1,3-divinyl-tetramethyldisilyl chalcogenides.

Ankin. Vahradian

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/508

This online database contains the full-text of PhD dissertations and Masters’ theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.
1,3-DIVINYL-TETRAMETHYLDISILYL CHALCOGENIDES

By

Ankin Vahradian

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Chemistry in partial fulfillment of the requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario
1981
To my wife,
and my parents.
TABLE OF CONTENTS

FOREWORD iv
LIST OF TABLES viii
LIST OF FIGURES ix
ABSTRACT xi

CHAPTER I
EXPERIMENTAL TECHNIQUES 1
1. THE VACUUM LINE 2
2. THE SEPARATION OF VOLATILE MATERIALS 4
3. STORAGE AND REACTION VESSELS 5
4. CLEANING OF RE-USABLE GLASSWARE 8
5. INSTRUMENTATION AND PHYSICAL METHODS 8
(a) Infrared spectroscopy 8
(b) Raman spectroscopy 9
(c) Nuclear magnetic resonance spectroscopy 9
(d) Mass spectrometry 10
(e) Vapour pressure 10

CHAPTER II
THE PREPARATION AND PURIFICATION OF STARTING MATERIALS 11

CHAPTER III
THE SYNTHESIS OF 1,3-DIVINYLTETRAMETHYLDISILYL CHALCOGENIDES 17
1. INTRODUCTION 18
(a) The nature of the silicon atom 18

2. EXPERIMENTAL 24
(a) Preparation of dilithium chalcogenides 24
(b) Reaction of chlorovinyl-dimethylsilane with water 26
(c) Reaction of VinMe₂SiCl with dilithium sulphide, selenide and telluride 27
(d) The reaction of \((\text{VinSiMe}_2)_2E\) with HCl \((E=S,\text{Se},\text{Te})\) 28

3. PHYSICAL PROPERTIES 29
4. DISCUSSION 30

CHAPTER IV. THE CHARACTERIZATION OF 1,3-DI-VINYLTETRAMETHYLDISILYL CHALCOGENIDES 33

1. \(^1H\) AND \(^{13}C\) NUCLEAR MAGNETIC RESONANCE SPECTRA 34
   (a) Description of CH₂=CH- proton resonance pattern 35
   (b) Methyl protons and carbon-13 chemical shifts 44
   (c) Coupling constants 52

2. VIBRATIONAL SPECTRA 58
   (a) Force constant calculations 67

3. THE MASS SPECTRUM OF \((\text{VinSiMe}_2)_2\text{O}\) 70

4. THE REACTIVITY OF 1,3-DIVINYLTETRAMETHYLDISILYL CHALCOGENIDES 70

5. EXPERIMENTAL 71
   (a) Reaction of \((\text{VinSiMe}_2)_2E\) with anhydrous HX \((X=\text{Cl},\text{Br})\) 71
   (b) Reaction of \((\text{VinSiMe}_2)_2\text{O}\) with aqueous HCN 71
   (c) Reaction of \((\text{VinSiMe}_2)_2\text{O}\) with SO₂F₂ 72
(d) Reaction of (VinSiMe₂)₂O with CCl₃SO₂ 72
(e) Reaction of (VinSiMe₂)₂O with CH₃SH 72
(f) Reaction of (VinSiMe₂)₂S with H₂S 73
(g) Reaction of (VinSiMe₂)₂Se with H₂Se 73

6. DISCUSSION 74

CHAPTER V
PARTIAL HALOGENATION OF SOME
SILANES AND GERMANES 78

1. INTRODUCTION 79

2. EXPERIMENTAL 79

(a) Synthesis of iodosilane, Me₃H₃-SiI 79
(b) Attempted preparation of Me₃SiSiMe₂Cl 81
(c) The preparation of H₃GeCl and H₂GeCl₂ 83
(d) The preparation of H₃GeBr 84
(e) The preparation of Me₃GeF and Me₂GeF₂ 85

3. DISCUSSION 86
REFERENCES 90

List of abbreviations
Me, methyl; Vin, vinyl or CH₂=CH; Bu, butyl; Ph, phenyl
v.p., vapour pressure; M, a group IV element
n.m.r., nuclear magnetic resonance; i.r. infrared;
R, Raman; p.p.m., parts per million
X, halogen; E, chalcogen; TMS, tetramethylsilane
ν, stretch; δ, deformation; ρ, rock
R.T., room temperature
LIST OF TABLES

I.1 Slush baths 4

III.1 Selected parameters of various silicon and carbon bonds 20

IV.1 The vinyl $^1H$ n.m.r. parameters of (VinSiMe$_2$)$_2$E species 43

IV.2 Changes in chemical shifts and coupling constants of (VinSiMe$_2$)$_2$E vs. (H$_3$-$n$SiMe$_n$)$_2$E species 54

IV.3 The coupling constants of the vinyl protons 57

IV.4 The i.r. and Raman spectra (cm$^{-1}$) of the (VinSiMe$_2$)$_2$E species 64

IV.5 The force constants of the Si-E bonds (E=O, S, Se, Te) 69
LIST OF FIGURES

I.1 The preparative vacuum system 3
I.2 Storage and reaction vessels 6

IV.1 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$O in C$_6$H$_{12}$ solution at 100.1 MHz 39
IV.2 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$S in C$_6$H$_{12}$ solution at 100.1 MHz 40
IV.3 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$Se in C$_6$H$_{12}$ solution at 100.1 MHz 41
IV.4 The $^1$H n.m.r. spectrum of neat (VinSiMe$_2$)$_2$Te at 100.1 MHz 42

IV.5 The $^{13}$C n.m.r. spectra of (VinSiMe$_2$)$_2$O (a); and (VinSiMe$_2$)$_2$S (b) in C$_6$H$_{12}$ solution 48
IV.6 The $^{13}$C n.m.r. spectra of neat (VinSiMe$_2$)$_2$Se (a); and (VinSiMe$_2$)$_2$Te (b) 49

IV.7 $^{13}$C chemical shifts as a function of the $^1$H chemical shifts (p.p.m.) 50
IV.8 The $^1$H and $^{13}$CH n.m.r. spectra of neat (VinSiMe$_2$)$_2$O (a); and (VinSiMe$_2$)$_2$S (b) 55
IV.9 The $^1$H and $^{13}$CH n.m.r. spectra of neat (VinSiMe$_2$)$_2$Se (a); and (VinSiMe$_2$)$_2$Te (b) 56

IV.10 The liquid phase infrared spectra of (VinSiMe$_2$)$_2$O (a); and (VinSiMe$_2$)$_2$S (b) 60
IV.11 The liquid phase infrared spectra of (VinSiMe$_2$)$_2$Se (a); and (VinSiMe$_2$)$_2$Te (b) 61
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.12</td>
<td>The liquid phase Raman spectrum of ((\text{VinSiMe}_2)_2\text{O})</td>
<td>62</td>
</tr>
<tr>
<td>IV.13</td>
<td>The liquid phase Raman spectrum of ((\text{VinSiMe}_2)_2\text{Se})</td>
<td>63</td>
</tr>
<tr>
<td>IV.14</td>
<td>The (^1\text{H n.m.r.} ) spectrum of ((\text{VinSiMe}_2)_2\text{Se}) with (\text{H}_2\text{Se} ) (excess)</td>
<td>77</td>
</tr>
</tbody>
</table>
ABSTRACT

The work in this thesis is concerned with the synthesis and characterization of some new vinylsilyl species.

The synthetic route involves the metathetical exchange reactions of chlorovinyldimethylsilane with the corresponding dilithium salts, Li₂E (E=O,S,Se,Te), which yield the corresponding (CH₂=CHSiMe₂)₂E. The products were characterized by the usual spectroscopic methods, i.e. ¹H n.m.r. and Raman, as well as by mass spectrometry where appropriate.

The reactivity of 1,3-divinyl-tetramethyldisilyl chalcogenides was studied by reacting them with some simple species such as HCl, HBr, aqueous HCN, SO₂F₂, CCl₃SCl, CH₃SH, H₂S and H₂Se.

Some of the spectroscopic features of (CH₂=CHSiMe₂)₂E were compared with those of some related species such as (HSiMe₂)₂E and (SiMe₃)₂E.

Partial halogenation reactions of some silanes and germanes were also carried out not only for the spectroscopic interest in the products, but also for their importance and utility in the synthesis of new silyl and germyl species.
CHAPTER I

EXPERIMENTAL TECHNIQUES
Halogeno-silanes and -germanes are among the most important intermediates in the synthesis of various silyl and germyl derivatives.

The reactivity of the functional groups is primarily affected by the nature and extent of the organic substituent at the silicon or germanium atom.

In conformity with their volatile nature, sensitivity to hydrolysis, and disagreeable odour, it was necessary to pay careful attention to the design of "gas-liquid" or "solid" handling equipment. Vacuum line techniques\(^1\)\(^-\)\(^4\), both for the preparation and transfer of the material, were of extreme importance. Where certain off-the-line procedures were required, the chemicals and equipment were handled in a nitrogen-filled glove bag.

