td>---</td>
<td>Mixture of SiH$_4$-Br$_n$ and arsine</td>
</tr>
<tr>
<td>Diglyme</td>
<td>3.9</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Discussion

Lithium tetra-arsinoaluminate shows a reactivity parallel to lithium tetrahydroaluminate reacting with halides of boron, carbon, silicon, germanium, tin, phosphorus, arsenic and sulphur, with protic acids and unsaturated carbon-oxygen and carbon-nitrogen linkages. It is the most effective reagent for the preparation of primary silyl- and germyl-arsines [reaction (1) and (2)].

\[
4\text{RB}_3 + \text{LiAl(AsH}_2^2\text{)}_4 = \text{LiBr} + \text{AlBr}_3 + 4\text{RAsH}_2 \quad \ldots \ldots \ldots \ldots \quad (1)
\]

where \( R = \text{SiH}_3, \text{GeH}_3, \text{Si}_2\text{H}_5, \text{MeSiH}_2, \text{MeGeH}_2, \text{Me}_3\text{Si}, \text{Me}_3\text{Ge} \) or \( \text{Me}_3\text{Sn} \).

\[
2\text{Me}_2\text{SiBr}_2 + \text{LiAl(AsH}_2^2\text{)}_4 = 2\text{Me}_2\text{Si(AsH}_2^2\text{)}_2 + \text{LiBr} + \text{AlBr}_3 \quad \ldots \ldots \ldots \ldots \quad (2)
\]

where \( R = \text{H}, \text{Me} \).

As Norman has pointed out for the corresponding phosphinoaluminates the mechanism may be either an \( S_N^2 \)-type or involve a four-centre transition state. No secondary or tertiary arsines were detected among the reaction products. These may be formed and be susceptible to further attack in the reaction medium, leading to involatile products. Treatment of the residue from a silylarsine preparation with hydrogen chloride gave some dichloro- and trichloro-silane, which indicates the presence of cross-linked polymeric substances. Disilylarsine has been prepared from \( \text{LiAl(AsH}_2^2\text{)}_4 \) by use of an excess of \( \text{LiAl(AsH}_2^2\text{)}_4 \) and longer reaction times (conditions which would facilitate displacement.
reactions) and in a different solvent, which may be important. It has been suggested that the reason for the formation of trisilylarsine in the $K^+\text{(AsH}_2^\text{-})^-$-$\text{SiH}_3\text{Br}$ system is the order of acidity $(\text{SiH}_3)_2\text{AsH} > \text{SiH}_3\text{AsH}_2 > \text{AsH}_3$ which has been attributed to the increasing solubility of the anions with increasing size. With the larger $[\text{Al(AsH}_2^\text{-})_4]^-$ anion the effect of silyl-substitution on solubility would probably be less important.

In each reaction, small amounts of the corresponding parent silane or germane and varying amounts of arsine were formed as by-products. The $\text{LiAl(AsH}_2^\text{-})_4$ solutions contain small amounts of Al-H bonded species (ca 5%) which may form the parent hydride either by reduction of the halide or by cleavage of the Si-As or Ge-As bonds of the product arsine. Lithium tetrahydroaluminate cleaves the bonds in silylarsine, germarylarsine, (table 5 and see chapter 5) and the corresponding phosphines to form silane or germane. By comparison with the corresponding $\text{LiAl(Ph}_2^\text{-})_4$ systems, possible sources of arsine are (i) aluminium halide-catalysed disproportionation of the product arsine similar to that observed with diborane; (ii) displacement reactions between the product arsine and unreacted $\text{LiAl(AsH}_2^\text{-})_4$ or (iii) lithium halide-induced cleavage of Si-As or Ge-As bonds similar to that observed for Si-Si and Ge-Ge bonds.

The results of the experiments listed in table 5 suggest that the major sources of arsine are (i) and (ii).

No digermanylarsine was isolated from the reaction with monobromo-digermane but digermanyl compounds are generally more unstable than the corresponding disilanyl derivatives. Both disilane and digermane
react with LiAlH$_4$ to give some monosilane and monogermane. Similar reactions in the monobromo-disilane and -digermane additions could account for the monosilane and monogermane observed. Monogermane reacts with LiAlH$_4$ to form an Al-Ge bonded species. Such species may account for the formation of digermane derivatives from reactions with bromogermanes containing Ge-H bonds. Monosilane does not react with LiAlH$_4$ and no corresponding disilanes are formed.

The infrared spectra of methylsilyl-, methylgermyl- and trimethylgermyl-arsines are displayed in table 3.2. A typical spectrum is shown in figure 3.1. The infrared spectrum of trimethylsilylarsine was published during the course of this work and the spectrum of trimethylstannyl-arsine is given in chapter 6. It was not possible to obtain satisfactory spectra for the bis-arsino-silanes due to hydrolysis. The assignments were made by comparison with other methylsilyl methylgermyl and trimethylgermyl compounds and other primary arsines.

The n.m.r. spectra of the compounds are displayed in table 3.3. The trends in chemical shifts and coupling constants are similar to those in analogous phosphines. Methyl or arsino substitution lowers the M-H chemical shift and the As-H chemical shifts move downfield as M = Si Ge → Sn in Me$_3$MAsH$_2$. Both these trends are consistent with anisotropic effects rather than inductive effects.

The n.m.r. spectrum of bis(arsino)silane, SiH$_2$(AsH$_2$)$_2$, shows the SiH$_2$ resonance split into a 1:4:6:4:1 pentet by the four protons on the arsenic atoms. The AsH$_2$ resonances are split into a broad 1:2:1 triplet by the two protons on silicon.
FIGURE 6 The Infrared Spectrum of Trimethylgermylarsine
The n.m.r. spectrum of methylsilylarsine, MeSiH₂AsH₂, shows the CH₃ resonance split into a 1:2:1 triplet by the two protons on the adjacent silicon atom. No long range coupling with the protons on arsenic was observed. The AsH₂ resonance is also split into a triplet by the protons on silicon. The SiH₂ resonance should be a triplet of quartets due to coupling with the two protons on arsenic and the three on carbon. Because of the similarity in coupling constants it appears as a 1:5:10:10:5:1 hextet. The n.m.r. spectrum of methylgermylarsine is similar. This simplification also occurs in the spectra of the analogous phosphines.⁷⁷,⁹⁷ In all the arsines the AsH₂ resonance was broadened presumably due to the high quadrupole moment of the arsenic nucleus.⁹⁸ This is also probably the reason behind the failure to detect any coupling between contiguous arsenic atoms and protons (As⁷⁵ is 100% abundant with a spin of ³⁄₂).
CHAPTER 4

The Preparation of Tertiary and Secondary Silicon Arsines

During the course of this work the preparation of a series of silicon arsines of the type $\text{Me}_{4-n} \text{Si(AsMe}_2\text{)}_n$, where $n = 1-3$, was reported. The arsines were prepared from lithium dimethylarsenide in excellent yields according to (1).

$$\text{Me}_{4-n} \text{SiCl} + n\text{LiAsMe}_0 \rightarrow \text{Me}_{4-n} \text{Si(AsMe}_2\text{)}_n + n\text{LiCl} \quad \ldots \ldots \quad (1)$$

A similar method (2) applied to the synthesis of secondary arsines gave very poor yields.$^{100}$

$$\text{Me}_3\text{SiCl} + \text{LiAsHMe} \rightarrow \text{Me}_3\text{SiAsHMe} + \text{LiCl} \quad \ldots \ldots \quad (2)$$

Recently a secondary methyl(silyl) phosphine was prepared from lithium tris(phosphino)hydroaluminate.$^{101}$ This chapter describes the synthesis of tertiary and secondary silicon arsines using lithium arsenides and arsinoaluminates.
Experimental

Alkylarsinoaluminate Reactions

Methylarsine (10.0 mmoles) and a few mls of diethylether were condensed at -196° onto a solution of lithium tetrahydroaluminate (1.9 mmoles) in ca 5 ml of diglyme. The mixture was warmed until it melted and a -78° bath placed around the reaction vessel. The mixture was stirred at this temperature for 30 minutes to ensure thorough mixing and then allowed to warm to room temperature. At this point the mixture was a dark green colour and was effervescing steadily. After 30 hours hydrogen evolution had ceased and the solution was brown in colour. The hydrogen (5.9 mmoles), excess methylarsine and diethyl ether were pumped out and bromosilane (8.0 mmoles) was condensed in. After 45 minutes at -45° the products were separated to give disilyl(methyl)arsine (3.3 mmoles), methylarsine (2.0 mmoles) and silane (1.1 mmoles).

Similar experiments using trimethylbromosilane in place of bromosilane gave a similar yield of bis(trimethylsilyl)methylarsine and methyl iodide gave 5.8 mmoles of dimethylarsine from 2.0 mmoles of the aluminate. 2.1 mmoles of a similar aluminate solution gave 1.8 mmoles of hydrogen and 6.5 mmoles of methylarsine on treatment with excess hydrogen sulphide for one hour.

Dimethylarsine (10.0 mmoles) and lithium tetrahydroaluminate (2.0 mmoles) were allowed to react under similar conditions to the methylarsine reaction evolving 5.9 mmoles of hydrogen. Reaction with bromosilane gave 5.7 mmoles of silyl(dimethyl)arsine. Similarly 2.0 mmoles of the aluminate gave 5.8 mmoles of trimethylsilyl(dimethyl)arsine with trimethylbromosilane, 1.9 mmoles of the aluminate gave
5.5 mmol of trimethylarsine with methyl iodide and 2.0 mmol of the aluminate gave 5.8 mmol of dimethylarsine and 1.1 mol of hydrogen with hydrogen sulphide.

**Ozonizer Discharge of Silane and Methylarsine**

Silane (10.0 mmol) and methylarsine (10.0 mmol) were circulated through the ozoniser at 0° for one hour. Non condensable gas was pumped off at -196° and the products passed through a -78° trap which retained disilyl(methyl)arsine and some silylarsine, identified by their n.m.r. spectra. The more volatile fraction contained silane, methylarsine, arsine and higher silanes.

**Disilylarsinoaluminate Reactions**

Typically, a lithium tetrahydroaluminate solution in ca. 4 ml of diglyme was added from a dropping funnel, chilled by a dry ice/acetone cold finger, to a solution of trisilylarsine in dimethyl ether at -78°. The mixture was then stirred for 30 minutes and allowed to warm slowly to room temperature and the silane, dimethyl ether and excess trisilylarsine pumped out and separated.

Lithium tetrahydroaluminate (2.1 mmol) consumed 16.5 mmol of trisilylarsine liberating ca 20 mmol of silane. The resultant solution was treated with excess hydrogen bromide for 2 hours at -45° yielding arsine (ca 16 mmol), bromosilane (ca 24 mmol) and ca 6 mmol of a 4:1 mixture of di and tribromosilane.

2.0 mmol of disilylarsinoaluminate treated with excess hydrogen sulphide for 1 hour gave 5.3 mmol of disilylarsine (whose $^1H$ nmr
spectrum showed the presence of ca. 6% disilylsulphide as an impurity) together with traces of mono- and tri-silylarsine. 2.1 mmoles of disilylsinoaluminate was treated with 8.2 mmoles of methyl iodide for 30 minutes at -45°. Separation of the products yielded 5.0 mmoles of disilyl(methyl)arsine and 0.3 mmoles of dimethyl(silyl)arsine. A similar experiment using trimethylbromosilane in place of methyl iodide gave a 54% yield of disilyl(trimethylsilyl)arsine.

Lithium Arsenide Reactions

Lithium arsenides were prepared immediately before use from the arsine and butyl-lithium.

Bromosilane (4.0 mmoles) was condensed into a solution of lithium dimethylarsenide (4.1 mmoles) in dimethyl ether and the mixture stirred at -78° for 45 minutes. Separation of the products gave 3.2 mmoles of silane and dimethylarsine.

Identical procedures using lithium diphenylarsenide and bromosilane or trimethylchlorosilane gave silyl(diphenyl)arsine (71%) and trimethylsilyl(diphenyl)arsine. Both reactions also gave small quantities of diphenylarsine and the appropriate silyl ether.

Similarly lithium phenylarsenide (4.0 mmoles) and bromosilane (4.0 mmoles) gave disilyl(phenyl)arsine (1.2 mmoles) and phenylarsine (1.8 mmoles) and lithium phenylarsenide (4.0 mmoles) and trimethylchlorosilane (4.0 mmoles) gave bis(trimethylsilyl)phenylarsine (1.4 mmoles) and phenylarsine (1.7 mmoles). In both reactions traces of silyl ethers were produced.
Lithium Silylarsenic Reactions

Methyl-lithium (4.0 mmol) in diethyl ether was dropped slowly into tris(trimethylsilyl)arsine (4.0 mmol) in 10 ml diethyl ether and the mixture stirred at room temperature for 4 hours. 4.0 mmol of methanethiol was condensed in and the mixture stirred for another 30 minutes. Fractionation yielded 1.9 mmol of bis(trimethylsilyl)arsine. Similarly lithium trimethylsilylmethylarsenide gave a 39% yield of trimethylsilylmethylarsine.

Treatment of lithium bis(trimethylsilyl)arsenide solutions with equimolar amounts of methyl iodide or bromosilane at -45°C for 30 minutes gave bis(trimethylsilylmethylarsine (60%), trimethylsilyl(dimethyl)arsine (50%), bis(trimethylsilyl)silylarsine, (Me$_3$Si)$_2$AsSiH$_3$, (47%) and trimethylsilyl(silyl)methylarsine, Me$_3$Si(SiH$_3$)AsMe, (55%) respectively.

Other reactions

No compounds containing silicon-arsenic bonds were isolated from the following mixtures after 10 hours at room temperature Me$_3$SiCl/AsH$_3$/Et$_3$N, Me$_3$SiCl/Me$_2$AsH/Et$_3$N, SiH$_3$Br/Me$_2$AsH/Et$_3$N and (Me$_3$Si)$_2$NH/AsH$_3$.

Characterisations

Known compounds were identified spectroscopically. (See chapter 1 for references). Disilylarsine was identified by its infrared and n.m.r. spectra. The infrared and n.m.r. spectra of the trimethylsilylmethylarsines and the new silicon arsines are given in tables 4.1-4.6. The new silicon arsines were characterised by molecular weight.
determinations, reaction with a hydrogen halide and alkaline hydrolysis. The silicon arsine was held at room temperature with a slight excess of hydrogen halide and the product silicon halide and arsine separated (table 4.7). The alkaline hydrolysis was performed by running dilute sodium hydroxide solution onto a measured amount of the silyl arsine and measuring the volume of hydrogen evolved. Only the Si-H containing arsines were hydrolysed.
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Me₃SiAsMe₂</th>
<th>(Me₃Si)₂AsMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>2989 sh</td>
<td>2986 sh</td>
<td>vas CH(As)</td>
</tr>
<tr>
<td>2966 s</td>
<td>2970 s</td>
<td>va CH(Si)</td>
</tr>
<tr>
<td>2923 s</td>
<td>2933 m</td>
<td>vs CH(As)</td>
</tr>
<tr>
<td>2910 sh</td>
<td>2910 m</td>
<td>vs CH(Si)</td>
</tr>
<tr>
<td>1430 w</td>
<td>1425 w</td>
<td>8as CH₃(As)</td>
</tr>
<tr>
<td>1405 w</td>
<td>1400 w</td>
<td>8as CH₃(Si)</td>
</tr>
<tr>
<td>1269 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1250 s</td>
<td>1244 s</td>
<td>8s CH₃</td>
</tr>
<tr>
<td>890 m</td>
<td></td>
<td>8CH₃(As)</td>
</tr>
<tr>
<td>860 s</td>
<td>830 s</td>
<td>8CH₃(Si)</td>
</tr>
<tr>
<td>825 s</td>
<td>820 s</td>
<td>8CH₃(As)</td>
</tr>
<tr>
<td>745 m</td>
<td>745 m</td>
<td>8CH₃(Si)</td>
</tr>
<tr>
<td>692 m</td>
<td>682 m</td>
<td>vas SiC</td>
</tr>
<tr>
<td>620 m</td>
<td></td>
<td>vs SiC</td>
</tr>
<tr>
<td>572 m</td>
<td>619 m</td>
<td></td>
</tr>
<tr>
<td>560 w</td>
<td>566 m</td>
<td></td>
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<tr>
<td>356*</td>
<td>352*</td>
<td>8SiAs</td>
</tr>
</tbody>
</table>