I.1 THE VACUUM LINE

The vacuum line (Fig. I.1) was constructed with Pyrex glass; it consisted of two manifolds (B,B') (volume ca. 150 ml each). Manifolds (B) and (B') were interconnected by four "U"-traps, and a central manifold (C) leading to two liquid nitrogen backing traps (E), a mercury diffusion pump (E'), and a rotary oil pump (G). Pressure readings between 1-760 Torr (0.13-101.33 kPa) were monitored by the mercury manometers (A,A') (±0.5 Torr); usual pressure readings recorded
were \(1.5 \times 10^{-2}\) Torr or \(2 \times 10^{-3}\) kPa. Pressure readings below 1 Torr (0.13 kPa) were recorded by a Pirani vacuum gauge (D). Because of the marked solubility of the compounds in hydrocarbon grease, high-vacuum Teflon-in-glass stopcocks and silicon-greased ground glass joints were utilized.

I.2 THE SEPARATION OF VOLATILE MATERIALS

The separation of volatile materials in the vacuum line was accomplished by trap-to-trap distillation using low temperature slush baths\(^1,4\). Table I.1 lists

<table>
<thead>
<tr>
<th>Material</th>
<th>Slush temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice/water</td>
<td>0</td>
</tr>
<tr>
<td>ice/salt water</td>
<td>0 to -15</td>
</tr>
<tr>
<td>carbon tetrachloride/liquid N(_2)</td>
<td>-23</td>
</tr>
<tr>
<td>chlorobenzene/liquid N(_2)</td>
<td>-45</td>
</tr>
<tr>
<td>chloroform/liquid N(_2)</td>
<td>-63</td>
</tr>
<tr>
<td>'dry-ice'/acetone (or methanol)</td>
<td>-78</td>
</tr>
<tr>
<td>toluene/liquid N(_2)</td>
<td>-96</td>
</tr>
<tr>
<td>1-bromobutane/liquid N(_2)</td>
<td>-112</td>
</tr>
<tr>
<td>methyl cyclohexane/liquid N(_2)</td>
<td>-126</td>
</tr>
<tr>
<td>n-pentane/liquid N(_2)</td>
<td>-132</td>
</tr>
<tr>
<td>iso-pentane/liquid N(_2)</td>
<td>-160</td>
</tr>
<tr>
<td>liquid N(_2)</td>
<td>-196</td>
</tr>
</tbody>
</table>

*All slush bath temperatures are estimated to ±5° C.*
the slush baths and their corresponding temperatures. The efficiency of separating two or more compounds depends upon the difference of their vapour pressures at different temperatures, the efficiency of the vacuum system, the quantity and relative composition of the mixture, and the rate of distillation. After one or more fractional condensations the purity of the separated compounds was confirmed by spectroscopic analysis.

1.3 STORAGE AND REACTION VESSELS

The storage and reaction vessels used in this work are shown in Figure 1.2. These were constructed of Pyrex-glass. The type of vessel used was determined by the stability, volatility and quantity of the substance in question, while experimental conditions, and the nature of the compound determined the type of stopcock fitted on the reaction or storage vessel.

Solid phase reactions in a solvent were conducted in vessel (A) (e.g. the reaction of lithium and arsenic in ammonia). Vessel (A) was modified to vessel (B) as shown in the diagram, in order to be used as a storage vessel for compounds with very low volatility such as (VinSiMe₂)₂Te. Vessel (C) was used as a storage vessel for simple hydrides and gases that
are stable at R.T. (e.g. SiH₄, GeH₄, HCl, H₂S). Low volatile liquids were stored in vessel (D) (e.g. VinSiMe₂Cl, BCl₃). Vessel (E) (1-4 mm o.d.) was used for sealed tube reactions and for sampling compounds to be utilized for spectroscopic analysis (e.g. raman, n.m.r.). For sealing these tubes, a sharp hot flame was used with an appropriate torch, and the flame was localized in a small area. When a compound has to be kept indefinitely for future use or when it is particularly unstable, it is best to keep it in a sealed tube at a temperature below that of R.T. A glass tube (5 mm o.d.) is attached to a MS 19 ball joint with a constriction at the neck (F), thus facilitating the process of sealing the tube. Furthermore, the use of vessel (F) reduces the use of expensive stopcocks. Opening of sealed tubes on the vacuum line was accomplished with the tube breaker (G). For small scale reactions at low pressures or in the condensed phase, a finger (H) (5-100 ml) fitted with a MS 19 ball joint and a Teflon-in-glass stopcock was used. Vessel (I), fitted with a MS 19 ball joint and an appropriate stopcock, was used to store dry solvents (e.g. Et₂O) under vacuum and in contact with a drying agent such as Li[AlH₄]₂. Vessel (K) was used for gas phase reactions.
I.4 CLEANING OF RE-USABLE GLASSWARE

The thorough cleaning of re-usable glassware is very important in a laboratory, because not only does it reduce waste but also it saves a considerable amount of time. For example, many reactive compounds, if stored in thoroughly clean vessels will not decompose, but their decomposition is apparently catalysed by traces of foreign material. The cleaning of glassware was achieved through such reagents as water, 10% HF, HCl:HNO₃ 3:1, NaOH/ethanolic solution, organic solvents, detergents, etc. Soaking and washing with a brush was found to be a very effective method in achieving the desired results. It cannot be overemphasized that efficient cleaning is no small matter when dealing with compounds such as volatile selenium and tellurium species that readily deposit metallic films that adhere strongly. After cleaning, the glassware was dried in an oven at 100°C.

I.5 INSTRUMENTATION AND PHYSICAL METHODS

(a) Infrared spectroscopy: Infrared spectra were recorded on Beckman I.R. 12 (4000-200 cm⁻¹) and Perkin-Elmer 180 Recorder Console spectrometers; using a 9 cm gas cell (Fig. I.2 J) equipped with KBr windows. A small finger, sealed into the front side of the cell, permitted distillation of small quantities of material into the cell. Gas pressures ranging from 1 to 15 Torr
were usually used. Low volatile liquids were recorded as smears between two CsI or KBr plates in an air tight device. Polyethylene plates were used when recording far-i.r. spectra. The positions of sharp peaks were accurate to ±1 cm⁻¹.

(b) **Raman spectroscopy**: Raman spectra were recorded on a Spectra Physics/Beckman 700 Laser-Raman spectrometer using the 5145 Å excitation of an argon ion laser. The samples were sealed under vacuum in Pyrex glass capillaries (ca. 50-100 mm long; ca. 2 mm o.d.) and polarization measurements were carried out by examining the spectrum with incident light respectively parallel and perpendicular to the axis of a polarcoid analyzer. The depolarization values thus obtained were directly proportional to the true values. Accuracies of ±2 cm⁻¹ were routinely obtained on sharp peaks. The important peaks were expanded to give frequencies accurate to ±0.5 cm⁻¹.

(c) **Nuclear magnetic resonance spectroscopy**

(¹H n.m.r. and ¹³C n.m.r.): The proton spectra were recorded on a JEOL C-60HL spectrometer operating at a resonance frequency of 60 MHz at R.T. Chemical shifts are given in p.p.m. (δ±0.02 p.p.m.) to low field of internal TMS in CCl₄ solution (5%V/V). Chemical shifts were also measured relative to cyclo-
hexane where appropriate. Deviations for coupling constants of neat liquids were $J(\text{HH}) \pm 0.05\, \text{Hz}$, $J(\text{CH}) \pm 0.20\, \text{Hz}$. The carbon-$\text{I}^3$ spectra were obtained on a Bruker CPX 100 (FT model) spectrometer, operating at a resonance frequency of 22,639 MHz, at a probe temperature of 35°C. All spectra were recorded under $^1\text{H}$ noise-decoupling conditions. The samples were sealed in capillaries (ca. 2 mm o.d.) as neat liquids or in cyclohexane solution, and the capillaries were placed coaxially in 5 mm tubes containing tetramethylsilane (TMS) as a standard and CDC$_3$ (CCl$_4$ for proton spectra, to ensure good sample spinning) which served as a lock.

(d) Mass spectrometry: The mass spectra were obtained on a Varian MAT CH5 double focusing spectrometer, equipped with an INCOS 2000 computer system. The spectra were recorded at 70 ev. Molecular ions were also obtained using field ionization techniques where appropriate. The samples were admitted into the spectrometer from a small finger with a 3 mm Teflon-in-glass stopcock. Sealed tubes were broken using a tube breaker (Fig. 1.2G) on a small vacuum line connected to the inlet system of the spectrometer.

(e) Vapour pressures: The vapour pressures of the various species under investigation were obtained by allowing them to expand against a mercury manometer.
CHAPTER II

THE PREPARATION AND PURIFICATION OF STARTING MATERIALS
The following compounds were obtained either through commercial sources, or were prepared by known synthetic procedures. As the synthesis of these compounds was not of primary interest, they are considered 'starting materials'. The purity of these materials was confirmed spectroscopically or by vapour pressure measurements (V.P.) where appropriate.

**ALUMINIUM, Al:** commercial; used as obtained.

**ALUMINIUM TRIIODIDE, AlI₃:** commercial; stored under N₂ at R.T.; resublimed and dried under vacuum.

**AMMONIA, NH₃:** commercial; pumped off under vacuum through a trap held at -78⁰ and dried over sodium or lithium.

**ANTIMONY TRIFLUORIDE, SbF₃:** commercial; dried in a 65⁰ oven for five hours or longer before use.

**ANTIMONY PENTACHLORIDE, SbCl₅:** commercial; used as obtained.

**ARSENIC, As:** commercial; used as obtained.

**BORON TRICHLORIDE, BCl₃:** commercial; degassed at -112⁰ prior to use and stored at R.T. in vessel 'D' fitted with a Teflon-in-glass stopcock; i.r.

**BROMOTRIMETHYLGEMANE, Me₃GeBr:** commercially available; degassed at -78⁰ and stored in vessel 'D' at R.T.; i.r.; n.m.r. 7,8

**BROMOTRIMETHYLSILANE, Me₃SiBr:** commercially available; degassed at -78⁰ before use and stored at R.T.
in vessel 'D'; i.r.\textsuperscript{9,10}, n.m.r.\textsuperscript{11}

**Chlorodimethylvinylsilane**, CH\textsubscript{2}=CHSiMe\textsubscript{2}Cl: commercially available\textsuperscript{a}; degassed at -78\degree and stored at R.T. in vessel 'D'; i.r./\textsuperscript{12}, n.m.r.\textsuperscript{13}

**Chlorotrimethylsilane**, Me\textsubscript{3}SiCl: commercially available\textsuperscript{b}; distilled through traps held at -45\degree, -78\degree, and -196\degree. The pure Me\textsubscript{3}SiCl was condensed in the -78\degree trap and stored at R.T. in vessel 'D'; i.r.\textsuperscript{14}, n.m.r.\textsuperscript{11}, v.p.\textsuperscript{1}

**Dichlorodimethylgermane**, Me\textsubscript{2}GeCl\textsubscript{2}: commercially available\textsuperscript{b}; degassed at -78\degree and stored in vessel 'D' at R.T.; i.r./\textsuperscript{15,16}, n.m.r.\textsuperscript{17}

**Germane**, GeH\textsubscript{4}: commercially available\textsuperscript{e}; purified by passage through traps held at -126\degree and degassed at -196\degree. Stored at R.T. in vessel 'C'; i.r.\textsuperscript{16}, n.m.r.\textsuperscript{17}, v.p.\textsuperscript{1}

**Hexamethyldisilane**, Me\textsubscript{3}SiSiMe\textsubscript{3}: commercially available\textsuperscript{a}; degassed at -78\degree and stored at R.T.; i.r./\textsuperscript{19,20}, n.m.r.\textsuperscript{21}

**Hydrogen chloride**, HCl: commercially available\textsuperscript{e}; degassed at -196\degree and stored in vessel 'C' at R.T.; i.r.\textsuperscript{22}

**Hydrogen iodide**, HI: hydrogen iodide was prepared in the following manner\textsuperscript{23}. A reaction vessel (ca. 250 ml, type 'I') fitted with a stirring bar and a dropping funnel was charged with red phosphorus (10g) or with phos-
phosphorus pentoxide (40g). In order to reduce contamination of the vacuum line by iodine vapour, the adaptor to the vacuum line was plugged with glass wool. After thoroughly evacuating the system, a solution consisting of iodine (4g) and hydroiodic acid (80g or ca. 50ml) was added in drops. The reaction was carried out at R.T. The reaction products were passed through traps held in series at -23°, -78°, and -196°. Pure HI was collected in the -196° trap. Stored at R.T. in vessel 'D'; i.e. 22

HYDROGEN SELENIDE, H₂Se AND D₂Se: hydrogen selenide was prepared in the following manner 24. A finely powdered mixture of aluminium (3.3 g) and selenium (5.6 g) was placed in a small crucible, and a strip of burning magnesium ribbon was plunged into it in order to form Al₂Se₃. After cooling, the products and the crucible were placed in a reaction vessel fitted with a dropping funnel and an adaptor, in order to be able to attach it to the vacuum line. After evacuating the system, distilled water, H₂O or D₂O, was slowly added into the reaction vessel. H₂Se was immediately formed, and after passing it through a trap held at -78° it was collected in another trap held at -196°. Thereafter it was stored at R.T. in vessel 'C'.

HYDROGEN SULPHIDE, H₂S AND D₂S: prepared 25 by an analogous procedure to that for H₂Se, and stored in vessel 'C'.
at R.T.

IODINE, I₂: commercially available; resublimed and degassed at -78° before use.

IODOGERMANANE, H₃GeI: prepared by the reaction of germane with iodine, stored at -78° or -196° in vessel 'D'. Accidental explosions of the reaction carried out in sealed tubes were avoided by using reaction vessels equipped with Teflon-in-glass stopcocks.

LEAD (II) OXIDE, PbO: commercially available; used as obtained.

LITHIUM, Li: commercially available; cleaned with petroleum ether before use.

LITHIUM ALUMINIUM HYDRIDE, Li[AlH₄]: commercially available; used as supplied.

LITHIUM OXIDE, Li₂O: commercially available; used as supplied.

LITHIUM SULPHIDE, Li₂S: commercially available or prepared from the elements in liquid ammonia.

METHANETHIOL, CH₃SH: commercially available; degassed at -196° prior to use; stored at R.T. in vessel 'D'; i.r.

SELENIUM, Se: commercially available; used as supplied.

SILANE, SiH₄: commercially available; degassed at -196° and stored at R.T.; i.r., n.m.r.
SOLVENTS: dimethyl ether\textsuperscript{g} was used as supplied. Diethyl ether\textsuperscript{e} and n-butyl ether\textsuperscript{a} were dried and stored over Li\ce{[AlH_4]} in vessel 'I' at R.T. prior to use. Spectral grade\textsuperscript{c,h} carbon tetrachloride and cyclohexane were vacuum distilled and stored in vessel 'D' at R.T.

SULPHUR, S\textsubscript{8}: commercially available\textsuperscript{8}; used as supplied.

TELLURIUM POWDER, Te: commercially available\textsuperscript{d}; used as supplied.

TETRAMETHYLSILANE, Me\textsubscript{4}Si: commercially available\textsuperscript{f}; stored in vessel 'D' at R.T.; n.m.r.\textsuperscript{29}

COMMERCIAL SUPPLIES

c. Anachemia Chemicals Ltd., Montreal, P.Q.
d. The British Drug Houses Ltd., Poole, Dorset, U.K.
f. Laramie Chemical Co., Laramie, Wy.
g. Matheson Gas Products, East Rutherford, N.J.
h. NMR Specialties Inc., New Kensington, Pa.
i. Ozark-Mahoning Co., Tulsa, Okla.
j. PCR Inc., Gainesville, Fla.
CHAPTER III

THE SYNTHESIS OF

1,3-DIVINYLTETRAMETHYLDISILYL

CHALCOGENIDES
III.1 INTRODUCTION

(a) The nature of the silicon atom: Silicon is a member of Group IV in the periodic table, sharing this position with carbon, germanium, tin, and lead. As is well known, carbon (1s², 2s², 2p²) commonly forms four single covalent bonds and can be considered as undergoing sp³ hybridization with its orbitals directed towards the corners of a tetrahedron. Similarly, although the second row element silicon ([Ne] 3s², 3p², 3d⁰) has nine orbitals of its M shell available for bonding, it nevertheless generally prefers to utilize only four of its valence orbitals in bonding. This is because the 3s and 3p orbitals are energetically more stable than the 3d orbital. Thus, the concept of sp³ hybridization in silicon and its subgroup can still be used to rationalize the same tetrahedral bonding as in carbon. Differences in the properties which give silicon (and its subgroup) its distinctive feature, and serve to differentiate it from carbon, may be rationalized by accounting for two fundamental features. First, silicon's filled L-shell shields its valence orbitals from attractive nuclear forces to a greater extent than that of carbon's K-shell. Thus, the valence electrons in silicon are lost more readily than those in carbon, and silicon is said to be more electro-
positive than carbon. Therefore, many silicon bonds have a rather high ionic character (Table III.1).

This fact explains why silicon-oxygen and silicon-halogen bonds undergo heterolytic fission so readily, and their failure to rupture homolytically at high temperature\(^{31}\). By contrast, the bond energy of the C-Si bond (76.0 Kcal mol\(^{-1}\)) is somewhat lower than the C-C value (82.6 Kcal mol\(^{-1}\)). Similarly, the difference between the Si-H (76.0 Kcal mol\(^{-1}\)) and the C-H bond (98.8 Kcal mol\(^{-1}\)) is even greater. Furthermore, because silicon is more electropositive than either carbon or hydrogen, ionic fission of these bonds always proceeds by nucleophilic attack directly on silicon, and by electrophilic attack on its partner, or by a more or less concerted mechanism.