* From raman spectra. Both bands were polarised and the band at 352 cm⁻¹ in (Me₃Si)₂AsMe contains both vs SiAs and vas SiAs.
<table>
<thead>
<tr>
<th>$\text{SiH}_3\text{AsMe}_2$</th>
<th>$(\text{SiH}_3)_2\text{AsMe}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2986 m</td>
<td>2989 m</td>
<td>$\nu$ $\text{CH}$</td>
</tr>
<tr>
<td>2933 m</td>
<td>2930 m</td>
<td>$\nu$ $\text{CH}$</td>
</tr>
<tr>
<td>2168 s</td>
<td>2165 s</td>
<td>$\nu$ $\text{SiH}$</td>
</tr>
<tr>
<td>1433 m</td>
<td>1432 w</td>
<td>$\delta$ $\text{CH}_3$</td>
</tr>
<tr>
<td>1262 m</td>
<td>1255 m</td>
<td>$\delta$ $\text{CH}_3$</td>
</tr>
<tr>
<td>936 s</td>
<td>930 s</td>
<td>$\delta$ $\text{SiH}_3$ and $\rho$ $\text{CH}_3$</td>
</tr>
<tr>
<td>880 s</td>
<td>880 s</td>
<td>$\delta$ $\text{SiH}_3$ and $\rho$ $\text{CH}_3$</td>
</tr>
<tr>
<td>873 sh</td>
<td>847 sh</td>
<td>$\rho$ $\text{SiH}_3$</td>
</tr>
<tr>
<td>850 m</td>
<td></td>
<td>$\nu$ $\text{AsC}$</td>
</tr>
</tbody>
</table>
**TABLE 4.3**

Infrared Spectrum of Trimethylsilyl(methyl)arsine

<table>
<thead>
<tr>
<th>Me₃SiAsHMe</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2980 sh</td>
<td>uas CH (As)</td>
</tr>
<tr>
<td>2970 s</td>
<td>uas CH (Si)</td>
</tr>
<tr>
<td>2939 m</td>
<td>us CH (As)</td>
</tr>
<tr>
<td>2907 m</td>
<td>us CH (Si)</td>
</tr>
<tr>
<td>2080 s</td>
<td>u AsH</td>
</tr>
<tr>
<td>1405 w</td>
<td>sas CH₃</td>
</tr>
<tr>
<td>1245 s</td>
<td>s s CH₃</td>
</tr>
<tr>
<td>925 m</td>
<td>AsH bond</td>
</tr>
<tr>
<td>898 m</td>
<td></td>
</tr>
<tr>
<td>878 sh</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td>839 s</td>
<td></td>
</tr>
<tr>
<td>748 m</td>
<td></td>
</tr>
<tr>
<td>690 m</td>
<td>uas SiC</td>
</tr>
<tr>
<td>620 m</td>
<td>vs SiC</td>
</tr>
<tr>
<td>559 m</td>
<td>uAsC</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>(Me₃Si)₂AsSiH₃</th>
<th>Me₃SiAs(SiH₃)₂</th>
<th>Me₃SiAs(Me)SiH₃</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2960 s</td>
<td>2964 s</td>
<td>2970 s</td>
<td>2940 m</td>
<td>vₛ CH (As)</td>
</tr>
<tr>
<td>2898 m</td>
<td>2905 m</td>
<td>2902 m</td>
<td>vₛ CH (Si)</td>
<td></td>
</tr>
<tr>
<td>2155 s</td>
<td>2165 s</td>
<td>2163 s</td>
<td>v SiH</td>
<td></td>
</tr>
<tr>
<td>2070 w</td>
<td></td>
<td></td>
<td>AsH imp.</td>
<td></td>
</tr>
<tr>
<td>1406 w</td>
<td>1400 w</td>
<td>1401 w</td>
<td>S₃s CH₃</td>
<td></td>
</tr>
<tr>
<td>1258 m</td>
<td>1254 w</td>
<td>1249 m</td>
<td>Sₛ CH₃</td>
<td></td>
</tr>
<tr>
<td>1070 w</td>
<td>1060-1100 w</td>
<td>1180 w</td>
<td>SiO imp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>932 s</td>
</tr>
<tr>
<td>926 s</td>
<td>935 s</td>
<td>890 s</td>
<td>S SiH₃</td>
<td></td>
</tr>
<tr>
<td>870 s</td>
<td>876 s</td>
<td>873 s</td>
<td>and</td>
<td></td>
</tr>
<tr>
<td>840 s</td>
<td>846 s</td>
<td>863 sh</td>
<td>ρ CH₃</td>
<td></td>
</tr>
<tr>
<td>750 m</td>
<td>749 m</td>
<td>755 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>689 s</td>
<td>688 s</td>
<td>690 s</td>
<td>vₘ s SiC</td>
<td></td>
</tr>
<tr>
<td>619 m</td>
<td>623 m</td>
<td>620 m</td>
<td>υₘ s SiC</td>
<td></td>
</tr>
<tr>
<td>579 m</td>
<td>585 m</td>
<td>581 m</td>
<td>ρ SiH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>560 m</td>
<td>v AsC</td>
</tr>
<tr>
<td>540 m</td>
<td>545 m</td>
<td>540 m</td>
<td>ρ SiH₃</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 4.5
Infrared Spectra of the Silicon(phenyl)arsines

<table>
<thead>
<tr>
<th></th>
<th>$\text{SiH}_3\text{AsPh}_2$</th>
<th>(SiH$_3$)$_2\text{AsPh}$</th>
<th>$\text{Me}_3\text{SiAsPh}_2$</th>
<th>(Me$_3$Si)$_2\text{AsPh}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3067</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3052</td>
<td>m</td>
<td>3066 s</td>
<td>3060 m</td>
<td>3060 s</td>
<td>vCH(Ph)</td>
</tr>
<tr>
<td>3026</td>
<td>sh</td>
<td>3055 m</td>
<td>3052 m</td>
<td>3049 s</td>
<td></td>
</tr>
<tr>
<td>3011</td>
<td>w</td>
<td>3010 w</td>
<td>3009 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2972 m</td>
<td>2978 s</td>
<td></td>
<td>vas CH$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2901 m</td>
<td>2906 m</td>
<td></td>
<td>vs CH$_3$</td>
</tr>
<tr>
<td>2156</td>
<td>s</td>
<td>2163 s</td>
<td></td>
<td></td>
<td>v SiH</td>
</tr>
<tr>
<td>1579</td>
<td>s</td>
<td>1584 s</td>
<td>1581 s</td>
<td>1580 s</td>
<td>vCC</td>
</tr>
<tr>
<td>1480</td>
<td>s</td>
<td>1478 s</td>
<td>1482 s</td>
<td>1480 s</td>
<td></td>
</tr>
<tr>
<td>1431</td>
<td>s</td>
<td>1435 s</td>
<td>1435 m</td>
<td>1430 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1408 w</td>
<td>1410 m</td>
<td></td>
<td>$\delta$as CH$_3$</td>
</tr>
<tr>
<td>1380</td>
<td>m</td>
<td>1374 w</td>
<td>1381 w</td>
<td>1379 w</td>
<td>v CC</td>
</tr>
<tr>
<td>1332</td>
<td>w</td>
<td>1330 w</td>
<td>1332 w</td>
<td>1327 w</td>
<td></td>
</tr>
<tr>
<td>1305</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\beta$CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1180</td>
<td>m</td>
<td>1183 m</td>
<td>1181 m</td>
<td>1181 w</td>
<td>$\delta$s CH$_3$</td>
</tr>
<tr>
<td>1159</td>
<td>w</td>
<td>1162 w</td>
<td>1159 w</td>
<td></td>
<td>$\beta$CH</td>
</tr>
<tr>
<td>1098</td>
<td>sh</td>
<td>1105 m</td>
<td></td>
<td></td>
<td>SiO imp.</td>
</tr>
<tr>
<td>1079</td>
<td>s</td>
<td>1067 s</td>
<td>1071 s</td>
<td>1076 m</td>
<td>$\beta$CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1060 sh</td>
<td>SiO imp.</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>SiH$_3$AsPh$_2$</th>
<th>(SiH$_3$)$_2$AsPh</th>
<th>Me$_3$SiAsPh$_2$</th>
<th>(Me$_3$Si)$_2$AsPh</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020 s</td>
<td>1020 m</td>
<td>1019 s</td>
<td>1021 m</td>
<td></td>
<td>β CH</td>
</tr>
<tr>
<td>995 s</td>
<td>998 s</td>
<td>1000 m</td>
<td>992 m</td>
<td></td>
<td>α CCC</td>
</tr>
<tr>
<td>982 w</td>
<td>967 w</td>
<td>964 w</td>
<td>968 m</td>
<td></td>
<td>γ CH</td>
</tr>
<tr>
<td>926 s</td>
<td>930 s</td>
<td>888 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>874 s</td>
<td>878 s</td>
<td>845 s</td>
<td>840 s</td>
<td></td>
<td>δ SiH$_3$, ρ CH$_3$ and γ$^2$CH</td>
</tr>
<tr>
<td>878 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>789 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>739 s</td>
<td>736 s</td>
<td>732 s</td>
<td>733 s</td>
<td></td>
<td>γ CH</td>
</tr>
<tr>
<td>696 s</td>
<td>696 s</td>
<td>696 s</td>
<td>699 s</td>
<td></td>
<td>υas SiC$_3$ and γCH</td>
</tr>
<tr>
<td>660 w</td>
<td>665 w</td>
<td>661 w</td>
<td>623</td>
<td>619</td>
<td>γ CH</td>
</tr>
<tr>
<td>540 w</td>
<td>538 m</td>
<td></td>
<td></td>
<td></td>
<td>ρ SiH$_3$</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{SiH}$</th>
<th>$\delta_{SiCH}$</th>
<th>$\delta_{AsCH}$</th>
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</thead>
<tbody>
<tr>
<td>$SiH_3AsMe_2$</td>
<td>3.75</td>
<td>---</td>
<td>0.94</td>
</tr>
<tr>
<td>$(SiH_3)_2AsMe$</td>
<td>3.80</td>
<td>---</td>
<td>0.89</td>
</tr>
<tr>
<td>$SiH_3AsPh_2$</td>
<td>4.21</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$(SiH_3)_2AsPh$</td>
<td>4.15</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$Me_3SiAs(SiH_3)_2$</td>
<td>3.79</td>
<td>0.32</td>
<td>---</td>
</tr>
<tr>
<td>$(Me_3Si)_2AsSiH_3$</td>
<td>3.69</td>
<td>0.30</td>
<td>---</td>
</tr>
<tr>
<td>$Me_3SiAs(Me)SiH_3$</td>
<td>3.70</td>
<td>0.30</td>
<td>0.92</td>
</tr>
<tr>
<td>$Me_3SiAsPh_2$</td>
<td>---</td>
<td>0.24</td>
<td>---</td>
</tr>
<tr>
<td>$(Me_3Si)AsPh$</td>
<td>---</td>
<td>0.29</td>
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</tbody>
</table>
### TABLE 4.7

Molecular Weights, Cleavage and Hydrolysis Reactions of the Silicon Arsines

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mmoles</td>
<td>Mmoles</td>
<td>Mmoles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Me₃SiX</td>
<td>SiH₃X</td>
</tr>
</tbody>
</table>

|                  |                |                |        |        |        |        |        |        |        |
| SiH₃AsMe₂        | 135            | 136            | 0.5    | ---    | 0.5    | 0.5    | 0.8    | 2.4    |
| (SiH₃)₂AsMe     | 155            | 152            | 0.5    | ---    | 1.0    | 0.5    | 0.9    | 5.3    |
| SiH₃AsPh₂       | 242            | 250            | 0.5    | ---    | 0.5    | 0.4    | 1.0    | 2.9    |
| (SiH₃)₂AsPh     | 202            | 214            | 0.5    | ---    | 0.9    | 0.4    | 1.0    | 5.7    |
| Me₃SiAs(SiH₃)₂  | 216            | 210            | 0.7    | 0.7    | 1.3    | 0.7    | 1.0    | 5.6    |
| (Me₃Si)₂AsSiH₃  | 241            | 252            | 0.7    | 1.4    | 0.7    | 0.7    | 1.0    | 2.9    |
| Me₃SiAs(Me)SiH₃ | 192            | 194            | 0.2    | 0.2    | 0.2    | 0.2    | 0.2    | 0.6    |
| Me₃SiAsPh₂      | 289            | 292            | 1.0    | 1.0    | ---    | 1.0    | ---    | ---    |
| (Me₃Si)₂AsPh    | 305            | 298            | 1.0    | 1.9    | ---    | 1.9    | ---    | ---    |
Discussion

Both methyl- and dimethyl-arsine reacted with lithium tetrahydroaluminate (1,2) in a similar manner to arsine

\[
\begin{align*}
\text{nMeAsH}_2 + \text{LiAlH}_4 & \rightarrow \text{LiAl(AsHMe)}_{n-2-n} + \text{nH}_2 \quad \cdots \cdots \cdots \cdots \cdots (1) \\
n\text{Me}_2^2\text{AsH} + \text{LiAlH}_4 & \rightarrow \text{LiAl(AsMe}_2_{n-2-n} + \text{nH}_2 \quad \cdots \cdots \cdots \cdots \cdots (2)
\end{align*}
\]

The amount of hydrogen evolved suggested that the stoichiometry was best represented by \( n = 3 \). For the corresponding reaction with dimethylphosphine \( n \) was 2. This probably results from the lower acidity of dimethylphosphine rather than any steric factor because tris-di-organo-phosphino- and -arsino-aluminates have been prepared by the lithium tetrahydroaluminate cleavage of P-P and As-As bonds. Further indications of the formation of \( \text{LiAl(AsHMe)}_3 \) and \( \text{LiAl(AsMe}_2)_3 \) came from the amounts of methyl- and dimethyl-arsine respectively recovered when the methyl- and dimethyl-arsinoaluminates were treated with the weakly acidic anhydrous hydrogen sulphide and also by the amounts of dimethyl- and trimethyl-arsine liberated on treatment with methyliodide.

Bromosilane and bromo(trimethyl)silane reacted with the dimethylarsinoaluminate to give dimethyl(silyl)arsine and dimethyl(trimethyl-silyl)arsine respectively (3).

\[
\begin{align*}
\text{LiAl(AsMe}_2)_3 + 4\text{R}_3\text{SiBr} & \rightarrow 3\text{R}_3\text{SiAsMe}_2 + \text{R}_3\text{SiH} + \text{LiBr} + \text{AlBr}_3 \\
\end{align*}
\]
(R = H, Me)

Under similar circumstances, the methylarsinoaluminate did not give methyl(silyl)arsine and methyl(trimethylsilyl)arsine but gave disilyl-(methyl)arsine, (SiH₃)₂AsMe, and bis-trimethylsilyl(methyl)arsine, (Me₃Si)₂AsMe. In these reactions, considerable amounts of methyl-arsine were also formed suggesting that the arsines containing an As-H bond were probably formed but immediately underwent disproportionation (4).

\[
\text{LiAl(AsHMe)}_3H + 4R_3SiBr = 3R_3SiAsHMe + R_3SiH + LiBr + AlBr₃
\]

\[
2R_3SiAsHMe = (R_3Si)₂AsMe + MeAsH₂ \ldots \ldots (4)
\]

The ease with which methyl(trimethylsilyl)arsine disproportionates has been noted by other workers and the reaction of bromosilane with methylaminoaluminate gave methyl(disilyl)- rather than methyl(silyl)-amine.

For many years the effect of an electric discharge on a gaseous mixture of silane and arsine was the only method of preparing silyl-arsine, SiH₃AsH₂, and primary arsine derivatives of methylsilanes have been synthesised in a similar manner. In neither case was there significant indication of the products undergoing disproportionation. Thus, in an attempt to isolate methyl(silyl)arsine, a mixture of silane and methylarsine was subjected to a silent electric discharge but the only identifiable silicon arsines were disilyl(methyl)arsine and silyl-arsine. Thus it appears that methyl(silyl)arsine may be intrinsically
unstable or its disproportionation is autocatalytic.