Silicon has a second distinctive feature, which arises from its second row position in Group IV of the periodic table. It has relatively low-lying empty 3d orbitals, which may be utilized in chemical bonding. These empty d-orbitals may be utilized in the formation of sp\(^3\)d and sp\(^3\)d\(^2\) hybridization. Silicon, however, is thought to never utilize more than two of these d-orbitals, hence the coordination number never exceeds six\(^{31,32}\). In the nd-orbital hypothesis the appearance of \(n\)-acceptor properties of M (M=Group
Table III.1  Selected parameters of various silicon and carbon bonds.*

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electroneg. of Z</th>
<th>Ionicity of Si-Z %</th>
<th>Bond energy of Si-Z Kcal mol⁻¹</th>
<th>Ionicity of C-Z %</th>
<th>Bond energy of C-Z Kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.8</td>
<td>0</td>
<td>53</td>
<td>12</td>
<td>76.0</td>
</tr>
<tr>
<td>H</td>
<td>2.1</td>
<td>2</td>
<td>76</td>
<td>4</td>
<td>98.8</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
<td>12</td>
<td>76</td>
<td>0</td>
<td>82.6</td>
</tr>
<tr>
<td>O</td>
<td>3.5</td>
<td>50</td>
<td>108</td>
<td>22</td>
<td>85.5</td>
</tr>
<tr>
<td>N</td>
<td>3.0</td>
<td>30</td>
<td>77</td>
<td>7</td>
<td>72.8</td>
</tr>
<tr>
<td>S</td>
<td>2.5</td>
<td>12</td>
<td>70</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>4.0</td>
<td>70</td>
<td>135</td>
<td>43</td>
<td>116.0</td>
</tr>
<tr>
<td>Cl</td>
<td>3.0</td>
<td>30</td>
<td>91</td>
<td>7</td>
<td>81.0</td>
</tr>
<tr>
<td>Br</td>
<td>2.8</td>
<td>22</td>
<td>74</td>
<td>2</td>
<td>68.0</td>
</tr>
<tr>
<td>I</td>
<td>2.5</td>
<td>8</td>
<td>56</td>
<td>0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

*Reference 33

IVW elements) is the result of partial transfer of lone pair(s) or π-electrons of X (X=an atom with lone pair(s) or an unsaturated group) to the nd-orbitals of M (p→d)π interaction. The ability of the substituent X to form (p→d)π M-X bonds is known to be proportional to the resonance constants δR of the substituent. In this respect, resonance hybrids, such as (a)-(c) shown
below, have been proposed to account for the shortening of the Si-X bond length, compared to the calculated value. However, the relationship between the resonance concept and the view of a \((p\rightarrow d)_\pi\) bond is complicated by the polarity of the \(\sigma\)-bond, which, in addition to exerting a direct influence on the \(\pi\)-orbitals, brings about changes in the hybridization of the \(\sigma\)-bonding orbitals. Nevertheless, the larger the halogen atom the less the amount of \((p\rightarrow d)_\pi\) bonding, possibly because of increasingly poorer overlap. Replacement of the Si atom by Ge leads to less appreciable \((p\rightarrow d)_\pi\) interaction, presumably, in part due to the presence of a radial node in the 4d orbitals. The linking of vinyl groups to the silicon atom leads to such a class of compounds, wherein the \(\sigma\)-carbon of the vinyl group is analogous to the ipso carbon of the phenyl ring, and the vinyl \(\sigma\)-carbon is related to the ortho phenyl carbon in the corres-
ponding PhX compounds, e.g.

\[ \beta \alpha \]

\[ \text{SiX}_3 \]

The earlier research of silyl species containing phenyl or vinyl groups has been motivated by the need for polymeric materials of greater thermal stability than the conventional organic polymers. Added motivation however, for research in the vinyl-metal field came from the increasing interest in chemical bonding in organometallic compounds. Chemical evidence for \((p \rightarrow d)_\pi\) bonding between silicon and a vinyl group has been inferred from anti-Markownikoff rule of addition of hydrogen halides to vinyltrimethylsilane\(^\text{30}\), i.e.

\[
\text{Me}_3\text{SiCH}=\text{CH}_2 + \text{HX} \rightarrow \text{Me}_3\text{SiCH}_2\text{CH}_2\text{X} \quad (1)
\]

The positive inductive effect of the \(\text{Me}_3\text{Si}\) group which operates in favour of the Markownikoff rule, i.e. \(\text{Me}_3\text{Si}^+\text{CH}=\text{CH}_2\) is outweighed by the participation of the \(\pi\)-electrons of the vinyl group in the d-orbitals of silicon, i.e. \(\text{Me}_3\text{Si}^-\text{CH}=\text{CH}_2^+\). However,
the latter effect can be overcompensated by the positive inductive effect of a methyl group in the α-position, \( \text{Me}_3\text{SiC(Me)}\text{=CH}_2 \), so that the addition of hydrogen halides yields products with Markownikoff's orientation \( \text{Me}_3\text{SiClMe}_2 \). This implies that the Si-C bond, which possesses partial double bond character, is even capable of participating in conjugation, otherwise it would hardly be possible to explain the anti-Markownikoff addition of organolithium compounds to triphenylvinylsilane, which occurs only with highly conjugated systems\(^{39}\). Replacement of a methyl group by siloxy groups leading to vinylmethysiloxane is reflected in the reactivity of the heavy atom skeleton C=C-Si-O. Namely, the reactivity is the result of at least three mechanistic effects: (a) weakening of the positive inductive effect of the silyl group, (b) \((p\rightarrow d)^\pi\) interaction between silicon and the vinyl group, and (c) competitive \((p\rightarrow d)^\pi\) conjugation of silicon with the two electron pairs of oxygen. The operation of the latter effect has been shown by the increased reactivity of the double bond in 3-vinylheptamethyltrisiloxane as compared with that in vinyl pentamethyldisiloxane, as a result of the weakening of the original \((p\rightarrow d)^\pi\) bond between the vinyl group and silicon\(^{40}\). Similar conclusions
have been reached on the basis of infrared and nuclear magnetic studies\textsuperscript{41,42}.

In order to better understand the effect of the silicon atom upon the behaviour of a proximate organic functional group and vice versa, a systematic study of unexplored organosilyl groups linked to a Group IV element was undertaken. Thus the present chapter describes the preparation of a series of bis(vinylidimethylsilyl) chalcogenides; (1,3-divinyl-tetramethyldisilylethylene) chalcogenides; (VinMe\textsubscript{2}Si\textsubscript{2})\textsubscript{2}E where E = O, S, Se, Te; Vin = -CH=CH\textsubscript{2}, and their spectroscopic characterization. The synthetic route involves the metathetical reactions of chlorevinylidimethylsilane with the corresponding dilithium salt, Li\textsubscript{2}E. The siloxane (VinMe\textsubscript{2}Si)\textsubscript{2}O, the only known compound\textsuperscript{43} of this series, was readily prepared by the hydrolysis of VinMe\textsubscript{2}SiCl. While VinMe\textsubscript{2}SiCl was commercially available, the dilithium salts Li\textsubscript{2}E (E = S, Se, Te) were prepared from the elements in liquid ammonia. Spectral evidence was sought for tentative structural assignments of the title compounds by examining the infrared, Raman, $^1$H and $^{13}$C n.m.r. spectroscopic features, as well as the mass spectra where appropriate.

III.2 EXPERIMENTAL

(a) Preparation of dilithium chalcogenides
$$2\text{Li} + \text{E} \overset{\text{liq. NH}_3}{\underset{-78}{\longrightarrow}} \text{Li}_2\text{E} \quad (\text{E}=\text{S,Se,Te}) \quad (2)$$

In a typical experiment the reaction vessel was a bulb (volume about 70 ml) the neck of which was extended into a tube (ca. 10 cm; 10 mm o.d.) terminating in a high-vacuum Teflon-in-glass stopcock and glass joint for attachment to the vacuum line. The reactor was evacuated and purged with dry nitrogen. The stopcock plug was removed in a dry box, and clean lithium wire (0.0694 g; 10.00 mmol), powdered selenium (0.3960 g; 5.02 mmol), and a small magnetic stirring bar were added to the reactor. The stopcock was replaced and the vessel was then thoroughly evacuated on the vacuum line. Dry ammonia (about 12 ml) was then distilled into the vessel held at -196°C. The stopcock was closed and the reaction mixture was allowed to stand at -78°C with occasional shaking until the blue color of dissolved lithium was discharged (about 10-12 hours). This was slower if the lithium wire had an oxide coating. With frequent cautious warming and shaking, while monitoring the pressure of the ammonia, the reaction time could be decreased greatly. Upon completion of the reaction, the ammonia was distilled out of the reactor under vacuum and the residual solid was heated to 150-155°C in vacuo for
5-6 hours. The dilithium selenide thus prepared is light grey and should show no signs of residual lithium or selenium; polyselenides impart a characteristic red colour to the material. Hydrolysis gave typically 98% of the selenium content required for \( \text{Li}_2\text{Se} \) as \( \text{H}_2\text{Se} \). The dilithium telluride was prepared in a similar manner from lithium wire (0.0694 g; 10 mmol) and powdered tellurium (0.6390 g; 5.01 mmol). It is characteristically a darker grey than the selenide, it appeared homogeneous. Dilithium sulphide, available commercially, was found to contain dilithium oxide, and hence it was prepared as above from lithium wire (0.0694 g; 10 mmol) and sulphur powder (0.162 g; 5.05 mmol). It is a characteristically yellow compound, which slowly hydrolyzes to \( \text{Li}_2\text{O} \) and \( \text{H}_2\text{S} \). Hence the dilithium salts were stored under nitrogen at R.T.

(b) Reaction of chlorodimethylvinylsilane with water

\[
2\text{VinMe}_2\text{SiCl} + \text{H}_2\text{O} \rightarrow (\text{VinMe}_2\text{Si})_2\text{O} + 2\text{HCl}
\] (3)

Typically, \( \text{VinMe}_2\text{SiCl} \) (5.37 mmol) was condensed, under vacuum conditions, into a reaction tube (ca. 20 ml) containing 8 ml of degassed distilled water.
The stopcock was closed and the contents were allowed to react at R.T. with occasional shaking. After about 40 minutes the volatile material was distilled through a series of 'U'-traps held at -23°, -45°, and -196°. The trap at -23° retained the excess water, while that at -45° contained (VinMe₂Si)₂O. Traces of (VinMe₂Si)₂O were also collected in the trap at -196°, and the amount increased with longer fractionation time and back pumping. The fraction at -45° was then collected in a storage vessel, and then passed through a loosely packed tube with small amounts of phosphorus V oxide supported on glass wool. Double passes of the oxide through P₄O₁₀ afforded complete removal of the water as indicated by the absence of ν(OH) in the infrared spectrum. In the presence of larger amounts of P₄O₁₀ it appears that (VinMe₂Si)₂O reacts with P₄O₁₀ to form presumably phosphates of the type (VinMe₂Si)₃PO₄ and/or (-PO₃SiMe₂Vin⁻)ₙ.⁴⁷,⁴⁸ The yield of (VinMe₂Si)₂O, based on the VinMe₂SiCl consumed, was 89%. Informative identification of (VinMe₂Si)₂O was obtained from the mass spectrum, which gave the major peak at m/e 171 (100%) (C₇H₁₅Si₂O)⁺ corresponding to homolytic cleavage of methyl groups from the molecular ion P⁺-CH₃.

(c) Reaction of VinMe₂SiCl with dilithium sulphide, selenide, and telluride
Diethyl ether (ca. 15 ml) and VinMe₂SiCl (1.807 g; 15 mmol) were distilled in vacuo into the reaction vessel held at -196° and containing dilithium selenide (ca. 8.00 mmol) prepared as above. The mixture was allowed to warm to R.T. and stirred for about seventy hours. After this time the volatile material was distilled in vacuo out of the reactor and fractionated through traps held at -45° and -196°. Diethyl ether and traces of unreacted VinMe₂SiCl were identified in the -196° trap. The contents of the trap that was maintained at -45° were redistilled through traps held in series at -23°, -45°, and -196°. The former trap retained pure bis(vinylidimethylsilyl) selenide \[ (\text{VinMe}_2\text{Si})_2\text{Se} , 3.80 \text{ mmol} , 80\% \text{ yield} \]. Bis(vinylidimethylsilyl)oxide was found in the trap held at -45° (identified by the characteristic strong band at 1049 cm⁻¹ in the i.r. spectrum of the gas). High yields of bis(vinylidimethylsilyl)telluride \((\text{VinMe}_2\text{Si})_2\text{Te} \), in the range of 70-85% were obtained by an analogous procedure using \(\text{Li}_2\text{Te} \) (ca. 6.00 mmol), diethyl ether (ca. 15 ml) and VinMe₂SiCl (10.50 mmol). Yields of 85-90% of bis(vinylidimethylsilyl) sulphide were analogously obtained using \(\text{Li}_2\text{S} \) (ca. 5.00 mmol), diethyl ether (ca. 15 ml) and VinMe₂SiCl (10.00 mmol).

(d) Reaction of \((\text{VinMe}_2\text{Si})_2\text{E} \) \(\text{E} = \text{S} , \text{Se} , \text{Te} \) with HCl
The reaction of bis(vinylidimethylsilyl)chalcogenides with an excess of gaseous hydrogen chloride indicated the protolytic cleavage of the S–E (E=S, Se, Te) bond.

\[(\text{VinMe}_2\text{Si})_2\text{E} + 2\text{HCl} \rightarrow 2\text{VinMe}_2\text{SiCl} + \text{E}_2\text{H} \tag{4}\]

Typically, \((\text{VinMe}_2\text{Si})_2\text{S}\) (1.25 mmol) and HCl (3.20 mmol) were condensed in vacuo into a small vessel (ca. 30 ml; type 'D'), equipped with a Teflon-in-glass stopcock) held at -196°. The reactants were then allowed to warm to R.T. for about 30 minutes. After this time the products were fractionally distilled through a series of traps held at -78° and -196°. \(\text{VinMe}_2\text{SiCl}\) was recovered in the former trap (2.40 mmol; 92% yield), identified by \(^1\text{H}\) n.m.r.\(^{13}\) and vibrational\(^{12}\) spectroscopy. \(\text{E}_2\text{H}\) and unreacted HCl were condensed into the latter trap. HCl was identified by vibrational\(^{22}\) spectroscopy, the products of this reaction provided an indirect evidence for the monomeric nature of \((\text{VinMe}_2\text{Si})_2\text{E}\) where \(\text{E}=\text{S}, \text{Se}, \text{Te}\).

III.3 PHYSICAL PROPERTIES

Bis(vinylidimethylsilyl) chalcogenides are all liquids, the oxide and the sulphide are clear colourless liquids, while the selenide is pale yellow, and the telluride is very deep yellow or gold in colour. The sulphide, selenide, and telluride are of lower volatility than the oxide, with revolting
and persisting odours. Their volatility is sufficient that they could be easily handled under vacuum conditions, provided contact with silicon-grease was kept to a minimum. They are very easily oxidized upon exposure to air or moisture, with the liberation of hydrogen chalcogenide, \( H_2E \) (\( E=S,Se,Te \)). They are stable at R.T. and all the chalcogenides were kept in sealed tubes.

III.4 DISCUSSION

Exchange reactions of type (5) represent one of the most widely encountered types of chemical transformations, characteristic of inorganic, organic, and organometallic compounds, e.g.

\[
AX + BY_{\text{solvent}} \rightarrow BX + AY \tag{5}
\]

The use of this type of metathesis between Group IV halides and dilithium salts has been demonstrated previously for the synthesis of a number of disilyl and digermyl chalcogenides\(^{49,50}\), \((\text{Me}_3-n\text{H}_n\text{M})_2E\) where \( M=\text{Si,Ge}; E=O,S,Se,Te; n=0\rightarrow 3 \). In this study this approach was extended to the synthesis of otherwise inaccessible vinyl-containing species, i.e.

\[
2\text{VinMe}_2\text{SiCl} + \text{Li}_2E \rightarrow (\text{VinMe}_2\text{Si})_2E + 2\text{LiCl} \tag{6}
\]

\( E=S,Se,Te \)
The reactions were carried out at R.T. in diethyl ether as solvent. Upon the basis of the observed material balance the yields of the products are high (ca. 80-90%), and the only significant loss of material was due to the susceptible nature of the Si-Cl and Si-E bond to hydrolysis. The presence of disilazane (VinMe₂Si)₂NH was often observed in the mass spectrum in cases where the dilithium salt contained ammonia. e.g.

\[
\begin{align*}
\text{P m/e 161 (Me₆Si₂NH)}^+ & \text{ 5%}, \\
\text{P-CH₃ m/e 146 (Me₅Si₂NH)}^+ & \text{ 100%}
\end{align*}
\]

The use of a slight excess of chalcogen and removal of solvated ammonia from Li₂E (7) resulted in complete conversion of VinMe₂SiCl into the corresponding Si-E species. The oxide, (VinMe₂Si)₂O was readily obtained.

\[
\text{2Li} + \text{E liq. ammonia} \xrightarrow{\Delta} \text{Li₂EₙNH₃} \xrightarrow{-78^°} \text{Li₂E} \xrightarrow{160-185^°} \text{nNH₃}
\]

(7)

by the hydrolysis of the chloride. The ease of its formation is, in part, to be found in the exceptionally high Si-O thermochemical bond energy. Another way
of obtaining (VinMe₂Si)₂O is by the reaction between Li₂O and VinMe₂SiCl in diethyl ether. Structural characterization of all the chalcogenides was obtained by ¹H and ¹³C n.m.r. and vibrational spectroscopy and, in the case of the oxide, from its electron impact mass spectrum.
CHAPTER IV