Silylarsine did not react with lithium tetrahydroaluminate in an analogous manner to methylarsine, but, as has been found with silylphosphine, there was cleavage of the silicon-group V element bond to give silane as the main volatile product (See chapter 3). Advantage was taken of this mode of reaction, in that a disilylarsinoaluminate was produced by the slow addition of lithium tetrahydroaluminate to a large excess of trisilylarsine (5).

\[ \text{LiAlH}_4 + n(SiH_3)_2As \rightarrow \text{LiAl}[As(SiH_3)_2]_{n-1}H_4 + n\text{SiH}_4 \quad (5) \]

The value of n was not easily ascertained as large amounts of silane were simultaneously produced by the condensation of trisilylarsine (6).

\[ m(SiH_3)_2As = m\text{SiH}_4 + (Si_2AsH_5)_m \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6) \]

The addition of anhydrous hydrogen bromide to the reaction mixture resulted in the cleavage of the Si-As and Al-As bonds in the disilylarsinoaluminate and the Si-As bonds in the polymeric (Si_2AsH_5)_m. The liberation of tribromosilane may be indicative of cross-linking in the polymer or may result from an aluminium halide catalysed redistribution of mono- and di-bromosilanes.

Despite the doubt of the exact stoichiometry of the disilylarsinoaluminate, it was utilised in the preparation of several disilylarsines. Treatment with hydrogen sulphide gave disilylarsine, (SiH_3)_2AsH.
Not surprisingly, since most readily available protic reagents cleave the Si-As bond, some such cleavage took place yielding disilyl-sulphide. Treatment of the disilylarsinoaluminate with methyl iodide gave disilyl(methyl)arsine and with bromo(trimethyl)silane gave disilyl(trimethylsilyl)arsine as expected (7).

\[
\text{LiAl}[\text{As(SiH}_3\text{)}_2]_n\text{H}_{4-n} + RX = n(\text{SiH}_3)\text{AsR} + (4-n)\text{RH} + \text{LiX} + \text{AlX}_3
\]

\[
\ldots\ldots (7)
\]

\[(R = \text{Me or Me}_3\text{Si}; X = \text{I or Br})\]

The formation of some silyl(dimethyl)arsine indicates that the \((\text{SiH}_3)_3\text{As/LiAlH}_4\) reaction is not specific and that some \((\equiv\text{Al})_2\text{AsSiH}_3\) species are present as well as \(\equiv\text{Al}\text{As(SiH}_3\text{)}_2\). Treatment of the disilyl-arsinoaluminate with bromo-germane did not yield disilyl(germyl)arsine as might be expected. Instead, the main product was trisilylarsine and the only identifiable germanium-containing product was trigermylarsine. Thus the instability to disproportionation already observed for the germyl(silyl)phosphines apparently extends to the arsines. This contrasts with the group VI derivatives of which germyl(silyl)-sulphide and -selenide and their methylated analogues have been prepared.

The reaction of lithium phenylarsenide with bromosilane and trimethylchlorosilane does not give any of the secondary arsines according to (8). The products were moderate yields of disilyl(phenyl)arsine...
\[ R_3SiX + LiAsHPh \rightarrow R_3SiAsHPh + LiX \] ........................ (8)

\[ R = H, Me; X = Br, Cl \]

and bis(trimethylsilyl)phenylarsine respectively. These may be formed either by the disproportionation of the \( R_3SiAsHPh \) species as was found for \( Me_3SiAsHMe \)\(^{100} \) (9) or by reaction of the secondary arsine with the

\[ 2R_3SiAsHPh \rightarrow (R_3Si)_2AsPh + PhAsH_2 \] ........................ (9)

arsenide anion as was found in the \( SiH_3Br/KAsH_2 \) reaction (10).

\[ R_3SiAsHPh + LiAsHPh \rightarrow LiAsPhSiR_3 + PhAsH_2 \] ........................ (10)

\[ LiAsPhSiR_3 + R_3SiX \rightarrow (R_3Si)_2AsPh + LiX \]

Although alkali metal arsenides have not been useful for the preparation of As-H containing silylarsines, dimethyl(trimethylsilyl)arsine was obtained in excellent yields from the reaction of trimethylchlorosilane with lithium dimethylarsenide.\(^{99} \) Similar reactions gave good yields of silyl \( (SiH_3) \) arsines as well as trimethylsilylarsines (11).

\[ R_3SiCl + LiAsR' \rightarrow R_3SiAsR' + LiCl \] ........................ (11)

\[ (R = H, Me; R' = Me, Ph) \]
Lithium silylarsenides were prepared by making use of the ability of methyl or butyl lithium to cleave the Si-As bond (12).

\[
\begin{align*}
\text{Me}_3\text{Si})_3\text{As} + \text{RLi} & = \text{Me}_3\text{SiR} + \text{LiAs(SiMe}_3)\_2 \\
\text{(12)} \\
\text{(Me}_3\text{Si})_2\text{AsMe} + \text{RLi} & = \text{Me}_3\text{SiR} + \text{LiAs(Me)SiMe}_3 \\
\end{align*}
\]

On acidification the secondary arsines \(\text{(Me}_3\text{Si})_2\text{AsH}\) and \(\text{Me}_3\text{SiAsHMe}\) respectively were formed. The reactions of methyl and silyl halides with \(\text{LiAs(SiMe}_3)\_2\) gave \((\text{Me}_3\text{Si})_2\text{AsMe}\) and \((\text{Me}_3\text{Si})_2\text{As(SiH}_3)\) respectively while with \(\text{LiAs(Me)(SiMe}_3)\) they gave \(\text{Me}_3\text{SiAsMe}_2\) and \(\text{Me}_3\text{SiAs(SiH}_3)\text{Me}\) respectively.

The vibrational spectra of trimethylsilyl(di)ethylarsine, \(\text{Me}_3\text{SiAsMe}_2\), and of bis-trimethylsilyl(methyl)arsine, \((\text{Me}_3\text{Si})_2\text{AsMe}\), are presented in table 41 together with assignments made on the basis of band intensities, Raman polarisation data, and comparisons with the spectra of mono-, bis-, and tris-trimethylsilylarsine, \(88\) methylarsine, \(52\) and dimethylarsine. The infrared spectra of the corresponding silyl-(di)ethylarsine \(\text{SiH}_3\text{AsMe}_2\) and disilyl(methyl)arsine, \((\text{SiH}_3)_2\text{AsMe}\), are presented in table 42 with assignments made by comparison with the methyl- and silyl-arsines. \(65, 86\) It is of interest that the Si-As and As-C stretching modes of all four silylarsines all can be assigned close to 350 and 560 cm\(^{-1}\) respectively as they can in the silyl-, trimethyl- silyl-, and methyl-arsines. This suggests that all are probably pyramidal molecules with bond angles similar to those already found in.
trisilyl-, trimethylsilyl-, and trimethyl-,\textsuperscript{113} arsines with little likelihood of the planarity once suggested for silylarsines.\textsuperscript{65}

On a similar basis, the infrared spectra of trimethylsilyl(methyl)-arsine, $\text{Me}_3\text{SiAsHMe}$ (Table 43); silyl(trimethylsilyl)methylarsine, $\text{Me}_3\text{SiAs}\text{Me}$, disilyl(trimethylsilyl)arsine, $\text{Me}_3\text{SiAs} \text{(SiH}_3\text{)}_2$, and bis(trimethylsilyl)silylarsine, $(\text{Me}_3\text{Si})_2\text{As} \text{(SiH}_3\text{)}$ (Table 4.4); and silyl-(diphenyl)arsine, $(\text{SiH}_3\text{)}\text{AsPh}_2$, disilyl(phenyl)arsine, $(\text{SiH}_3\text{)}_2\text{AsPh}$, trimethylsilyl(diphenyl)arsine, $\text{Me}_3\text{SiAsPh}_2$, and bis(trimethylsilyl)-phenylarsine, $(\text{Me}_3\text{Si})_2\text{AsPh}$ (Table 4.5 are assigned with varying degrees of certainty.

All the silicon arsines showed the expected parent peaks in their mass spectra. The data on splitting patterns was unreliable because extensive hydrolysis occurred even when the spectrometer was pre-dried by the initial passage of monochlorosilane. However, in several runs there was some evidence of the formation of disilanes suggesting that the loss of the central arsenic atom may be a significant pathway as was found in the corresponding decomposition of the phosphines.\textsuperscript{91}
CHAPTER 5

The Preparation of Tertiary and Secondary Germanium Arsines

Germanium arsines have received relatively little attention in comparison to their silicon and tin analogues. During the course of this work the only synthetic studies reported were the preparation of trimethylgermyl(dimethyl)arsine from lithium dimethylarsénide and trimethylchlorogermaine, the preparation of germylarsine, its specifically deuterated analogues and trigemylarsine by reaction of a silyl arsine with a halogermaine and the preparation of digemylarsine by the water catalysed disproportionation of germylarsine. This chapter describes the preparation of a number of tertiary and secondary germanium arsines by various methods and the thermal decomposition of some Ge-H and As-H containing germanium arsines.
EXPERIMENTAL

The Reactions of Bromogermandes with Lithium Methylarsinoaluminates

Dimethylarsine (ca. 15 mmoles) in diethyl ether was run into a diglyme solution of lithium tetrahydroaluminate (2.1 mmoles) at room temperature. The solution effervesced and started to turn green in colour. The mixture was stirred and after 1 hr had acquired a brown colour. After 30 hr., hydrogen (6.1 mmoles), diethylether and unreacted dimethylarsine were pumped out and bromogermane (8.0 mmoles) condensed in. The mixture was held at -45° for 30 min. and the products separated giving germyl(dimethyl)arsine (4.9 mmoles).

Trimethylgermyl(dimethyl)arsine was prepared in similar yield by the same procedure using trimethylbromogermane.

A solution of lithium methylarsinoaluminate (2.0 mmoles) in diglyme was prepared as described above (also see chapter 4). 8.0 mmoles of trimethylbromogermane was condensed in and the mixture held at -45° for 30 minutes. Fractionation of the products gave 1.8 mmoles of trimethylgermane, 1.9 mmoles of methylarsine, 2.1 mmoles of trimethylgermyl(methyl)arsine and 1.8 mmoles of bis(trimethylgermyl)methylarsine.

The Reaction of Arsines on N-trimethylgermyldimethylarsine

Phenylarsine (2.5 mmoles) in diethyl ether (ca 5 ml) was slowly added to a stirred ether (ca 5 ml) solution of N-trimethylgermyldimethylamine (5.0 mmoles) at room temperature evolving dimethylamine. The mixture was stirred for 30 min. and separated to give bis-trimethylgermyl(phenyl)arsine (1.7 mmoles).
Methylarsine (2.5 mmoles) was condensed onto an ether (ca 5 ml) solution of N-trimethylgermyldimethylamine (5.0 mmoles) at -78°. The mixture was warmed to room temperature and recooled repeatedly until an infrared spectrum of the volatiles no longer contained a band attributable to an As-H stretch. Fractionation yielded bis(trimethylgermyl)methylarsine (2.1 mmoles).

Similarly dimethylarsine (2.5 mmoles) and N-trimethylgermyldimethylamine (2.5 mmoles) gave trimethylgermyl(dimethyl)arsine (2.2 mmoles).

N-trimethylgermyldimethylamine (5.0 mmoles) was condensed into arsine (20 mmoles) and held at -96° for 15 min. Separation of the products yielded tris(trimethylgermyl)arsine (1.5 mmoles) and arsine (18.3 mmoles).

**The Reactions of Bromogermanes with Lithium Arsenides**

Bromogermane (4.0 mmoles) was condensed into lithium dimethylarsenide (4.0 mmoles) in dimethyl ether at -78° and the mixture stirred for 45 min. Fractionation yielded germyl(dimethyl)arsine (3.1 mmoles). With lithium diphenylarsenide, the yield of germyl(diphenyl)arsine was 69%. From the corresponding reactions with trimethylbromogermane, the yields of trimethylgermyl(dimethyl)arsine and trimethylgermyl(diphenyl)arsine were 84 and 72% respectively.

Trimethylbromogermane (4.0 mmoles) and lithium methylarsenide (4.1 mmoles) gave trimethylgermyl(methyl)arsine (0.9 mmoles), bis(trimethylgermyl)methylarsine (1.3 mmoles) and methylarsine (1.5 mmoles) under similar conditions. Similarly trimethylbromogermane (1.9 mmoles)
and lithium phenylarsenide (2.0 mmoles) gave trimethylgermyl(phenyl)-
arsine (0.3 mmoles), bis(trimethylgermyl)phenylarsine (0.7 mmoles) and
phenylarsine (0.7 mmoles).

The Reactions of Trimethylhalogermanes with Methylarsine and Arsine

Trimethylbromogermane (2.0 mmoles), methylarsine (1.0 mmoles) and triethylamine (2.0 mmoles) were condensed into a finger (10 ml capacity) and allowed to warm to room temperature. A white precipitate formed and after 15 min. the infrared spectrum of the volatiles from the reaction mixture were recorded showing the presence of considerable amounts of unreacted starting materials. The mixture was returned to the reaction vessel and the infrared spectrum taken periodically. After 30 hrs. no further reaction appeared to be taking place and bis(trimethylgermyl)methylarsine (0.4 mmole) was separated from unreacted starting materials. In another experiment a mixture of trimethylchlorogermane (3.0 mmoles) and arsine (5.0 mmoles) were allowed to warm slowly to room temperature. At just below 0° a white precipitate appeared. The products were separated giving tris(trimethylgermyl)arsine (0.5 mmole). The experiment was repeated using benzene, hexane and diethyl ether as solvents but there was no increase in yield.

Exchange Reactions

Typically, silyl(dimethyl)arsine (5.0 mmoles) and chlorogermane (5.0 mmoles) were held together at room temperature. After 1 hr. the reaction vessel was surrounded by a -96° slush bath and chlorosilane (5.0 mmoles) distilled out leaving a pure sample of germyl(dimethyl)arsine (5.0 mmoles).
Germyl(diphenyl)arsine, trimethylgermyl(dimethyl)arsine, trimethylgermyl(diphenyl)arsine, digermyl(methyl)arsine, digermyl(phenyl)arsine, bis(trimethylgermyl)methylarsine, bis(trimethylgermyl)phenylarsine, trigermylarsine, and tris(trimethylgermyl)arsine were all prepared in 95% yield, based on halogermane consumption, in similar exchange reactions using the appropriate chlorogermane and silicon arsenic.

In similar preparations of bis(arsino)dimethylgermane, bis(dimethylarsino)dimethylgermane and tris(dimethylarsino)methylgermane, the halosilane was removed every 20 min. and replaced with more of the silicon arsenic. Yields were 75, 86 and 84% respectively.

A series of reactions of silyl(dimethyl)arsine with fluoro-, chloro-, bromo-, and iodo-(trimethyl)germane were examined. Reaction was complete with the fluoride after 15 min. and with the chloride after 50 min. The bromide took 3 hr and left traces of the silylarsine while even after 2 days the iodide reaction had proceeded less than 5%.

Silylarsine (4.0 mmoles) and methyltrichlorogermane (1.0 mmoles) were held at room temperature for 15 min. A yellowish-brown solid appeared on the walls of the reaction vessel and the products were separated giving arsine (1.1 mmoles), silylarsine (0.5 mmoles), disilylarsine (0.2 mmoles), trisilylarsine (0.4 mmoles) and traces of silane. The solid was insoluble in diethylether, monoglyme, benzene, methylene dichloride, carbon tetrachloride and hexane. The reaction was repeated at -63° and gave a similar mixture of products but the rate of decomposition of silylarsine was slower. The reaction with
dichlorogermane gave a similar mixture of products and was not investigated further.

Disilylarsine (1.0 mmole) and trimethylchlorogermane (2.0 mmole) were held at -45° for 70 min. and the products separated to give tris(trimethylgermyl)arsine (0.6 mmole), arsine (0.3 mmole), chlorosilane (2.0 mmoles) and a trace of trimethylchlorogermane.

The Reaction and Reaction of Lithium Trimethylgermylarsenides

Methyl-lithium (4.0 mmoles) in diethyl ether was dropped slowly into tris(trimethylgermyl)arsine (4.0 mmoles) in diethyl ether (10 ml) and the mixture stirred at room temperature for 5 hr. Excess hydrogen sulphide was condensed in and the mixture stirred at -63° for 1 hr. Fractionation yielded bis(trimethylgermyl)arsine (2.1 mmoles) and tetramethylgermane (ca 3.7 mmoles). Similar procedures using bis(trimethylgermyl)methylarsine and bis(trimethylgermyl)phenylarsine gave trimethylgermyl(methyl)arsine (45%) and trimethylgermyl(phenyl)arsine (39%) respectively. Treatment of the bis(trimethylgermyl)arsenide solution with methyl iodide gave a 65% yield of bis(trimethylgermyl)methylarsine.