THE CHARACTERIZATION OF

1,3-DIVINYLTETRAMETHYLDISILYL CHALCOGENIDES

$(\text{VinMe}_2\text{Si})_2\text{E}$ where $\text{E}=\text{O}, \text{S}, \text{Se}, \text{Te}$
IV.1 $^1{\text{H}}$ AND $^{13}{\text{C}}$ NUCLEAR MAGNETIC SPECTRA

Over the last two decades nuclear magnetic resonance spectroscopy (n.m.r.) has occupied a leading position among the various spectroscopic methods, and in fact, it now appears to be recognized as an independent scientific discipline. The fundamental feature of the n.m.r. spectra is the appearance of two parameters, the chemical shifts of equivalent nuclei and the spin-spin coupling constants between magnetically non-equivalent nuclei. Both parameters, the chemical shift and the coupling constant, are closely associated with the electronic structure of a molecule. The $^1{\text{H}}$ chemical shifts are dependent on both magnetic and electric fields, and are very sensitive to the nature and spatial orientation of substituents. Similarly, the carbon-$^{13}$ chemical shifts indicate both the type and structural environment of each carbon atom. Electronegativity, hybridization, and diamagnetic anisotropy effects all affect the carbon-$^{13}$ chemical shifts just as they do for protons, but in a more complex fashion.\textsuperscript{51,52,53} The chemical shifts of related compounds may be compared in terms of contributions from magnetically anisotropic atoms or bonds, inductive effects, and others as appropriate. The coupling constants are dependent on electric
fields, but independent of magnetic fields, and are sensitive to conformation, bond angles, bond lengths, and to the electronegativity of substituents. Both the chemical shift and the coupling constant also depend on external factors such as solvent and temperature.

The usefulness of the chemical shifts and the coupling constants in providing an insight into the electron distribution and bonding characteristics as well as the conformation of molecules is well documented. There has been much concern about the bonding between silicon and electronegative elements or groups. However, the nature of this bonding and, in particular, its variation with the Group IV elements remains a matter for speculation. Quantification of the transmission of substituent effects governing the changes of the n.m.r. parameters presented herein for the new species (CH$_2$=CHSiMe$_2$)$_2$E is, therefore, very difficult.

(a) **Description Of The CH$_2$=CH- Proton Resonance Pattern**

Figures IV.1 - IV.4 at 100.1 MHz and Figures IV.8 and IV.9 at 60 MHz show the $^1$H resonance spectra of the four 1,3-divinyl-tetramethyldisilyl chalcogenides, each featuring the resonance pattern characteristic
of the vinyl group. The vinyl group possesses three magnetically non-equivalent hydrogen nuclei, and constitutes a typical ABC spin system. The protons of the vinyl group of the series of compounds may be labeled as follows:

\[
\begin{array}{c}
\text{SiMe}_2 \\
\text{G} \\
\text{SiMe}_2
\end{array}
\]

The proton A is trans to C and cis to SiMe₂, while the proton B is cis to C and trans to SiMe₂. Thus, A, B, and C all experience different environments and exhibit different chemical shifts. However, the resonance pattern of the CH₂=CH- group is not just a chemical shift phenomenon, but arises because of the spin-spin coupling between the three protons.

A proposal has been made of analyzing or synthesizing the proton resonance pattern of an ABC three spin system which is approached as follows. First, for one nucleus of spin 1/2 there are two energy states \( \alpha \) and \( \beta \) which can be connected with the corresponding transition, i.e.
The actual transition may be symbolized with a vertical bar \( \bar{1} \). Second, for two interacting nuclei with a spin of \( 1/2 \), which constitute an \( AB \) case, the energy diagram is as shown below.

\[
\begin{array}{c}
\alpha \beta \\
\alpha \alpha \\
\downarrow \\
\downarrow \\
\end{array} \quad \begin{array}{c}
\uparrow \beta \beta \\
\uparrow \beta \alpha \\
\end{array}
\]

(symbol)

An alternate way of looking at this diagram for the two nuclei, is the resultant of the symbolic multiplication:

\[
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} \times \begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= \begin{pmatrix}
\alpha \alpha \\
\alpha \beta \\
\beta \alpha \\
\beta \beta
\end{pmatrix}
\]

Thirdly, consider three nuclei with spin of \( 1/2 \), which constitute an \( ABC \) case. This system results from the multiplication:

\[
\begin{pmatrix}
\alpha \\
\beta \\
\gamma
\end{pmatrix} \times \begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= \begin{pmatrix}
\alpha \alpha \alpha \\
\alpha \alpha \beta \\
\alpha \beta \alpha \\
\alpha \beta \beta \\
\beta \alpha \alpha \\
\beta \alpha \beta \\
\beta \beta \alpha \\
\beta \beta \beta
\end{pmatrix}
\]

The resultant energy diagram shows that unsymmetrical three-spin system has eight energy levels, and at
high magnetic fields generates 12 strong transitions. The corners of the cube may be taken to represent the eight energy levels, so that when the cube is oriented with one body diagonal vertical, the energy levels are grouped 1,3,3,1 corresponding to states \(-3/2, -1/2, +1/2, +3/2\). The three sets of four parallel edges represent the A, B, and C quartets of transition lines. The three body diagonals represent "combination" lines which are indistinguishable from the other 12 lines in some cases. Apparently, in the \(^1\)H n.m.r. spectra of 1,3-divinyl-tetramethyldisilyl chalcogenides, Figures IV.1-IV.4, the 12 resonance lines are clearly observed and determination of the chemical shifts of the three protons and the coupling constants \((J_{AC}, J_{AB}, J_{BC})\) is a rather involved procedure as compared to other cases, and ideally should be approached by direct computer calculation. However, for the purposes of this study an assignment of the observed frequencies, intensities, and chemical shifts of the \(\text{CH}_2=\text{CH}\) resonance lines was based on comparisons with published vinyl compounds as listed in Table IV.1. The numbering of the resonance lines of the spectra bare a similarity to that of vinyltrimethyilsilane, \(\text{CH}_2=\text{CHSiMe}_3\). The spectra of the vinyl protons of the related silyl species have been analyzed using
Figure IV.1 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$O in C$_6$H$_{12}$ solution at 100.1 MHz.
Figure IV.2 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$S in $^6$H$_{12}$ solution at 100.1 MHz.
Figure IV.3 The $^1$H n.m.r. spectrum of (VinSiMe$_2$)$_2$Se in C$_6$H$_{12}$ solution at 100.1 MHz.
Figure IV.4 The $^1$H n.m.r. spectrum of neat $(\text{VinSiMe}_2)_2\text{Te}$ at 100.1 MHz.
Table IV.1 The vinyl $^1$H n.m.r. parameters of (VinSiMe$_2$)$_2$E species.

<table>
<thead>
<tr>
<th>LINE</th>
<th>(CH$_2$=CHSiMe$_2$)$_2$O</th>
<th>(CH$_2$=CHSiMe$_2$)$_2$S</th>
<th>(CH$_2$=CHSiMe$_2$)$_2$Se</th>
<th>(CH$_2$=CHSiMe$_2$)$_2$Te</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HEIGHT (PPM)</td>
<td>FREQUENCY (Hz)</td>
<td>HEIGHT (PPM)</td>
<td>FREQUENCY (Hz)</td>
</tr>
<tr>
<td>1</td>
<td>150.27</td>
<td>629.72</td>
<td>60.43</td>
<td>639.45</td>
</tr>
<tr>
<td>2</td>
<td>375.09</td>
<td>614.83</td>
<td>182.86</td>
<td>624.96</td>
</tr>
<tr>
<td>3</td>
<td>204.41</td>
<td>611.67</td>
<td>127.53</td>
<td>621.03</td>
</tr>
<tr>
<td>4</td>
<td>1206.67</td>
<td>596.75</td>
<td>472.04</td>
<td>606.54</td>
</tr>
<tr>
<td>5</td>
<td>168.28</td>
<td>594.18</td>
<td>222.96</td>
<td>602.08</td>
</tr>
<tr>
<td>6</td>
<td>1224.37</td>
<td>590.09</td>
<td>515.60</td>
<td>596.86</td>
</tr>
<tr>
<td>7</td>
<td>397.54</td>
<td>581.41</td>
<td>199.87</td>
<td>587.57</td>
</tr>
<tr>
<td>8</td>
<td>915.09</td>
<td>578.79</td>
<td>408.70</td>
<td>584.59</td>
</tr>
<tr>
<td>9</td>
<td>131.90</td>
<td>575.21</td>
<td>101.16</td>
<td>582.29</td>
</tr>
<tr>
<td>10</td>
<td>400.96</td>
<td>572.59</td>
<td>212.78</td>
<td>579.40</td>
</tr>
<tr>
<td>11</td>
<td>286.45</td>
<td>560.75</td>
<td>147.73</td>
<td>566.18</td>
</tr>
<tr>
<td>12</td>
<td>236.89</td>
<td>554.65</td>
<td>124.68</td>
<td>560.99</td>
</tr>
</tbody>
</table>