The Reaction of Germylarsine with Lithium Tetrahydroaluminate

Germylarsine (4.5 mmoles) was condensed onto a diglyme solution of lithium tetrahydroaluminate (1.1 mmoles) and allowed to warm to room temperature. After the solvent melted the solution started to effervesce and acquired a green then brown colour. After 30 min. the solution was refrozen and hydrogen (0.5 mmole) pumped out. The mixture was warmed, and volatile products were removed and separated giving germane (3.2
mmoles), arsine (0.8 mmoles) and a trace of digermane. Methanethiol (4.5 mmoles) was added to the reaction vessel and the mixture held at -45° for 45 min. yielding germane (0.6 mmole) arsine (3.1 mmole) and digermane (0.1 mmole). A similar solution treated with methyl iodide gave methylarsine, methylgermane and digermane in the ratio 5:1:1.

The Pyrolysis of Germanium Arsines

Pyrolyses were carried out in sealed thick-walled glass tubes for 24 hr at 100°. The tube was then broken open on the vacuum line, volatile products distilled out and separated, and any involatile residues treated with hydrogen chloride for 2 hr.

Trimethylgermylarsine (2.0 mmoles) on pyrolysis for 24 hr at 100° gave arsine (0.7 mmole) and tris(trimethylgermyl)arsine (0.7 mmole) as volatile products with only a trace of a pink residue in the tube which gave no volatile products on treatment with hydrogen chloride.

Germyl(dimethyl)arsine (4.0 mmole) gave germane (1.5 mmoles) and unreacted germyl(dimethyl)arsine (0.6 mmole) as the volatile products. Treatment of the lilac coloured viscous-liquid residue with hydrogen chloride gave chlorogermaine (0.2 mmole), dichlorogermaine (0.9 mmole), trichlorogermaine (0.2 mmole) and dimethylarsine (2.5 mmoles) leaving an apparently unaffected purple solid.

Bis(arsino)dimethylgermane (3.0 mmoles) gave arsine (3.9 mmoles) as the only volatile product. The yellow solid residue on treatment with hydrogen chloride gave dimethyldichlorogermaine (2.8 mmoles). The solid was moderately soluble in benzene from which it was recrystallised. Molecular weight determinations varied between 670 and 810 on
different samples. The infrared spectrum in a KBr pellet showed broad medium intensity peaks at 2990, 1440, 1244, 850 and 620 cm$^{-1}$. The PMR spectra of different samples showed peaks at & 0.58, 0.62 and Q 64 with relative intensities which varies with the sample.

Characterisations

Known compounds were identified spectroscopically. New germanium arsines were characterised by molecular weight determinations, infrared and n.m.r. spectra as well as analysis by their cleavage reactions with hydrogen halides (HCl or HBr) at room temperature for 30 minutes. Tables 5.1 - 5.6 Mass spectra were not satisfactory owing to oxidation taking place in the spectrometer.
### Infrared Spectra of the Secondary Germanium Arsines

<table>
<thead>
<tr>
<th>(Me₃Ge)₂AsH</th>
<th>Me₃GeAsHMe</th>
<th>Me₃GeAsHPh</th>
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</tr>
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<td>2973 s</td>
<td>ν as CH(Ge)</td>
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<td>2912 s</td>
<td>2908 s</td>
<td>ν s CH(Ge)</td>
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<td>ν AsH</td>
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<td>1241 m</td>
<td>1238 m</td>
<td>δ s CH₃(Ge)</td>
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<td>947 m</td>
<td>958 m</td>
<td>942</td>
<td>AsH bend</td>
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<td>824 s</td>
<td>830 s</td>
<td>823 s</td>
<td>ρ CH₃(Ge)</td>
</tr>
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<td>752 m</td>
<td>749 m</td>
<td>759 m</td>
<td></td>
</tr>
<tr>
<td>597 s</td>
<td>595 s</td>
<td>595 s</td>
<td>ν as GeC</td>
</tr>
<tr>
<td>576 m</td>
<td>570 m</td>
<td>577 w</td>
<td>υ s GeC</td>
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In addition Me₃GeAsHMe showed the following bands: 1259 (m), δCH₃(As); 887 (s), ρCH₃(As); 570 (m) νAsC; and Me₃GeAsHPh showed the following bands 3062 (m), 3050 (m), 3025 (m), 3010 (m), νCH(Ph); 1577 (s), 1476 (s), 1437 (m), 1380 (w) νCC; 1184 (w), 1156 (w), 1070 (m), 1019 (s), 1437 (m), 1380 (w) 734(s), 727 (s), 697 (s), 656 (sh), γCH; 462 (s), α CCC.
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<th>(Me₃Ge)₂AsMe</th>
<th>Me₃GeAsMe₂</th>
<th>Me₂Ge(AsMe₂)₂</th>
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<td>2820 w</td>
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TABLE 5.4

The Infrared Spectra of the Germanium(phenyl)arsines

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<th>(GeH\textsubscript{3})\textsubscript{2}AsPh</th>
<th>Me\textsubscript{3}GeAsPh\textsubscript{2}</th>
<th>(Me\textsubscript{3}Ge)\textsubscript{2}AsPh</th>
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<td>v GeH</td>
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<td>1475 s</td>
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<td>1329</td>
<td>1337</td>
<td>1330</td>
<td></td>
<td></td>
<td>β CH</td>
</tr>
<tr>
<td>1265</td>
<td></td>
<td>1250 s</td>
<td>1245 s</td>
<td>δsCH\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>1182 w</td>
<td>1186 w</td>
<td>1180 w</td>
<td>1180 w</td>
<td></td>
<td>βCH</td>
</tr>
<tr>
<td>1158 w</td>
<td>1152 w</td>
<td>1157 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1070 m</td>
<td>1069 m</td>
<td>1068 m</td>
<td>1071 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1020 s</td>
<td>1019 s</td>
<td>1017 s</td>
<td>1020 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>998 m</td>
<td>1000 m</td>
<td>995 m</td>
<td>998 m</td>
<td>α CCC</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Frequency</th>
<th>Time</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>880 m</td>
<td>910 s</td>
<td>905 w</td>
<td>$\gamma$ CH</td>
</tr>
<tr>
<td>860 s</td>
<td>863 s</td>
<td></td>
<td>$\delta$ GeH$_3$</td>
</tr>
<tr>
<td>798 s</td>
<td>801 s</td>
<td></td>
<td>$\rho$ CH$_3$</td>
</tr>
<tr>
<td>735 s</td>
<td>738 s</td>
<td>730 s</td>
<td>$\gamma$ CH</td>
</tr>
<tr>
<td>696 s</td>
<td>697 s</td>
<td>691 s</td>
<td>$\nu$ as GeC</td>
</tr>
<tr>
<td>665 w</td>
<td>670 w</td>
<td>660 w</td>
<td>$\nu$ s GeC</td>
</tr>
<tr>
<td>491 w</td>
<td>480 w</td>
<td></td>
<td>$\rho$GeH$_3$</td>
</tr>
<tr>
<td>477 s</td>
<td>459 s</td>
<td>470 s</td>
<td>$\alpha$ CCC</td>
</tr>
</tbody>
</table>

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### TABLE 5.5

**N.m.r. Parameters of the Germanium Arsines**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{GeH}$</th>
<th>$\delta_{GeCH}$</th>
<th>$\delta_{AsCH}$</th>
<th>$\delta_{AsH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_3$AsMe$_2$</td>
<td>3.96</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>(GeH$_3$)$_2$AsMe</td>
<td>3.98</td>
<td>-</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>GeH$_3$AsPh$_2$</td>
<td>4.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(GeH$_3$)Ph</td>
<td>4.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Me$_3$GeAsMe$_2$</td>
<td></td>
<td>0.29</td>
<td>0.97</td>
<td>-</td>
</tr>
<tr>
<td>(Me$_3$Ge)$_2$AsMe</td>
<td>-</td>
<td>0.36</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>Me$_3$GeAsPh$_2$</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Me$_3$Ge)$_2$AsPh</td>
<td>-</td>
<td>0.44</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>Me$_2$Ge(AsMe$_2$)$_2$</td>
<td>-</td>
<td>0.44</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>MeGe(AsMe$_2$)$_3$</td>
<td>-</td>
<td>0.58</td>
<td>1.10</td>
<td>-</td>
</tr>
<tr>
<td>(Me$_3$Ge)$_2$AsH</td>
<td>-</td>
<td>0.40</td>
<td>-</td>
<td>0.42</td>
</tr>
<tr>
<td>Me$_3$GeAsHMe$^*$</td>
<td>-</td>
<td>0.38</td>
<td>1.03</td>
<td>1.25</td>
</tr>
<tr>
<td>Me$_3$GeAsHPh</td>
<td>-</td>
<td>0.39</td>
<td>-</td>
<td>1.08</td>
</tr>
<tr>
<td>Me$_2$Ge(AsH$_2$)$_2$</td>
<td>-</td>
<td>0.50</td>
<td>-</td>
<td>1.30</td>
</tr>
</tbody>
</table>

* $J_{HCASH} = 6.9$ Hz

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TABLE 5.6

Molecular Weights and Cleavage Reactions of the Germanium Arsines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol Wt.</th>
<th>Reaction with Hydrogen Halide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calc.</td>
</tr>
<tr>
<td>( \text{GeH}_3\text{AsMe}_2 )</td>
<td>171</td>
<td>180</td>
</tr>
<tr>
<td>( \text{GeH}_3\text{AsMe} )</td>
<td>228</td>
<td>241</td>
</tr>
<tr>
<td>( \text{GeH}_3\text{AsPh}_2 )</td>
<td>305</td>
<td>304</td>
</tr>
<tr>
<td>( \text{GeH}_3\text{AsC}_6\text{H}_5 )</td>
<td>299</td>
<td>303</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsMe}_2 )</td>
<td>230</td>
<td>223</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsMe} )</td>
<td>342</td>
<td>325</td>
</tr>
<tr>
<td>( \text{Me}_2\text{Ge(AsMe}_2 )</td>
<td>323</td>
<td>312</td>
</tr>
<tr>
<td>( \text{MeGe(AsMe}_2 )</td>
<td>402</td>
<td>402</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsPh}_2 )</td>
<td>330</td>
<td>346</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsPh} )</td>
<td>411</td>
<td>387</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsH} )</td>
<td>312</td>
<td>311</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsHMe} )</td>
<td>202</td>
<td>215</td>
</tr>
<tr>
<td>( \text{Me}_3\text{GeAsHPh} )</td>
<td>255</td>
<td>267</td>
</tr>
<tr>
<td>( \text{Me}_2\text{Ge(AsH}_2 )</td>
<td>260</td>
<td>256</td>
</tr>
</tbody>
</table>

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Discussion

Germyl(dimethyl)arsine, GeH₃AsMe₂, and trimethylgermyl(dimethyl)-arsine, Me₃GeAsMe₂, were prepared by the action of bromogermane or trimethylbromogermane with lithium dimethylarsinoaluminate \( (1) \).

\[
\text{LiAl(AsMe₂)₃H} + 4\text{R}_3\text{GeBr} = 3\text{R}_3\text{GeAsMe}_2 + \text{R}_3\text{GeBr} + \text{LiBr} + \text{AlBr}_3
\]  

The yields are comparable to those obtained for the corresponding silicon arsines. (Chapter 4).

The reaction of trimethylbromogermane with lithium methylarsinoaluminate gave a moderate yield of trimethylgermyl(methyl)arsine, Me₃GeAsHMe, \( (2) \) together with bis(trimethylgermyl)methylarsine, \( (\text{Me₃Ge})_2\text{AsMe} \).

\[
\text{LiAlH(AsHMe)₃} + 4\text{Me₃GeBr} \rightarrow 3\text{Me₃GeAsHMe} + \text{Me₃GeH} + \text{LiBr} + \text{AlBr}_3
\]  

A number of trimethylgermylarsine derivatives were prepared by the cleavage of the Ge-N bond in N-trimethylgermyldimethylamine by primary and secondary arsines \( (3) \). The reaction of a large excess of

\[
2\text{Me₃GeNMe}_2 + \text{RAsH}_2 = (\text{Me₃Ge})_2\text{AsR} + 2\text{Me₂NH}
\]  

\[
\text{Me₃GeNMe}_2 + \text{R₂AsH} = \text{Me₃GeAsR}_2 + \text{Me₂NH}
\]  

\((\text{R} = \text{Me, Ph})\)

AsH₃ with N-trimethylgermyldimethylamine failed to produce any primary...
or secondary germylarsines and even with liquid arsine as the solvent the only product was tris(trimethylgermyl)arsine.  

Germyl(dimethyl)-, trimethylgermyl(dimethyl)-, germyl(diphenyl)- and trimethylgermyl(diphenyl)-arsines were also prepared in good yields using lithium arsenides (4).

\[
\text{LiAsR}_2 + R'_3\text{GeBr} = R'_3\text{GeAsR}_2 + \text{LiBr} \quad \ldots \ldots \ldots \quad (4)
\]

\[ R = \text{Me, Ph, } R' = \text{Me, H} \]

The secondary arsines trimethylgermyl(methyl)arsine and trimethylgermyl(phenyl)arsine were prepared from the lithium arsenides in low yields (5). This method was even less effective than the methylarsino-

\[
\text{LiAsHR} + \text{Me}_3\text{GeBr} \rightarrow \text{Me}_3\text{GeAsHR} + \text{LiBr} \quad \ldots \ldots \ldots \quad (5)
\]

\[ R = \text{Me, Ph} \]

aluminate method and gave even more of the bis(trimethylgermyl)derivatives. As was the case for the silicon arsines there are probably two mechanisms operative (6) and (7).

\[
2\text{Me}_3\text{GeAsHR} \rightarrow (\text{Me}_3\text{Ge})_2\text{AsR} + \text{RAsH}_2 \quad \ldots \ldots \ldots \ldots \ldots \quad (6)
\]

\[
\text{Me}_3\text{GeAsHR} + \text{LiAsHR} \rightarrow \text{LiAsR}((\text{Me}_3\text{Ge}) + \text{RAsH}_2 \quad \ldots \ldots \ldots \ldots \ldots \quad (7)
\]
\[ \text{LiAsR(GeMe}_3\text{)} + \text{Me}_3\text{GeBr} \rightarrow \text{(Me}_3\text{Ge)}_2\text{AsR} + \text{LiBr} \]

Another method for preparing germylarsines involved the elimination of a hydrogen halide from a halogermane and an arsine by a tertiary amine \( (8) \). In general, the yields were poor and the method is particularly unsuitable for GeH\(^3\) containing arsines which rapidly decompose in the presence of a strong base. An attempt to prepare primary and secondary arsines by the reaction of trimethylchlorogermane with a large excess of arsine in the presence of triethylamine gave only tris(trimethylgermyl)arsine.

A more suitable general method of preparing germanium arsines, involved exchange reactions between a halogermane and a silylarsine \( (9) \).

\[ \text{SiH}_3\text{AsR}_2 + \text{R'}_3\text{GeX} = \text{R'}_3\text{GeAsR}_2 + \text{SiH}_3\text{X} \]

\[ (\text{SiH}_3\text{)}_2\text{AsR} + 2\text{R'}_3\text{GeX} = (\text{R'}_3\text{Ge)}_2\text{AsR} + 2\text{SiH}_3\text{X} \quad (9) \]

\[ (\text{SiH}_3\text{)}_3\text{As} + 3\text{R'}_3\text{GeX} = (\text{R'}_3\text{Ge)}_3\text{As} + 3\text{SiH}_3\text{X} \]

\[(R = \text{Me, Ph}; \ R' = \text{H, Me})]\n
The silylarsines were prepared by methods that can be applied to germyl-
arsines but the yields based on the halogeno-silanes and -germanes are not quantitative. The exchange reactions, by contrast, are essentially quantitative in the relatively expensive halogenogermanes. The reaction proceeded more readily for fluoro- than for chloro- than for bromo-germanes with the iodogermanes inactive. The difference in the bond energies of Si-As and Ge-As bonds is not known but the above order follows the same trend as the difference in the Si-X and Ge-X bond energies (Table 7). Because of their easier preparation, the chlorides

<table>
<thead>
<tr>
<th>Bond Energies (Kcals/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Si</strong></td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Br</td>
</tr>
<tr>
<td>I</td>
</tr>
</tbody>
</table>

were usually used in the preparation of germyl(dimethyl)arsine, GeH₃AsMe₂, digermyl(methyl)arsine, (GeH₃)₂AsMe, trimethylgermyl(dimethyl)arsine, Me₃GeAsMe₂, bis(trimethylgermyl)methylarsine, (Me₃Ge)₂AsMe, germyl-(diphenyl)arsine, GeH₃AsPh₂, digermyl(phenyl)arsine, (GeH₃)₂AsPh, trimethylgermyl(diphenyl)arsine, Me₃GeAsPh₂, bis(trimethylgermyl)-phenylarsine, (Me₃Ge)₂AsPh, and tris(trimethylgermyl)arsine, (Me₃Ge)₃As.