The spectra were recorded at 100.1 MHz in cyclohexane solution at room temperature. The numbering of the lines is tentative. The frequencies (591.35-592.63 Hz) for the telluride deviate from its accuracy because the sample contained some oxide.
the method of Castellano and Waught\textsuperscript{58} modified by Cavanaugh\textsuperscript{59}. Differences in the appearance of the resonance pattern are observed when the spectra recorded at 100.1 MHz (Figures IV.1-IV.4) and 60 MHz (Figures IV.6-IV.9) are compared. However, even at high-field strength (100.1 MHz) significant complicating effects are still present. Closer examination of the spectra (Figures IV.1-IV.4) shows that replacement of S (Se or Te) by the more electronegative oxygen with smaller magnetic anisotropy leads to some collapse of the (ABC) spectrum, such that the lines 4 and 5 appear as a single line. In all cases the proton H\textsubscript{C} on the a-carbon experiences the largest deshielding which increases progressively as the chalcogen changes from oxygen to tellurium. The changes in the chemical shift values of the resonance lines involving the protons A and B are small (the chemical shifts relate to individual protons by means of the relation \( J_{\text{trans}} > J_{\text{cis}} > J_{\text{gem}} \)) between the sulhide, selenide, and telluride. The largest shift along the series can be seen between the oxide and the sulphide.

(b) \textbf{Methyl Protons And Carbon-13 Chemical Shifts}

The observed methyl proton and carbon-13 parameters of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{E}\) vs. \((\text{H}_3\text{SiMe}_n)_2\text{E}\) where
E=O,S,Se,Te; and m=2,3 are given in Table IV.2. The

$^1H$ and $^{13}C$ n.m.r. spectra are shown in Figures IV.1-

IV.4 and Figures IV.5-IV.6, respectively. The $^1H$ n.m.r. 
spectra of $(VinSiMe_2)_2E$ show that the methyl reso-
nance is a single peak, indicating the absence of any 
observable coupling with the vinyl proton $(H_c)$ on the 
$\alpha$-carbon. The values of the proton chemical shifts of 
the methyl group $^1H \delta$ (Me) of $(VinSiMe_2)_2E$ fall generally between the values of those obtained for $(HSiMe_2)_2E$ 
and $(SiMe_3)_2E^{60}$. The general trend of decreasing of 
$^1H \delta$(Me) in the sequence E=Te→Se→S→O persists in 
the three series of compounds. Similar trends for other 
Group IV species have been discussed in terms of a 
major contribution from diamagnetic anisotropy of the 
substituents and related intramolecular effects$^{61}$. 

Closer examination of $^1H \delta$(Me) of the vinyl species 
reveals that the values are essentially the same as 
those for $(HSiMe_2)_2E$ where E=O,S,Te and $(SiMe_3)_2E$ 
where E=S,Se,Te. Thus, the largest deviation in the 
magnitude of $^1H \delta$(Me) is shown between the selenides 

$[(VinSiMe_2)_2Se(0.45 \text{ p.p.m.})$ and $(HSiMe_2)_2Se (0.55 \text{ p.p.m.})]$ 
and oxides $[(VinSiMe_2)_2O (0.12 \text{ p.p.m.})$ and $(SiMe_3)_2O$ 
$(0.06 \text{ p.p.m.})]$ with chemical shift differences of 
0.06 p.p.m. While the shift of $^1H\delta$(Me) values form 
0.06→0.12→0.14 p.p.m. in the series $(SiMe_3)_2O$ →
\[ \text{CH}_2\text{=CHSiMe}_2\text{O} \rightarrow \text{HSiMe}_2\text{O} \quad (0.14 \text{ p.p.m.}) \] implies weakening of the oxygen-silicon (p→d) bond, the magnitude of \( ^1\text{H} \delta(\text{Me}) \) values for the selenides \((\text{SiMe}_3)_2\text{Se} 0.42 \rightarrow (\text{CH}_2\text{=CHSiMe}_2)_2\text{Se} 0.45 \rightarrow (\text{HSiMe}_2)_2\text{Se} 0.51 \text{ p.p.m.}\) suggests that the vinyl group behaves as do the methyl, although the electronegativity of the vinyl group has been inferred to be comparable to that of a hydridic hydrogen atom\(^{62}\). The effect of the vinyl group is, however, large upon the carbon-13 chemical shifts, such that the trend of shielding parallels only that of \((\text{SiMe}_3)_2\text{E}\). The magnitude of the values indicate that the methyl carbon in the vinyl-containing species are more shielded and the shielding increases as it does for the protons in the series \(\text{Te}(3.60) \rightarrow \text{Se}(2.67) \rightarrow \text{S}(2.28) \rightarrow \text{O}(-0.44) \) p.p.m. As can be seen from Figure IV.7, there is, in general, a linear relationship between the \(^{13}\text{C} \) and \(^1\text{H} \) chemical shifts for \(\text{E} = \text{S, Se, and Te}\). The linear correlation suggests that similar factors are responsible for the observed trends in the \(^{13}\text{C} \) and \(^1\text{H} \) chemical shifts.

The straightforward assignment of the \(^{13}\text{C} \) n.m.r. peaks of the \(\text{CH}_2\text{=CH-} \) group was based on the relative intensities of the \(^{13}\text{C} \) signals and comparison with the \( \delta(^{13}\text{C}) \) values for the related species\(^{63}\). As can be
seen from Table IV.2 and Figures IV.5 and IV.6. The carbon-13 resonances of the sp² carbons appear considerably down-field relative to those of the sp³ carbon. The shielding of the sp³ carbons is much more sensitive to substituent changes than the sp² carbons. Thus as the chalcogen changes from oxygen to tellurium there is a slight successive down-field shift in the \( ^{13}\text{C}(\text{sp}^2) \) resonances matching a larger similar shift in the sp³ resonances. The effect of chalcogen change is markedly attenuated upon \( \delta ^{13}\text{C}(\text{sp}^2) \) such that the values of \( \delta (\text{O}_2) \) and \( \delta (\text{O}_\alpha) \) are relatively small between the selenide and telluride (\( \Delta = 0.02 \) p.p.m.) and the sulphide and selenide (0.07 p.p.m.), respectively. In contrast to the successive down-field shift of the \( ^{13}\text{C}(\text{sp}^2) \) resonances from oxygen to tellurium, the internal chemical shift \( \Delta = \delta (\text{O}_\alpha) - \delta (\text{O}_2) \) increases from Se (7.04) → S (7.17) → Te (7.21) → O (7.98) p.p.m. It has been suggested that the internal chemical shift is a measure of a double bond polarization in the concept of (a) and if other ef-

\[
\begin{align*}
\text{H} & \overset{\delta}{\rightarrow} \text{H} \\
\text{C} & = \text{C} \\
\text{H} & \overset{\beta}{\underset{\alpha}{\rightarrow}} \text{H}
\end{align*}
\]

(a)
Figure IV.5 The $^{13}$C n.m.r. spectra of (VinSiMe$_2$)$_2$O (a) and (VinSiMe$_2$)$_2$S (b) in C$_6$H$_{12}$ solution.
Figure IV.6. The $^{13}C$ n.m.r. spectra of neat (Vinylidene) and (Vinylidene) (a) and (b).
Figure IV.7 $^{13}$C chemical shifts as a function of the $^1$H chemical shifts (p.p.m.). The points $\bullet$ and $\circ$ refer to $(CH_2=CHSiMe_2)_2E$ and $(SiMe_3)_2E$ respectively.
### Table IV.2 Changes in chemical shifts and coupling constants of \((\text{CH}_2=\text{OHSiMe}_2)_2\text{E}^*\) vs. \((\text{H}_3\text{SiMe}_n)_2\text{E}\) species.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(1^1\text{H}\delta(\text{Me}))</th>
<th>(1^3\text{C}\delta(\text{Me}))</th>
<th>(1^3\text{C}\delta(\text{CH}_2))</th>
<th>(1^3\text{C}\delta(\text{CH}))</th>
<th>(1^3\text{C}\delta(\text{Me}))</th>
<th>(J^{1^3\text{CH}}(\text{Me}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.12</td>
<td>-0.44</td>
<td>130.85</td>
<td>138.83</td>
<td>118.0</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>0.36</td>
<td>2.28</td>
<td>131.92</td>
<td>139.09</td>
<td>119.6</td>
<td>0.38</td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>2.67</td>
<td>132.12</td>
<td>139.16</td>
<td>120.7</td>
<td>0.51</td>
</tr>
<tr>
<td>7</td>
<td>0.60</td>
<td>3.58</td>
<td>132.14</td>
<td>139.35</td>
<td>121.5</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The spectra were recorded at ambient temperature at 60 and 100.1 MHz*. The values were partially taken from ref. 8.
facts remain constant, increased polarization should increase the \( \Delta \) value. Nevertheless, the deshielding or the chemical shift of the \( C_\gamma \) is presumably controlled by the \( \pi \)-electron density and that of \( C_\alpha \) by \( \delta \)-electron density, though other effects may also contribute.