The method was also applicable to the formation of compounds containing more than one arsenic moiety bonded to one of germanium (10).
\[ n \text{SiH}_3 \text{AsMe}_2 + \text{Me}_{4-n} \text{GeX} = \text{Me}_{4-n} \text{Ge(AsMe}_2)^n + n \text{SiH}_3 \text{X} \ldots \ldots \quad (10) \]

The ease of substitution decreased as \( n \) increased. It was not possible to prepare tetrakis(dimethylarsino)germane even with tetrafluorogermane as the starting material.

The exchange method has a limited application to the preparation of As-H containing germyl arsines (11).

\[ \text{SiH}_3 \text{AsH}_2 + R_3 \text{GeX} = R_3 \text{GeAsH}_2 + \text{SiH}_3 \text{X} \]

\[(R_3 = \text{H}_3, \text{Me}_3, \text{MeH}_2; \text{ref. 3}) \quad (12)\]

\[ 2 \text{SiH}_3 \text{AsH}_2 + \text{Me}_2 \text{GeCl}_2 = \text{Me}_2 \text{Ge(AsH}_2)^2 + 2 \text{SiH}_3 \text{Cl} \]

However, when the reaction was attempted with methyltrichlorogermane or dichlorogermane, the preferred reaction, even at low temperature, was the condensation of silylarsine to trisilylarsine. This was found to take place when silylarsine was reacted with tin halides. (See Chapter 6). Further reaction then took place to give intractable materials which were not easily characterised. Condensation also took place in the reaction of disilylarsine with trimethylchlorogermane so that tris(trimethylgermyl)arsine, rather than the bis-derivative was formed (13).

\[ 3(\text{SiH}_3)^2 \text{AsH} + 6 \text{Me}_3 \text{GeCl} = 2(\text{Me}_3 \text{Ge})_3 \text{As} + 6 \text{SiH}_3 \text{Cl} \ldots \ldots \quad (13) \]

Another route to digermylarsines was provided by the cleavage of
the Ge-As bond in tris(trimethylgermyl)arsine, bis(trimethylgermyl)methylarsine or bis(trimethylgermyl)phenylarsine by methyl-lithium to give lithium trimethylgermylarsenides (14).

\[(\text{Me}_3\text{Ge})_2\text{AsR} + \text{MeLi} \rightarrow \text{Me}_4\text{Ge} + \text{LiAsR}\text{(GeMe}_3\text{)} \] ......... (14)

\[R = \text{Me}_3\text{Ge}, \text{Me}, \text{Ph}.\]

Acidification or reaction with methyl iodide gave bis-trimethylgermylarsine, \((\text{Me}_3\text{Ge})_2\text{AsH}\), bis-trimethylgermyl(methyl)arsine, trimethylgermyl(methyl)arsine, \(\text{Me}_3\text{GeAsHMe}\), or trimethylgermyl(phenyl)arsine \(\text{Me}_3\text{GeAsHPh}\).

The Ge-As bond was also cleaved by the action of lithium tetrahydroaluminate on germylarsines. By analogy with the corresponding reactions of silyl-phosphine and -arsine (chapter 3) the formation of germane and lithium arsinoaluminates was expected (15).

\[\text{nGeR}_3\text{AsR'}_2 + \text{LiAlH}_4 = \text{nGeR}_3\text{H} + \text{LiAl(AsR'}_2\text{)}_\text{n}_4-\text{n} \] .... (15)

\[(R, R' = H, Me)\]

Germane (or trimethylgermane) was indeed evolved, but other reactions also occurred since arsine (or dimethylarsine), hydrogen, and small amounts of digermane were also volatile products. The liberation of arsines suggested that among the several possible complex reactions, some of the germylarsines or germane probably reacted with
aluminate ions to give germylaluminates, containing an \((\text{Al-GeH}_3)^-\) entity. The presence of both arsino- and germyl-aluminates in the solution resulting from the reaction of \(\text{GeH}_3\text{AsH}_2\) with \(\text{LiAlH}_4\) was indicated by the production of both methylarsine and methylgermane on treating with methyliodide. Further, treatment with methanethiol, which is an acid that is too weak to cleave the Ge-As bond in germylarsine, gave arsine and germane. In both these reactions the complexity was emphasized by the formation of small quantities of digermane. The infrared spectrum of the resultant solution from the reaction of \(\text{GeH}_3\text{AsMe}_2\) with \(\text{LiAlH}_4\) gave a band attributable to a Ge-H stretch at 1975 cm\(^{-1}\) which is close to that found for the \(\text{AlH}_3\text{GeH}_3^-\) ion. Species such as \(\text{BH}_3\text{GeH}_3^-\) and \(\text{GeH}_3^-\) have bands at 1930 and 1740 cm\(^{-1}\) respectively, while \((\text{GeH})_x\) type polymers have bands closer to 2100 cm\(^{-1}\). Thus, although the Ge-As bond is cleaved to give arsino-aluminates as with the Si-As bond, it seems clear that germyl-aluminates are also formed. The mechanism for the formation of digermane in these systems is not known but Ge-Ge bonded species have been observed in other systems containing aluminum alkyls. Thus, although the reactions of silylarsines with lithium tetrahydroaluminate provided synthetic routes to silylarsine derivatives, the corresponding reactions with germylarsines are too complicated to have practical application.

The germanium arsines containing Ge-H and/or As-H bonds were less stable than their fully organo-substituted analogues. Trimethylgermylar sine, when heated at 100°C for 24 hr have arsine as the volatile product while treatment of the involatile residue with hydrogen chloride
resulted in the formation of trimethylchlorogermane (16).

\[
3\text{Me}_3\text{GeAsH}_2 \xrightarrow{\text{heat}} 2\text{AsH}_3 + (\text{Me}_3\text{Ge})_2\text{As} \quad \xrightarrow{3\text{HCl}} \quad 3\text{Me}_3\text{GeCl} + \text{AsH}_3
\]

Germyl(dimethyl)arsine when similarly heated gave off germane consistent with decomposition mainly occurring as in (17).

\[
2\text{GeH}_3\text{AsMe}_2 \rightarrow \text{GeH}_4 + \text{GeH}_2(\text{AsMe}_2)_2
\]

\[
2\text{GeH}_2(\text{AsMe}_2)_2 \rightarrow \text{GeH}_4 + \text{GeH}(\text{AsMe}_2)_3
\]

This mode of decomposition has been noted for germyl-phosphines and -selenides and is a familiar feature of the chemistry of silane derivatives. On treatment with HCl, di- and tri-chlorogermane were evolved as expected and also some monochlorogermane which suggested that some germyl(dimethyl)arsine was still present. On heating bis(arsino)dimethylgermane, Me₂Ge(AsH₂)₂, the volatile product is arsine. Dimethyl-dichlorogermane was evolved from the involatile residue when it was treated with HCl, indicating the presence of the Me₂Ge moiety. The infrared spectrum of the involatile residue exhibited bands attributable to Me stretching, deformation, and rocking modes for methyl groups attached to germanium; showed bands in the Ge-C stretching region; and gave no bands in the As-H stretching region. The PMR spectrum showed three peaks in the expected region for Me attached to Ge. The relative
intensities varied from sample to sample suggesting the presence of more than one compound. This was supported by the variable values obtained for molecular weight determinations. The thermal decomposition of $\text{Me}_2\text{Ge(Ph}_2\text{)}_2$ was reported recently$^{123}$. The major product, with mercury catalysis, was a Ge-P cage molecule, $(\text{Me}_2\text{Ge})_6\text{P}_4$, while with mercury excluded a mixture of products resulted. With mercury manometers in the vacuum line it is quite likely that similar products result from the thermal decomposition of the arsine analogue $\text{Me}_2\text{Ge(AsH}_2\text{)}_2$. 

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CHAPTER 6

The Preparation of Tin Arsines

Before this work only tertiary arsines containing tin-arsenic bonds had been reported.\textsuperscript{15-18} The preparation of trimethylstannylarsine using LiAl(AsH\textsubscript{2})\textsubscript{4} is described in chapter 1, but the yields were low.

Recent reports on tertiary tin arsines describe the preparation of the compounds (R\textsubscript{3}Sn\textsubscript{n}AsR\textsubscript{3-n}, [n = 1-3, R = Me or Ph] from R\textsubscript{3}SnCl and R\textsubscript{3-n}AsH\textsubscript{n} in the presence of triethylamine\textsuperscript{124} and the preparation of R\textsubscript{4-n}Sn(AsR\textsubscript{2})\textsubscript{n}, [n = 1-4 R = Me or Ph] from alkali metal arsenides\textsuperscript{124} or silicon arsines\textsuperscript{125} and tin halides.

This chapter describes the preparation of primary, secondary and tertiary tin arsines by a variety of methods.
Experimental

Reaction of Trimethylbromostannane with Arsino-Potassium

Typically, trimethylbromostannane (ca 9 mmoles) and arsino-potassium (10.1 mmoles) each in diethylether, were mixed together slowly and held at -78° for 3 hr. After this time, arsine and solvent were distilled off as the vessel was warmed to room temperature. Tris (trimethylstannyl)arsine (ca 2.7 mmoles) was then distilled from the reaction vessel.

In a similar manner, trimethylbromostannane (ca 10.5 mmoles) was mixed with excess arsino-potassium (39 mmoles). Arsine was pumped away at -78° and the residue treated with excess hydrogen sulphide for 1 hr. After removal of solvent, distillation gave trimethylstannylarsine (2.3 mmoles), bis(trimethylstannyl)arsine (0.9 mmmole), and tris(trimethylstannyl)arsine (0.8 mmoles). A similar residue, when treated with methyl iodide gave trimethylstannyl(dimethyl)arsine, bis(trimethylstannyl)methylarsine, and tris(trimethylstannyl)arsine.

Reaction of Trimethylbromostannane with Lithium Phenylarsenide

Trimethylbromostannane (3.0 mmoles) was condensed into a solution of lithium phenylarsenide (3.0 mmoles) and the mixture stirred at -78° for 45 minutes yielding 1.2 mmoles of bis(trimethylstannyl)phenylarsine and 1.4 mmoles of phenylarsine.

Further Anion Reactions

(a) Tris(trimethylstannyl)arsine (2.4 mmmole) and monoglyme were trapped onto potassium (5.0 mmoles) and the system allowed to warm to room temperature. The monoglyme solution changed colour from blue to
various shades of brown. Excess hydrogen sulphide was immediately added and after 10 mins. the volatile materials, which included arsine, tetramethylstannane and trimethylstannane (identified by n.m.r. spectra), were pumped away. Bis(trimethylstannyl)arsine (0.8 mmoles) was then distilled, by gentle warming, from the reaction vessel. (b) In a similar manner, bis(trimethylstannyl)phenylarsine (3.0 mmoles) and potassium (5.9 mmoles) in monoglyme gave, after treatment with H₂S and pumping off volatile products, trimethylstannyl(phenyl)arsine (1.0 mmoles).

(c) In a similar manner, bis(trimethylstannyl)methylarsine (2 mmoles) and potassium (4 mmoles) in monoglyme gave only a small amount of bis(trimethylstannyl)methylarsine in the less volatile fraction.

(d) Methyl-lithium (4.0 mmoles) in diethyl ether was dropped slowly into tris(trimethylstannyl)arsine (4.0 mmoles) in 10 mls of diethyl ether and the mixture stirred at room temperature for 4 hours. Methanethiol (4.0 mmoles) was condensed in and the mixture stirred for another 30 minutes. Fractionation yielded bis(trimethylstannyl)arsine (1.2 mmoles)

Unsuccessful Reactions

Trimethylchlorostannane 2.0 mmoles, triethylamine (2.0 mmoles) and arsine (10.0 mmoles) at room temperature for 2 hours gave tris(trimethylstannyl)arsine (0.5 mmoles), and trimethylstannyl(diethyl)amine (3.0 mmoles) and arsine (10 mmoles) at -96° for 30 minutes gave tris(trimethylstannyl)arsine (0.7 mmoles) as the only tin arsines.

Reaction of Trimethylchlorostannane with Silyl(dimethyl)arsine

Typically, silyl(dimethyl)arsine (ca. 10.1 mmoles) and a small quantity of diethylether were distilled onto trimethylchlorostannane
(ca. 10 mmoles) and allowed to warm from \(-196^\circ\) to room temperature. Chlorosilane (identified by its i.r. spectrum\(^{31}\)) and the ether were pumped away leaving trimethylstannyl(dimethyl)arsine (10.1 mmoles) which was poured into a \(^1\)H n.m.r. tube attached as a side-arm to the reaction vessel.

**Reaction of Trimethylchlorostannane with Disilyl(methyl)arsine, Silyl-(diphenyl)arsine, and Disilyl(phenyl)arsine**

As described above, the reaction of trimethylchlorostannane (ca. 20 mmoles) with disilyl(methyl)arsine (ca. 10.5 mmoles) gave bis(trimethylstannyl)methylarsine (ca. 9.9 mmoles); trimethylchlorostannane (ca. 7.3 mmoles) with silyl(diphenyl)arsine (7.1 mmoles) gave trimethylstannyl(diphenyl)arsine (7.1 mmoles); and trimethylchlorostannane (14.9 mmoles) with disilyl(phenyl)arsine (7.4 mmoles) gave bis(trimethylstannyl)phenylarsine (7.5 mmoles).

**Reaction of Trimethylchlorostannane with Silylarsine**

(a) Silylarsine (ca. 1 mmoles) and diethylether were distilled onto trimethylchlorostannane (.2 g ca. 1 mmoole) and allowed to warm to \(-78^\circ\) when arsine was evolved. On warming to room temperature, trisilylarsine was distilled off leaving mainly unreacted trimethylchlorostannane.

(b) An equimolar amount of silylarsine was distilled onto trimethylchlorostannane in an n.m.r. tube which was then sealed. The \(^1\)H n.m.r. spectrum only showed peaks attributable to arsine,\(^{25}\) trisilylarsine,\(^{66}\) and trimethylchlorostannane\(^{76}\). (c) An equimolar amount of silylarsine was distilled onto trimethylbromostannane in an n.m.r. tube which was then sealed. The \(^1\)H n.m.r. spectrum taken immediately the tube had

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warmed to room temperature, only showed peaks attributable to the starting materials. After 1 hr. the only peaks were those attributable to trisilylarsine and arsine (in a ratio of ca. 3:2) and unchanged trimethylbromostannane.

Reaction of Trimethylbromostannane with Trimethylstannylarsine

Equimolar amounts of trimethylbromostannane and trimethylstannylarsine were held at room temperature in a 10 ml. reaction vessel. Arsine was evolved and after ca. 6 hr. the remaining mixture consisted only of tris(trimethylstannyl)arsine and trimethylbromostannane.

Reaction of Trimethylstannyl(diethyl)amine with Phenylarsine

Typically, phenylarsine (2.5 mmoles) in diethylether was slowly added to a stirred solution of trimethylstannyl(diethyl)amine (5 mmoles) at room temperature. Diethylamine was pumped off at room temperature along with the solvent. Bis(trimethylstannyl)phenylarsine (1.9 mmoles) was then distilled, from the reaction vessel.

Reaction of Trimethylstannyl(diethyl)arsine with Methylarsine

Typically, gaseous methylarsine (2.5 mmoles) was slowly admitted over a stirred diethylether solution of trimethylstannyl(diethyl)amine (5 mmoles) at room temperature. Diethylamine and solvent were pumped away after 40 minutes at room temperature. Bis(trimethylstannyl)methylarsine (1.4 m moles) was then distilled, from the reaction vessel.

Characterisations

Known compounds were identified spectroscopically. The infrared and n.m.r. spectra of $\text{Me}_3\text{SnAsMe}_2$, $(\text{Me}_3\text{Sn})_2\text{AsMe}$, $\text{Me}_3\text{SnAsPh}_2$, $(\text{Me}_3\text{Sn})_2\text{AsPh}$...
and (Me₃Sn)₃As were reported recently. The spectra of trimethylstannyl-arsine, bis(trimethylstannyl)arsine and trimethylstannyl(phenyl)arsine are given in tables 6.1 and 6.2. The tin arsines were further characterised by molecular weight determinations (table 6.3) and by reaction with a slight excess of hydrogen bromide at room temperature for 30 minutes. Table 6.3 lists the quantity of tin arsine used and the amounts of tin halide and arsine produced.
### TABLE 6.1

The Infrared Spectra of the Tin Arsines

<table>
<thead>
<tr>
<th>Me₃SnAsH₂</th>
<th>(Me₃Sn)₂AsH</th>
<th>Me₃SnAsHPh</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2975 s</td>
<td>2979 s</td>
<td>2979 s</td>
<td>v as CH</td>
</tr>
<tr>
<td>2908 m</td>
<td>2902 m</td>
<td>2909 s</td>
<td>v as CH</td>
</tr>
<tr>
<td>2076 s</td>
<td>2089 s</td>
<td>2084 s</td>
<td>v AsH</td>
</tr>
<tr>
<td>1415 m</td>
<td>1420 m</td>
<td>1433 s</td>
<td>s as CH₃</td>
</tr>
<tr>
<td>1185 m</td>
<td>1186 m</td>
<td>1184 s</td>
<td>sₕ CH₃</td>
</tr>
<tr>
<td>950 m</td>
<td>938 w</td>
<td>959 m</td>
<td>AsH₂ def or AsH bend</td>
</tr>
<tr>
<td>766 m</td>
<td>760 m</td>
<td>765 s</td>
<td>ρ CH₃</td>
</tr>
<tr>
<td>715 w</td>
<td>710 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>570 vw</td>
<td></td>
<td></td>
<td>AsH₂ wag</td>
</tr>
<tr>
<td>519 s</td>
<td>522 s</td>
<td>520 s</td>
<td>v as SnC</td>
</tr>
<tr>
<td>499 m</td>
<td>502 m</td>
<td>501 s</td>
<td>v s SnC</td>
</tr>
</tbody>
</table>

Me₃SnAsHPh showed the following bands attributable to the phenyl group:
3061 s, 3098 m (υCH); 1583 s, 1484 s, 1335 w, 1320 w (υCC); 1300 w, 1155 w, 1072 m, 1023 s (β CH); 998 m(α CCC); 842 w, 736 s, 693 s, 665 w (γ CH); 616 w (α CCC) and 452s.
**TABLE 6.2**

N.m.r. Parameters of the Tin Arsines and Other Trimethylstannyl Derivatives

<table>
<thead>
<tr>
<th>Compounds</th>
<th>J117 SnCH</th>
<th>J119 SnCH</th>
<th>J117 SnCH</th>
<th>J119 SnCH</th>
<th>Compounds</th>
<th>J117 SnCH</th>
<th>J119 SnCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃SnAsH₂</td>
<td>0.31</td>
<td>47.5</td>
<td>50</td>
<td>Me₃SnCl</td>
<td>56.1</td>
<td>58.5</td>
<td></td>
</tr>
<tr>
<td>Me₃SnAsHPh</td>
<td>0.34</td>
<td>48</td>
<td>50</td>
<td>Me₃SnBr</td>
<td>55.8</td>
<td>58.4</td>
<td></td>
</tr>
<tr>
<td>Me₃SnAsMe₂</td>
<td>0.22</td>
<td>47</td>
<td>49.5</td>
<td>Me₃SnI</td>
<td>55.6</td>
<td>58.0</td>
<td></td>
</tr>
<tr>
<td>Me₃SnAsPh₂</td>
<td>0.21</td>
<td>48</td>
<td>50.5</td>
<td>(Me₃Sn)₂O</td>
<td>53.6</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td>(Me₃Sn)₂AsH</td>
<td>0.36</td>
<td>c</td>
<td>c</td>
<td>(Me₃Sn)₂S</td>
<td>53.9</td>
<td>56.3</td>
<td></td>
</tr>
<tr>
<td>(Me₃Sn)₂AsMe</td>
<td>0.39</td>
<td>47.5</td>
<td>50</td>
<td>(Me₃Sn)₂Se</td>
<td>53.5</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td>(Me₃Sn)₂AsPh</td>
<td>0.35</td>
<td>48</td>
<td>50</td>
<td>Me₃SnSMe</td>
<td>54.5</td>
<td>59.9</td>
<td></td>
</tr>
<tr>
<td>(Me₃Sn)₃As</td>
<td>0.37</td>
<td>47.5</td>
<td>50</td>
<td>Me₃SnSeMe</td>
<td>53.4</td>
<td>55.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Me₃Sn)₃P</td>
<td>49.7</td>
<td>52.2</td>
<td></td>
</tr>
</tbody>
</table>

(a) § AsH 1.1  (b) § AsH not observed  (c) not observed  (d) Ref. 76  (e) Ref. 126  (f) Ref. 127.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Wt.</th>
<th>Reaction with H Br</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>mmoles compound</td>
</tr>
<tr>
<td>Me₃SnAsH₂</td>
<td>238</td>
<td>1.0</td>
</tr>
<tr>
<td>Me₃SnAsHPh</td>
<td>335</td>
<td>1.1</td>
</tr>
<tr>
<td>Me₃SnAsMe₂</td>
<td>278</td>
<td>0.5</td>
</tr>
<tr>
<td>Me₃SnAsPh₂</td>
<td>400</td>
<td>0.7</td>
</tr>
<tr>
<td>(Me₃Sn)₂AsH</td>
<td>421</td>
<td>0.5</td>
</tr>
<tr>
<td>(Me₃Sn)₂AsMe</td>
<td>411</td>
<td>0.5</td>
</tr>
<tr>
<td>(Me₃Sn)₂AsPh</td>
<td>452</td>
<td>0.5</td>
</tr>
<tr>
<td>(Me₃Sn)₃As</td>
<td>547</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Discussion

Trimethylstannylarsine and bis(trimethylstannyl)arsine, \((\text{Me}_3\text{Sn})_2\text{AsH}\), can both be prepared from the reaction of trimethylbromostannane and arsinopotassium under controlled conditions. With equimolar amounts of reactants, tris(trimethylstannyl)arsine, \((\text{Me}_3\text{Sn})_3\text{As}\), was formed in good yield, as might be expected because a tertiary product is common in such anion reactions\(^{10}\). However, with a large excess of arsinopotassium, subsequent acidification with hydrogen sulphide led to the liberation of mono- and bis-trimethylstannylarsine,\(^{(1)}\). The mechanism of formation of related complex ions has been discussed for phosphine systems\(^{10,80}\). The rapid condensation of primary and secondary silyl- and germylarsines is a familiar feature of their chemistry\(^3\), so condensation to produce tris(trimethylstannyl)arsine is not unexpected. In addition, both under sealed-tube and vacuum-line conditions, trimethylhalostannanes catalysed such condensation processes,\(^{(2)}\)

\[
\begin{align*}
\text{[AsH}_2\text{]}^- \text{Me}_3\text{SnBr} \xrightarrow{\text{H}_2\text{S}} \text{Me}_3\text{SnAsH}_2 \\
\text{[(Me}_3\text{Sn)}_2\text{As]}^- \xrightarrow{\text{H}_2\text{S}} (\text{Me}_3\text{Sn})_2\text{AsH} 
\end{align*}
\]

\[
\begin{align*}
\text{SiH}_3\text{AsH}_2 \text{Me}_3\text{SnX} \quad \text{X = Cl, Br} \\
\begin{cases}
\text{SiH}_3\text{As} + 2\text{AsH}_3 \\
(\text{Me}_3\text{Sn})_3\text{As} + 2\text{AsH}_3
\end{cases}
\end{align*}
\]

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The isolation of bis(trimethylstannyl)phenylarsine as the only tin arsine product of the reaction between lithium phenylarsenide and trimethylbromostannane is consistent with the above observations and the poor yields of secondary silicon and germanium arsines using this method (Chapters 4 and 5).

Bis(trimethylstannyl)arsine and phenyl(trimethylstannyl)arsine were prepared when the corresponding trimethylstannylarsine anions, formed by reaction of dry potassium in diglyme (3) are immediately

\[
(Me_3Sn)_2AsR \xrightarrow{2K} [Me_3SnAsR]^- + Me_3Sn^- + 2K^+ \quad \ldots \ldots \quad (3)
\]

\[(R = Me_3Sn, Ph,Me)\]

acidified with hydrogen sulphide. Trimethylstannane and tetramethylstannane were also liberated.

The solutions, (3) presumed to contain the methyl(trimethylstannyl)arsine anion, \( [Me_3SnAsMe^-] \), did not give \( Me_3SnAsMeH \) on acidification. The latter presumably disproportionated to give only the starting material, \( (Me_3Sn)_2AsMe \) in the less volatile fraction. Similarly, when the solutions containing trimethylstannylarsine anions, (1) were treated with methyliodide, only bis(trimethylstannyl)methylarsine, (4) was found although trimethylstannyl(methyl)arsine might also have been expected from the

\[
\Gamma(Me_3Sn)_2As^- + MeI \rightarrow (Me_3Sn)_2AsMe + I^- \quad \ldots \ldots \quad (4)
\]

corresponding reaction with \( [Me_3SnAsH]^+ \). The formation of small amounts
of trimethylstannyl(dimethyl)arsine in this experiment could result from interaction with excess $[\text{AsH}_2]^-$ (5) followed by reaction with methyl iodide.

$$\text{Me}_3\text{SnAsHMe}^- + [\text{AsH}_2]^- \rightarrow \text{AsH}_3 + [\text{Me}_3\text{SnAsMe}]^- \ldots (5)$$

iodide.

The use of a lithium alkyl to cleave an Sn-As bond followed by acidification did not lead to better yields of As-H containing tin arsines than the potassium method.

Tin arsines have previously been prepared by methods outlined in equations (6) and (7)\textsuperscript{15, 124}. Even with a large excess of arsine used as the solvent it was not possible to prepare any As-H containing tin arsines by either of these methods. Trimethylstannyl(diethyl)amine

$$3\text{Me}_3\text{SnCl} + \text{AsH}_3 + 3\text{Et}_3\text{N} \rightarrow 3\text{Et}_3\text{NCl} + (\text{Me}_3\text{Sn})_3\text{As} \ldots (6)$$

$$\text{Me}_3\text{SnNMe}_2 + R_2\text{AsH} \rightarrow \text{Me}_3\text{SnAsR}_2 + \text{Me}_2\text{NH} \ldots \ldots (7)$$

\((R = \text{Ph, Me})\)

reacts smoothly with phenyl- and methyl-arsine (8) to give the tertiary arsines.

$$2\text{Me}_3\text{SnNET}_2 + R\text{AsH}_2 \rightarrow (\text{Me}_3\text{Sn})_2\text{AsR} + 2\text{Et}_2\text{NH} \ldots \ldots (8)$$

\((R = \text{Ph, Me})\)

The exchange reactions between silylarsines and methylhalogermanes resulted in the formation of mono- and bis-arsino-methylgermanes, (Chapter 5)
However, extension to the methylhalostannanes is not promising since trimethylhalostannanes so effectively catalysed the condensation of silylarsine or trimethylstannylarsine (2). In this the tin halides parallel bromosilane which also assists condensation rather than bromogermanes which exchange (Chapter 5). However, trimethylchlorostannane did react in a similar manner to trimethylhalo- and halo-germanes with silyl(dimethyl)-, silyl(diphenyl)-, disilyl(methyl)-, and disilyl(phenyl)-arsines forming trimethylstannyl(dimethyl)-, trimethylstannyl(diphenyl)-, bis(trimethylstannyl)phenyl- and bis(trimethylstannyl)phenyl-arsines respectively, (9 and 10), in excellent yields.

\[
\begin{align*}
\text{SiH}_3\text{AsR}_2 + \text{Me}_3\text{SnCl} & \rightarrow \text{Me}_3\text{SnAsR}_2 + \text{SiH}_3\text{Cl} \quad \ldots \ldots \quad (9) \\
(\text{SiH}_3)_2\text{AsR} + 2\text{Me}_3\text{SnCl} & \rightarrow (\text{Me}_3\text{Sn})_2\text{AsR} + 2\text{SiH}_3\text{Cl} \quad \ldots \ldots \quad (10)
\end{align*}
\]

\(R = \text{Me, Ph}\)

The infrared spectra of the new compounds are listed in table 6.1 together with assignments made by comparison with the spectra of phenyl-arsine, related silyl-, \(^{86, 88}\) germyl-\(^{87}\) and trimethylstannyl-arsines\(^{124}\) and other trimethylstannyl\(^{128}\) compounds.

The n.m.r. spectra are displayed in table 6.2. The SnCH chemical shifts and coupling constants confirm the characterisation of the new compounds as tin arsines. In particular the Sn-C-H coupling constants remain in a very narrow range regardless of the differing substitution on arsenic.
The coupling constants for other trimethylstannyl compounds fall into quite distinct and characteristic ranges depending on the group of the periodic table to which the element bonded to tin belongs, rather than being electronegativity dependent. Although As-H resonances are usually broad due to quadrupole relaxation, the failure to detect those in bis(trimethylstannyl)arsine and trimethylstannyl(phenyl) arsine was probably due to exchange processes taking place. In view of the failure to detect the Sn-C-H satellites in bis(trimethylstannyl)arsine, the value for the chemical shift for this compound must be regarded as provisional.
A number of reactions of silicon arsines had been studied\textsuperscript{9} prior to 1968 and these are listed below (1-7).

\begin{align*}
\text{Me}_3\text{SiAsMe}_2 + \text{HBr} &\rightarrow \text{Me}_3\text{SiBr} + \text{Me}_2\text{AsH} \\
2\text{Me}_2\text{SiAsMe}_2 + \text{H}_2\text{O} &\rightarrow (\text{Me}_3\text{Si})_2\text{O} + 2\text{Me}_2\text{AsH} \\
\text{Me}_3\text{SiAsMe}_2 + \text{ROH} &\rightarrow \text{Me}_3\text{SiOR} + \text{Me}_2\text{AsH} \\
2\text{Me}_3\text{SiAsMe}_2 + \text{BF}_3 &\rightarrow 2\text{Me}_3\text{SiF} + (\text{Me}_2\text{As})_2\text{BF} \\
2\text{Me}_3\text{SiAsMe}_2 + 2\text{PF}_5 &\rightarrow 2\text{Me}_3\text{SiF} + \text{PF}_3 + \text{Me}_2\text{AsAsMe}_2\cdot\text{PF}_5 \\
\text{Me}_3\text{SiAsMe}_2 + 2\text{CH}_3\text{I} &\rightarrow \text{Me}_3\text{SiI} + \text{Me}_4\text{AsI} \\
\text{Me}_3\text{SiAsMe}_2 + \text{CS}_2 &\rightarrow \text{Me}_3\text{SiSC(S)AsMe}_2
\end{align*}

Recently there has been more interest\textsuperscript{1,2} in the reactivity of M-As bonds (M = Si, Ge, Sn) and reactions with protic reagents\textsuperscript{107,114,121} (8-10), diborane\textsuperscript{92,93} (11) boron halides\textsuperscript{92,107} (12), phosphorus and arsenic halides\textsuperscript{107,129} (13-15) and halogens\textsuperscript{107} (16) have been reported.

\begin{align*}
2\text{R}_3\text{MAsR}_2 + \text{H}_2\text{S} &\rightarrow (\text{R}_3\text{M})_2\text{S} + 2\text{R}_2\text{AsH}
\end{align*}
\[ M = \text{Si, Sn}; R = \text{Me and } M = \text{Ge}; R = \text{H} \]

\[ \text{Me}_3\text{MAsMe}_2 + \text{RSH} \rightarrow \text{Me}_3\text{MSR} + \text{Me}_2\text{AsH} \] \hspace{1cm} (9)

\[ M = \text{Si, Sn} \]

\[ \text{GeH}_3\text{AsH}_2 + \text{H}_2\text{Se} \rightarrow (\text{GeH}_3)_2\text{Se} + \text{AsH}_3 \] \hspace{1cm} (10)

\[ \text{MH}_3\text{AsH}_2 + \text{B}_2\text{H}_6 \rightarrow \text{MH}_4 + \frac{1}{n}(\text{AsH}_2\text{BH}_2)_n \] \hspace{1cm} (11)

\[ M = \text{Si, Ge} \]

\[ \text{R}_3\text{MAsR}_2 + \text{R'}\text{BX} \rightarrow \text{R}_3\text{MX} + \frac{1}{n}(\text{R'BAsR}')_n \] \hspace{1cm} (12)

\[ M = \text{Si}; R = \text{Me}; R' = \text{Ph}; X = \text{Cl} \]

\[ M = \text{Si, Ge}; R = \text{H}, R' = X; X = \text{Cl, Br} \]

\[ \text{R}_3\text{MAsR}_2 + \text{R'}\text{EX} \rightarrow \text{R}_3\text{MX} + \text{R}_2\text{AsER}'_2 \] \hspace{1cm} (13)

\[ E = \text{P, As}; M = \text{Si}; R = \text{Me}; R' = \text{Me, Ph} \]

\[ E = \text{P, M = Sn}; R = \text{Ph}; R' = \text{Ph} \]

\[ 3\text{Me}_3\text{SiAsMe}_2 + \text{ECl}_3 \rightarrow 3\text{Me}_3\text{SiCl} + \text{E(AsMe}_2)_3 \] \hspace{1cm} (14)

\[ E = \text{P, As} \]

\[ (\text{Me}_3\text{Sn})_3\text{As} + 3\text{Ph}_2\text{ECl} \rightarrow 3\text{Me}_3\text{SnCl} + \text{As(EPh}_2)_3 \] \hspace{1cm} (15)

\[ E = \text{P, As} \]
\[ R_3M\text{As}R_2 + X_2 \rightarrow R_3MX + R_2\text{As}X \] \hspace{1cm} (16)

\[ M = \text{Si, Sn}; \hspace{1cm} X = \text{Br, I}; \hspace{1cm} R = \text{Me} \]

\[ M = \text{Ge}; \hspace{1cm} X = \text{I}; \hspace{1cm} R = \text{H} \]

This chapter describes some similar reactions of group IV arsines. Reactions with protic reagents were used for analysis of the arsines. Reactions with covalent halides gave arsines with As-\(\text{B}\), As-\(\text{Al}\), As-As and As-S bonds and with group IV amines gave mixed group IV arsines.
Experimental

Reactions with Chlorine

Trimethylsilyl(dimethyl)arsine (0.5 mmole), trimethylgermyl-(dimethyl)arsine (0.5 mmole) and trimethylstannyl(dimethyl)arsine (0.5 mmoles) were each sealed in a 2 mm. o.d. n.m.r. tube with ca 0.5 mmoles of chlorine and 0.5 mmoles of T.M.S. and allowed to warm slowly from -196° to room temperature. The n.m.r. spectra were recorded and showed peaks attributable to trimethylchlorosilane, trimethylgermane and trimethylchlorostannane respectively and chlorodimethylarsine. Integration of the spectra showed that the reactions had proceeded in yields over 90% in each case. The tubes were broken open and the characterisations confirmed by infrared spectroscopy.

Reactions with Group III Halides

Trimethylsilylarsine (0.4 mmole) and boron trichloride (0.4 mmole) were held together at -23° for 1 hour. The products were trimethylchlorosilane (0.4 mmole) and a solid which evolved some arsine and hydrogen chloride on treatment with water. Trimethylgermylarsine (0.3 mmole) reacted similarly to give trimethylchlorogermane (0.2 mmole). Boron trichloride (0.4 mmole) and trimethylstannyl(dimethyl)arsine (0.4 mmole) and trisilylarsine (0.4 mmoles) gave chlorosilane (1.1 mmoles) and arsenic boride.

Trisilylarsine (2.3 mmoles) and chlorodimethylborane (2.3 mmoles) were condensed together at -196° and allowed to warm in stages to room temperature. Chlorosilane (2.2 mmoles) was evolved. The residual solid exhibited bands in the infrared at 2920 (s), 2142 (s) 1390 (w), 1283 (m),
1060 (s), 1012 (s), 974 (s), 930-860 (vs) 560 w cm⁻¹ in KBr.

Trigermynes{2.0 mmoles) and chlorodimethylborane (2.0 mmoles) reacted similarly giving 1.7 mmoles chlorogermane and 0.1 mmoles of dichlorogermane. The residual solid exhibited bands in the infrared at 2900 (s), 2050 (s), 1410 (w) 1276 (m), 1001 (s), 965 (s), 900-850 (vs), 600-500 (w) cm⁻¹ in KBr.

Trisilylarsine (2.9 mmoles) and monobromodiborane (2.9 mmoles) similarly gave bromosilane (2.9 mmoles) and diborane (1.4 mmoles). The residual solid exhibited bands in the infrared at 2400 (s), 2351 (s), 2151 (s), 1100 (m), 890-860 (s), 548 (w) cm⁻¹ in KBr.

Trigermynes (1.9 mmoles) and monobromodiborane (1.8 mmoles) similarly gave bromogermane (1.5 mmoles), diborane (0.7 mmoles) and dibromogermane (0.2 mmoles). The residual solid exhibited bands in the infrared at 2395 (s), 2343 (s), 2057 (s), 850 (m) 600-500 w cm⁻¹ in KBr.

Trisilylethyl(dimethyl)arsine (5.0 mmoles) and dimethylaluminium chloride (5.0 mmoles Me₂AlCl) were warmed from -196° to room temperature. After 15 minutes trimethylchlorosilane (5.0 mmoles) was pumped off leaving a solid whose molecular weight and spectra were consistent with (Me₂Al-AsMe₂)₃.

Reactions With Group V Halides

Chlorodimethylarsine (4.0 mmoles) and trisilylarsine (4.0 mmoles) were warmed from -196° to -78° and held at -78° for 15 minutes. 3.9 mmoles of chlorosilane was taken off. On warming to room temperature 3.8 mmoles of silyl(dimethyl)arsine was evolved leaving a pale yellow solid which evolved a little arsine and darkened in colour on standing. About 30°
(based on SiH\textsubscript{3} groups recovered when reacted with HBr) of the solid could be dissolved in benzene. The solution showed no signs of decomposition during 1 hour. Infrared spectra of the extracted solid in benzene and KBr showed broad bands at 2140 cm\textsuperscript{-1} (υSiH) and 890-840 cm\textsuperscript{-1} (υSiH\textsubscript{3}) and Raman spectra showed bands at 350-340 cm\textsuperscript{-1} (υSiAs) and 270 cm\textsuperscript{-1} (υAs-As). The n.m.r. spectrum showed a broad peak at δ0.50. Trigermylarsine reacted almost identically giving a solid whose vibrational spectra showed bands at 2060 cm\textsuperscript{-1} (υGeH); 750-800 cm\textsuperscript{-1}(υGeH\textsubscript{3}) and 250-265 cm\textsuperscript{-1} (υGe-As and υAs-As) and its n.m.r. spectrum showed a broad feature at 84.46 which in one sample was resolved into three peaks at δ 4.44, 4.47 and 4.49 with relative intensities of 1.7:1.9:1.0.

**Reaction with Sulphur Dichloride**

Trimethylsilyl(dimethyl)arsine (2.0 mmoles) and sulphur dichloride (1.0 mmole) were sealed together in an n.m.r. tube with a little T.M.S. as an internal standard. After 5 minutes the n.m.r. spectrum showed the appearance of a peak attributable to trimethylchlorosilane and one at δ1.2 in the ratio 1.5:1.0. The sample was inadvertently destroyed before the reaction could be monitored further.

**Reactions With Group IV Halides**

These were monitored in sealed 2 mm. n.m.r. tubes using benzene as an internal standard. The products were identified by comparison of their n.m.r. spectra with literature values or authentic samples and the relative amounts determined by integration of the spectra. Trimethylgermyl(dimethyl)arsine (0.2 mmoles) and excess methyl iodide gave trimethyl-iodogermaine and tetramethylarsonium iodide (relative intensities after...
4 1/2 hours, 1:1.3). Bis(dimethylarsino)dimethylgermane (0.2 mmoles) and excess methyl iodide gave dimethylidiodogermane and tetramethylarsonium iodide (relative intensities after 5 hours, 1:4.1) and tris-(dimethylarsino)methylgermane (0.1 mmoles) and excess methyl iodide gave methyltriiiodogerame and tetramethylarsonium iodide (relative intensities after 3 hours, 1:11.8). Trimethylgermyl(dimethyl)arsine or trimethylstannyldimethyl)arsine and bromosilane or trimethylchlorosilane showed no reaction after 1 week. Both trimethylgermyl(dimethyl)arsine/trimethylbromostannane and trimethylstannyldimethyl)arsine/trimethylbromogermane mixtures had reached equilibrium within 3 days when the ratio of germanium arsine to tin arsine was 1:1.8.

Reactions with Group IV Dialkylamines

Bis(trimethylgermyl)arsine (3.0 mmoles) and trimethylstannyldimethyl)amine (3.0 mmoles) in 5 mls ether were warmed from -196° to room temperature and stirred for 20 minutes. The products were then separated to give 0.9 mmoles of tris(trimethylgermyl)arsine, 1.0 mmoles of bis(trimethylgermyl)trimethylstannyllarsine (Me₃Ge)₂AsSnMe₃, 0.6 mmoles of tris(trimethylstannyll)arsine and traces of an unidentified compound (possibly (Me₃Sn)₂AsGeMe₃) and 0.3 mmoles of arsine. Under identical conditions trimethylstannyldimethyl)amine (2.0 mmoles) and trimethylgermyl(methyl)arsine (2.0 mmoles) or trimethylgermyl(phenyl)arsine (2.0 mmoles) gave bis(trimethylgermyl)methylarsine (0.6 mmoles), trimethylgermyl(trimethylstannyll)methylarsine, Me₃GeAs(Me)SnMe₃, (0.7 mmoles) bis(trimethylstannyll)methylarsine (0.6 mmoles) and 0.2 mmoles of methylarsine or bis(trimethylgermyl)-phenylarsine (0.7 mmoles) trimethylgermyl(trimethylstannyll)phenylarsine,
Me₃GeAs(Ph)SnMe₃ (0.5 mmole) bis(trimethylstannyl)phenylarsine (0.7 mmole) respectively. The reactions of bis(trimethylgermyl)arsine (4.0 mmoles) with bis(dimethylamino)dimethylgermane or stannane (2.0 mmoles) gave involatile solids as the major products but 0.3 mmoles of Me₂Ge(As(GeMe₂))₂ and 0.2 mmoles of Me₂Sn(As(GeMe₃))₂ were isolated from the volatile products.

Bis(trimethylsilyl)arsine (2.0 mmoles) and trimethylgermyl- or trimethylstannyl-(dimethyl)amine (2.0 mmoles) gave only the symmetrical species on separation. Peaks attributable to the mixed species were detected in n.m.r. spectra of the products of identical solvent-free reactions before separation.

**Characterisations**

Known compounds were characterised spectroscopically. Molecular weights and analyses for the silyl- and germyl- arsinoboranes and polyarsines are given in table 7.1 and for the mixed germanium-tin arsines in table 7.2. The n.m.r. and infrared spectra of the mixed arsines are presented in tables 7.3 and 7.4.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Wt.</th>
<th>Reaction with HX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calc.</td>
</tr>
<tr>
<td>[(SiH₃)₂AsBH₂]₃</td>
<td>407</td>
<td>450</td>
</tr>
<tr>
<td>[(GeH₃)₂AsBH₂]₃</td>
<td>742</td>
<td>717</td>
</tr>
<tr>
<td>[(SiH₃)₂AsBMe₂]₃</td>
<td>547</td>
<td>534</td>
</tr>
<tr>
<td>[(GeH₃)₂AsBMe₂]₃</td>
<td>786</td>
<td>801</td>
</tr>
<tr>
<td>(SiH₃As)₅</td>
<td>526</td>
<td>530</td>
</tr>
<tr>
<td>(GeH₃As)₅</td>
<td>668</td>
<td>755</td>
</tr>
</tbody>
</table>

* mmoles of monomer based on MH₃Cl evolved during preparation
⁺ mmoles of MH₃As based on MH₃AsMe₂ evolved during preparation
TABLE 7.2

Molecular Weights and Cleavage Reactions of the Mixed Arsines

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me₃Ge)₂AsSnMe₃</td>
<td>470</td>
<td>475</td>
<td>0.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Me₃GeAs(Me)SnMe₃</td>
<td>381</td>
<td>372</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Me₃GeAs(Ph)SnMe₃</td>
<td>449</td>
<td>434</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Me₂Ge[As(GeMe₃)₂]₂</td>
<td>735</td>
<td>723</td>
<td>0.2</td>
<td>0.7</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Me₂Sn[As(GeMe₃)₂]₂</td>
<td>710</td>
<td>769</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

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TABLE 7.3

N.m.r. Parameters for the Mixed Arsines

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^7$GeCH</th>
<th>$^8$SnCH</th>
<th>$^8$SiCH</th>
<th>$^{117}$SnCH</th>
<th>$^{119}$SnCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Me}_3\text{Ge})_2\text{AsSnMe}_3$</td>
<td>0.37</td>
<td>0.37</td>
<td>---</td>
<td>47.5</td>
<td>50.0</td>
</tr>
<tr>
<td>$\text{Me}_3\text{GeAs(Me)SnMe}_3$</td>
<td>0.35</td>
<td>0.34</td>
<td>---</td>
<td>48.0</td>
<td>50.0</td>
</tr>
<tr>
<td>$\text{Me}_3\text{GeAs(Ph)SnMe}_3$</td>
<td>0.37</td>
<td>0.36</td>
<td>---</td>
<td>47.5</td>
<td>50.0</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Ge[As(GeMe}_3)_2$</td>
<td>0.37</td>
<td>0.35*</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Sn[As(GeMe}_3)_2$</td>
<td>0.36</td>
<td>0.35</td>
<td>---</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{AsGeMe}_3$</td>
<td>0.38</td>
<td>---</td>
<td>0.28</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{AsSnMe}_3$</td>
<td>---</td>
<td>0.38</td>
<td>0.30</td>
<td>n.o.</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

* $^8$Ge(CH$_3$)$_2$, n.o. = not observed

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**TABLE 7.4**

Infrared Spectra of the Mixed Arsines

<table>
<thead>
<tr>
<th></th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{(Me}_3\text{Ge)}_2\text{AsSnMe}_3$</td>
<td></td>
</tr>
<tr>
<td>2970 s</td>
<td>$\nu$ CH</td>
</tr>
<tr>
<td>2910 s</td>
<td>$\nu$ CH</td>
</tr>
<tr>
<td>1408 w</td>
<td>$\delta$ CH$_3$</td>
</tr>
<tr>
<td>1236 m</td>
<td>$\delta$ CH$_3$ (Ge)</td>
</tr>
<tr>
<td>1186 m</td>
<td>$\delta$ CH$_3$ (Sn)</td>
</tr>
<tr>
<td>830 s</td>
<td>$\rho$ CH$_3$</td>
</tr>
<tr>
<td>750 s</td>
<td>$\nu$ GeC</td>
</tr>
<tr>
<td>592 s</td>
<td>$\nu$ GeC and</td>
</tr>
<tr>
<td>565 m</td>
<td>$\nu$ SnC</td>
</tr>
<tr>
<td>520 s</td>
<td>$\nu$ AsC</td>
</tr>
<tr>
<td>501 m</td>
<td>$\nu$ SnC</td>
</tr>
</tbody>
</table>

$\text{Me}_3\text{GeAs(MeSnMe}_3$ showed bands at 2985 sh ($\nu$ CH); 1261 w ($\delta$ CH$_3$) and 888 s ($\rho$ CH$_3$) attributable to CH$_3$(As) and $\text{Me}_3\text{GeAs(Ph)SnMe}_3$ showed bands at 3060 m, 3040 m, $\nu$CH; 1578 s, 1480 s, 1380 w, 1340 w ($\nu$ CC); 1300 m, 1260 w, 1150 sh, 1070 m, 1020 s, ($\beta$ CH); 999 m ($\alpha$ CCC), 695 s, 660 w($\gamma$ CH) attributable to the phenyl group.

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Discussion

Reactions with Covalent Halides

Chlorine cleaved the M-As bond (M = Si, Ge, Sn) to give the two chlorides (1)

\[ \text{Me}_3\text{MAsMe}_2 + \text{Cl}_2 \rightarrow \text{Me}_3\text{MCl} + \text{Me}_2\text{AsCl} \quad \ldots \ldots \ldots \ldots \quad (1) \]

The arsines reacted with boron trichloride according to (2).

\[ \text{Me}_3\text{MAsR}_2 + \text{BCl}_3 \rightarrow \text{Me}_3\text{MCl} + \frac{1}{n}(\text{R}_2\text{AsBCl}_2)_n \quad \ldots \ldots \ldots \ldots \quad (2) \]

\[ M = \text{Si}, \text{Ge}; R = \text{H} \]

\[ M = \text{Sn}; R = \text{Me} \]

The reaction of trisilylarsine with boron trichloride proceeded with reaction of all the silicon-arsenic and boron-chlorine bonds (3).

\[ (\text{SiH}_3)_3\text{As} + \text{BCl}_3 \rightarrow 3\text{SiH}_3\text{Cl} + \text{AsB} \quad \ldots \ldots \ldots \ldots \quad (3) \]

With chlorodimethylboron and monobromodiborane a similar reaction gave disilylarsinoboranes (4 and 5). Trigermylarsine reacted similarly.

\[ (\text{MH}_3)_3\text{As} + \text{Me}_2\text{BCl} \rightarrow \frac{1}{n}(\text{MH}_3)_2\text{AsBMe}_2)_n + \text{MH}_3\text{Cl} \quad \ldots \ldots \quad (4) \]

\[ 2(\text{MH}_3)_3\text{As} + 2\text{B}_2\text{H}_5\text{Br} \rightarrow \frac{2}{n}[(\text{MH}_3)_2\text{AsBH}_2)_n + 2\text{MH}_3\text{Br} + \text{B}_2\text{H}_6] \quad (5) \]
Molecular weight determinations suggest that \( n = 3 \). The B-As stretching frequency in some arsinodiarylboranes has been assigned to the 1370-1430 cm\(^{-1}\) region, which seems rather high compared to the As-C region at 550-600 cm\(^{-1}\). It was not possible to assign the As-B stretches in the compounds prepared to any of the bands in the 500-1500 cm\(^{-1}\) region.

Trimethylsilyl(dimethyl)arsine reacted similarly with dimethyl-(aluminium)chloride (6):

\[
\text{Me}_3\text{SiAsMe}_2 + \text{Me}_2 + \text{Me}_2\text{AlCl} \rightarrow \text{Me}_3\text{SiCl} + \frac{1}{3}(\text{Me}_2\text{AlAsMe}_2)_3 \quad (6)
\]

The reactions of chlorodimethylarsine with equimolar amounts of trisilylarsine or trigermylarsine evolved chlorosilane or chlorogerme, consistent with (11) then silyl- or germyl-(dimethyl)arsine consistent with (8).

\[
(\text{MH}_3)_3\text{As} + \text{Me}_2\text{AsCl} \rightarrow (\text{MH}_3)_{2}\text{AsAsMe}_2 + \text{MH}_3\text{Cl} \quad (7)
\]

\[M = \text{Si, Ge}\]

with (8). There is no direct evidence for the proposed intermediates,

\[
(\text{MH}_3)_2\text{AsAsMe}_2 \rightarrow \text{MH}_3\text{AsMe}_2 + \frac{1}{n}(\text{MH}_3\text{As})_n \quad (8)
\]

1,1 disilyl,2,2 dimethyldiarsine, and its germyl analogue, but a mode of decomposition as in (8) has been noted for the more stable group IV substituted diphosphines. The other products \((\text{MH}_3\text{As})_n\) consisted mainly of insoluble polymers but small amounts of the pentamers, pentasilyl-
cyclopentaarsine, \((\text{SiH}_3\text{As})_5\) and the germyl analogue were extracted. The n.m.r. spectrum of the germyl compound which was resolved into three peaks suggests that the ring is puckered like its methyl analogue.\(^{133}\)

Trimethylsilyl(dimethyl)arsine reacted with sulphur dichloride to give trimethylchlorosilane consistent with (9). The other product

\[
2\text{Me}_3\text{SiAsMe}_2 + \text{SCl}_2 \rightarrow 2\text{Me}_3\text{SiCl} + (\text{Me}_2\text{As})_2\text{S} \quad \ldots \quad (9)
\]

was not characterised but the single peak in the n.m.r. suggests the product was probably bis(dimethylarsino)sulphane and precludes an Arbusov rearrangement to an As\(\text{III}\) compound such as \(\text{Me}_2\text{As(S)AsMe}_2\).

Reactions of silicon arsines with germanium and tin halides have been described in chapters 5 and 6. Germanium and tin arsines did not react with silicon halides. Germanium arsines reacted with methyl iodide in the same manner (10) as silicon\(^{9}\) and tin\(^{134}\) arsines.

\[
\text{Me}_{4-n}\text{Ge(AsMe}_2\text{)}_n + 2n\text{MeI} \rightarrow \text{Me}_{4-n}\text{GeI} + 2n\text{Me}_2\text{AsI} \quad \ldots \quad (10)
\]

The germanium arsine/tin halide and tin arsine/germanium halide reactions led to an equilibrium (11) with approximately twice as much tin arsine as germanium arsine.

\[
\text{Me}_3\text{SnAsMe}_2 + \text{Me}_3\text{GeBr} \rightleftharpoons \text{Me}_4\text{GeAsMe}_2 + \text{Me}_3\text{SnBr} \quad \ldots \quad (11)
\]
Reactions with Group IV Dialkylamines

These proceeded in the same manner as the reactions of alkyl and phenyl arsines. Thus the germyl arsines reacted with stannyl dimethylamines to evolve dimethylamine forming tin-arsenic bonds according to (12).

\[
\text{Me}_3\text{GeAsHR} + R_3\text{MNM}_{2} \rightarrow \text{Me}_3\text{Ge(Me}_3\text{M)AsR} + \text{Me}_2\text{NH} \quad \ldots \ldots (12)
\]

\[M = \text{Sn}; R = \text{Me}_3\text{Ge}, \text{Me}, \text{Ph}; R' = \text{Me}\]

The yields were not as high as the alkyl and aryl arsine reactions since the trimethylgermyl arsines are unstable towards condensation (13).

\[
2\text{Me}_3\text{GeAsHR} \rightarrow (\text{Me}_3\text{Ge})_2\text{AsR} + \text{RAsH}_2
\]

\[R = \text{Me}, \text{Ph} \quad (13)\]

\[
3(\text{Me}_3\text{Ge})_2\text{AsH} \rightarrow 2(\text{Me}_3\text{Ge})_3\text{As} + \text{AsH}_3
\]

The arsines formed in (13) reacted with the tin dialkylamines\(^5,7\) according to (14). With the more volatile arsine and methyl arsine this took place.

\[
R_{3-n}\text{AsH}_n + n\text{Me}_3\text{SnNM}_{2} \rightarrow (\text{Me}_3\text{Sn})\text{AsR}_{3-n} + n\text{Me}_2\text{NH} \quad \ldots \ldots (14)
\]

\[R = \text{Me}, \text{Ph}; n = 1-3\]
to a lesser extent than with phenylarsine. The mixed trimethylgermyl-(trimethylstannylic)arsines undergo a thermal redistribution (15) providing a further source of the symmetrical arsines.

\[ 2\text{Me}_3\text{Ge}(\text{Me}_3\text{Sn})\text{AsR} \rightarrow (\text{Me}_3\text{Ge})_2\text{AsR} + (\text{Me}_3\text{Sn})_2\text{AsR} \ldots \ldots \ (15) \]

Trimethylgermyl arsines further paralleled alkyl and aryl arsines in that they did not react to cleave silicon-nitrogen bonds.

Small yields of bis[bis(trimethylgermyl)arsine]dimethylgermane and the analogous stannane were prepared by this method according to (16),

\[ \text{Me}_2M\text{(NMe}_2\text{)}_2 + 2(\text{Me}_3\text{Ge})_2\text{AsH} \rightarrow \text{Me}_2M\text{As}(\text{GeMe}_3\text{)}_2 \text{H} + 2\text{Me}_2\text{NH} \ldots \ldots \ (16) \]

but attempts to prepare the tris-arsino derivatives were unsuccessful.

Bis(trimethylsilyl)arsine reacted similarly with germanium and tin amines to form very small amounts of the mixed species (17)

\[ (\text{Me}_3\text{Si})_2\text{AsH} + \text{Me}_3\text{MNMe}_2 \rightarrow (\text{Me}_3\text{Si})_2\text{AsMMe}_3 + \text{HNNMe}_2 \ldots \ldots \ (17) \]

\[ M = \text{Ge, Sn} \]

Bis(trimethylstannylic)arsine did not give any mixed arsines with trimethylgermyl(dimethyl)amine or trimethylsilyl(dimethyl)amine.
The methods used to prepare the arsines described in Chapters 3-6 can be classified into the following six types listed below with typical examples.

(a) The reaction of an arsinoaluminate with a group IV halide (1).

\[ \text{LiAl(AsH}_2\text{)}_4 + 4\text{Me}_3\text{GeBr} \rightarrow 4\text{Me}_3\text{GeAsH}_2 + \text{LiBr} + \text{AlBr}_3 \]  

(b) The reaction of an arsenide with a group IV halide (2).

\[ \text{LiAsPh}_2 + \text{SiH}_3\text{Br} \rightarrow \text{SiH}_3\text{AsPh}_2 + \text{LiBr} \]  

(c) The removal of a hydrogen halide from an arsine and a group IV halide using triethylamine (3).

\[ 3\text{Me}_3\text{SnCl} + \text{AsH}_3 + 3\text{Et}_3\text{N} \rightarrow (\text{Me}_3\text{Sn})_3\text{As} + 3\text{Et}_3\text{NHCl} \]  

(d) The reaction of an arsine with a group IV amine (4).

\[ 2\text{Me}_3\text{GeNM}e_2 + \text{MeAsH}_2 \rightarrow (\text{Me}_3\text{Ge})_2\text{AsMe} + 2\text{Me}_2\text{NH} \]  

(e) The reaction of a silicon arsine with a germanium or tin halide (5).
\[ \text{SiH}_3\text{AsMe}_2 + \text{Me}_3\text{SnCl} \rightarrow \text{Me}_3\text{SnAsMe}_2 + \text{SiH}_3\text{Cl} \]  \hspace{1cm} (5)

(f) Cleavage of one M-As bond in \((R_3M)_3\text{As}\) \((M = \text{Si, Ge, Sn})\) followed by reaction of the anion formed with a protic reagent or a halide. (6 and 7).

\[ \text{(Me}_3\text{Si})_3\text{As} + \text{LiMe} \rightarrow \text{LiAs(Me}_3\text{Si})_2 + \text{Me}_4\text{Si} \]  \hspace{1cm} (6)

\[ \text{LiAs(Me}_3\text{Si})_2 + \text{CH}_3\text{SH} \rightarrow \text{LiSCH}_3 + \text{(Me}_3\text{Si})_2\text{AsH} \]  \hspace{1cm} (7)

Table 5.1 lists the arsines prepared and the methods used.

**Primary Arsines**

These are best prepared by method (a). Method (e) gives good yields of germanium arsines but the ability of tin halides to catalyse the decomposition of primary arsines renders this method unsuitable for tin arsines. Silicon, germanium and tin arsines can be prepared in low yields by method (b).

**Secondary Arsines**

These are best prepared by method (f) while methods (a) and (b) give low yields.

**Tertiary Arsines**

Those of germanium and tin are best prepared by method (e) and method (b) is generally applicable. Methods (a), (d) and (f) are more tedious and do not give better yields than method (b). Method (d) is also unsuitable for the preparation of silicon arsines, presumably due
**TABLE 8.1**

Preparative Methods Used for the Arsines

<table>
<thead>
<tr>
<th>Arsine</th>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Arsines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₃AsH₂</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>Me₃SiH₂AsH₂*</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>Me₃SiAsH₂</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>SiH₃SiH₂AsH₂</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>SiH₂(AsH₂)₂*</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>Me₂Si(AsH₂)₂*</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>GeH₂AsH₂</td>
<td>a</td>
<td>3</td>
</tr>
<tr>
<td>MeGeH₂AsH₂*</td>
<td>a,e</td>
<td>3</td>
</tr>
<tr>
<td>Me₃GeAsH₂*</td>
<td>a,e</td>
<td>3</td>
</tr>
<tr>
<td>Me₂Ge(AsH₂)₂*</td>
<td>e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃SnAsH₂*</td>
<td>a,b</td>
<td>3,6</td>
</tr>
<tr>
<td><strong>Secondary Arsines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SiH₃)₂AsH</td>
<td>f</td>
<td>4</td>
</tr>
<tr>
<td>(Me₃Si)₂AsH</td>
<td>f</td>
<td>4</td>
</tr>
<tr>
<td>Me₃SiAsHMe</td>
<td>f</td>
<td>4</td>
</tr>
<tr>
<td>(Me₃Ge)₂AsH*</td>
<td>.f</td>
<td>5</td>
</tr>
<tr>
<td>Me₃GeAsHMe*</td>
<td>a,b,f</td>
<td>5</td>
</tr>
<tr>
<td>Me₃GeAsHPh*</td>
<td>b,f</td>
<td>5</td>
</tr>
<tr>
<td>(Me₃Sn)₂AsH*</td>
<td>b,f</td>
<td>6</td>
</tr>
<tr>
<td>Me₃SnAsHPh*</td>
<td>f</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Tertiary Arsines</strong></th>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Me₃R₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₃AsMe₂*</td>
<td>a,b</td>
<td>4</td>
</tr>
<tr>
<td>SiH₃AsPh₂*</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>Me₃SiAsMe₂</td>
<td>a,b</td>
<td>4</td>
</tr>
<tr>
<td>Me₃SiAsPh₂*</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>GeH₃AsMe₂*</td>
<td>a,b,e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃GeAsMe₂</td>
<td>b,e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃Ge(AsMe₂)₂</td>
<td>a,b,d,e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃GeAsPh₂*</td>
<td>b,d,e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃Ge(AsMe₂)₂</td>
<td>e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃Ge(AsMe₂)₃</td>
<td>e</td>
<td>5</td>
</tr>
<tr>
<td>Me₃SnAsMe₂</td>
<td>e</td>
<td>6</td>
</tr>
<tr>
<td>Me₃SnAsPh₂</td>
<td>e</td>
<td>6</td>
</tr>
</tbody>
</table>

* denotes new compound

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Table 8.1 (Continued)

<table>
<thead>
<tr>
<th>Arsine</th>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Me}_3\text{Ge})_2\text{AsMe})^*</td>
<td>a,b,c,d,e,f</td>
<td>5</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Ge})_2\text{AsPh})^*</td>
<td>b,d,e</td>
<td>5</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Sn})_2\text{AsMe})</td>
<td>d,e</td>
<td>6</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Sn})_2\text{AsPh})</td>
<td>b,d,e</td>
<td>6</td>
</tr>
</tbody>
</table>

3) **\(\text{Me}_3\text{As}\)**

<table>
<thead>
<tr>
<th>Arsine</th>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{SiH}_3)_3\text{As})</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Si})_3\text{As})</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>(\text{Me}_3\text{SiAs(\text{SiH}_3)})^*</td>
<td>f</td>
<td>4</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Si})_2\text{AsSiH}_3)^*</td>
<td>f</td>
<td>4</td>
</tr>
<tr>
<td>((\text{GeH}_3)_3\text{As})</td>
<td>e</td>
<td>5</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Ge})_3\text{As})</td>
<td>c,d,e</td>
<td>5</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Sn})_3\text{As})</td>
<td>b,c</td>
<td>6</td>
</tr>
</tbody>
</table>

**Other Arsines**

<table>
<thead>
<tr>
<th>Arsine</th>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{r}(\text{SiH}_3)_2\text{AsBH}_2)]^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>(\text{r}(\text{SiH}_3)_2\text{AsBMe}_2)]^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>([\text{GeH}_3)_2\text{AsBH}_2]_3^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>([\text{GeH}_3)_2\text{AsBMe}_2]_3^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>((\text{SiH}_3\text{As})_5)</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>((\text{GeH}_3\text{As})_5)^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Ge})_2\text{AsSnMe}_3)^*</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>(\text{Me}_3\text{GeAs(\text{Me})SnMe}_3)^*</td>
<td>d</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Me}_3\text{GeAs(\text{Ph})SnMe}_3)^*</td>
<td>d</td>
<td>7</td>
</tr>
</tbody>
</table>

* denotes new compound
to the high Si-N bond energy. Method (c) only gives good yields of the tin compounds and using the chlorides the yields decreased in the order Sn > Ge > Si which is in accord with the M-Cl bond energies. This suggests that silicon iodides might be suitable for this reaction but apparently yields are poor.
REFERENCES


VITA AUCTORIS

1947   Born in Aberdeen, Scotland, April 23rd.

1965   Completed secondary education at King Edward VI Grammar School, Chelmsford, England.

1968   Graduated from University of Southampton, England, with an Honours Bachelor of Science Degree in Chemistry.

Award  Science Research Council Studentship 1968-1969.