(c) Coupling Constants

The coupling constants \( J^{(13}C\text{H}) \) were measured from the well-resolved satellites of the methyl resonances (Figures IV.8 and IV.9). Satellites were also observed that arose from long-range spin-spin coupling involving \( ^{77}\text{Se} \) and \( ^{125}\text{Te} \) suggesting that exchange, if any, of silyl groups must be slow.

Earlier investigations of element-hydrogen spin-spin coupling have established that, the coupling constants increase with increasing s-character for the element-hydrogen bond. The s-character of the C-H bond generally depends on the hybridization of the carbon (e.g. \( sp^3 \) in \( CH_3^- \), \( sp^2 \) in \( CH_2=CH^- \), and \( sp \) in \( CH=CH^- \) group) and the electronegativity of other groups at carbon or neighbouring atoms, which tend to increase the s-character of the C-H bond. The \( ^{13}C\text{-H} \) coupling constants for the vinyl-containing species are presented in Table IV.2 and exhibits the expected trend. Apparently the trends emerge readily as they
do for the \( \delta(\text{Me}) \), such that the values fall between those for the system of \((\text{SiMe}_3)_2\text{E}\) and \((\text{HSiMe}_2)_2\text{E}\). Clearly, the effect of the chalcogen is substantial and leads to an increase in the \( ^{13}\text{C}-\text{H} \) coupling constants along the series \( \text{O}(118.0) \rightarrow \text{S}(119.5) \rightarrow \text{Se}(120.7) \rightarrow \text{Te}(121.5) \) Hz. This increase implies an increasing electronegativity from oxygen to tellurium which violates chemical sense and suggests that the s-character hypothesis (the Fermi contact term) might not dominate the coupling mechanism between the carbon and hydrogen. Nevertheless, it is interesting to observe that the efficiency of sulphur, selenium, and tellurium in transmitting the effects is greater relative to oxygen. Considering that \( \text{E} (\text{E}=\text{S,Se,Te}) \) has electron-accepting d-orbitals and lone-pair electrons available for electron donation, and that silicon also has electron-accepting d-orbitals, it appears possible that the hybrid orbitals in the heavy atom skeleton \( \text{C-Si-E} \) could be affected. In this way the larger values may reflect the larger fraction of s-character induced by silicon in the C-H bond as the chalcogen changes from oxygen to tellurium. On the other hand, substitution of methyl or vinyl group by hydrogen leads to an increase of the \( ^{13}\text{C}-\text{H} \) coupling constants indicating that both methyl and vinyl groups
are behaving as less electronegative groups than hydrogen. Whether this dependence of the $^{13}\text{C-}H$ coupling is a result of changes in the $s$-character of the orbitals involved, or due to angular distortion, or bond shortening is a matter of controversy.

The proton-proton coupling constants $J(\text{HH})$ for the vinyl group are given in Table IV.3. The assignment (Figure IV.3) and the determination are only tentative, and disclose the changes of the values as the chalcogen changes. While the coupling between the protons A and C ($^{3}\text{J}_{\text{AC}}$) increases as the chalcogen changes from oxygen to tellurium, as does $J(\text{HCH})$, the coupling between the protons A and B ($^{3}\text{J}_{\text{AB}}$) and between B and C ($^{2}\text{J}_{\text{BC}}$) decreases as does the sum of the three coupling constants $[^{1}\text{J}=39.11 \text{ (O)} \rightarrow 38.10 \text{ (S)} \rightarrow 37.93 \text{ (Se)} \rightarrow 37.64 \text{ (Te)}]$. Evidently, the magnitude of $^{1}\text{J}$ follows the effective electronegativity of the chalcogen (E) and it would be highly speculative to make further discussion, since the factors governing the magnitude of the coupling constants cannot be said to be fully understood and must be complex.
Figure IV.9 The $^1$H and $^{13}$CH n.m.r. spectra of neat 
$(\text{VinSiMe}_2)_2\text{Se}$ (a) and $(\text{VinSiMe}_2)_2\text{Te}$ (b).
Table IV.3 The coupling constants of the vinyl protons.*
The spectra were recorded at 100.1 MHz in
cyclohexane solution. The assignment and
the magnitude of the coupling constants
are tentative, see Figure IV.3.

<table>
<thead>
<tr>
<th>E</th>
<th>(^3J_{AC})</th>
<th>(^3J_{BC})</th>
<th>(^2J_{AB})</th>
<th>(\Sigma J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>18.03</td>
<td>14.89</td>
<td>6.19</td>
<td>39.11</td>
</tr>
<tr>
<td>S</td>
<td>18.42</td>
<td>14.49</td>
<td>5.19</td>
<td>38.10</td>
</tr>
<tr>
<td>Se</td>
<td>18.67</td>
<td>14.47</td>
<td>4.79</td>
<td>37.93</td>
</tr>
<tr>
<td>Te</td>
<td>18.92</td>
<td>14.43</td>
<td>4.29</td>
<td>37.64</td>
</tr>
</tbody>
</table>

* The corresponding coupling constants in CH\(_2\)=CHSi(CH\(_3\))\(_3\)
are \(^3J_{AC}= 20.4\), \(^3J_{BC}= 14.6\), and \(^2J_{AB}= 3.8\) with
\(\overline{J}= 38.8\), see reference 57.
IV.2 VIBRATIONAL SPECTRA

Vibrational spectroscopy is an important tool for the characterization of various species. Valuable information regarding molecular structures, intra- and intermolecular forces as well as molecular force constants can be extracted from vibrational spectral data. Many studies have been done on the vibrational spectra of vinyl derivatives of Group IV elements. Conflicting conclusions have been reached not only over the assignment of the vibrations of the vinyl group, but also on the extent of a vinyl-metalloid and metalloid-chalcogen \( \pi \)-interaction. The observed frequencies and intensities, changes of \( \nu(C=C) \) and the vibrations of the CH\(_2\)= group have been taken as a measure of the vinyl-metalloid \( \pi \)-interaction. Similarly, the observed \( \nu(M-C) \) frequency changes for compounds of the formula \((Et_3M)_nE\) (M=Si, Ge; E=element in Group V-IV; n=valence of E) have been interpreted in terms of the capacity of E for \((p-d)\pi\) bonding with M. It has been concluded that the \( \nu(M-C) \) frequencies are linearly related to the electronegativity of E. In the following discussion, the i.r. and Raman spectra of 1,3-divinyl-tetramethylsilylethylene chloride, \((CH_2=CHSiMe_2)_2E\), where E=O, S, Se, Te are examined consecutively. Representative spectra are presented.
in Figures IV.10-13. The observed frequencies and tentative assignments of the vibrational modes are summarized in Table IV.4. The vibrational assignments were made by comparison along the series 0→S→Se→Te and with those of (CH₂=CHSiMe₂)₂⁰⁴₃, CH₂=CHSiMe₂Cl₁₈, (CH₂=CH)₄Si₆₈, (CH₂=CH)₃B₆₉ and (CH₂=CH)₂F₇₀.

Features associated with CH stretches are expected to be at highest wavenumbers, and the three Raman bands are seen at νₓ(CH₂) ca. 3053, ν(CH) ca. 3008 and νₛ(CH₂) ca. 2969 cm⁻¹ with corresponding i.r. absorptions of weak to strong intensities. Except for the oxide, the νₛ(CH₂) stretching frequency is indistinguishable from the νₓ(CH₂) mode. The νₛ(CH₂) mode is observed as a very strong polarized band at ca. 2902 cm⁻¹ with a weak i.r. counterpart. The CH₂ scissors vibration is expected to give a band at about 1404 cm⁻¹ where the δₓ(CH₂) vibration appears. Similarly, the δ(CH) is obscured by the ν(Si-O) mode at 510 cm⁻¹. The δ(CH₂) is assigned at somewhat higher frequency at ca. 1440 cm⁻¹ as a very weak absorption. The remaining vibrations appearing at: ρ(CH) ca. 1264, δ₁ₓ(CH) ca. 1000, δ₂ₓ(CH₂) ca. 947 and δₛ(CH₂) ca. 1242 cm⁻¹ are unambiguously assigned. This assignment is in agreement with previous
Figure IV.10 The liquid phase infrared spectra of (CH₂=CHSiMe₂)₂O (a) and (CH₂=CHSiMe₂)₂S (b).
Figure IV.11 The liquid phase infrared spectra of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}\) (a); and \((\text{CH}_2=\text{CHSiMe}_2)_2\text{Te}\) (b).
Figure IV.12  The liquid phase Raman spectrum of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\).
Figure IV.13 The liquid phase Raman spectrum of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}\).
Table IV.4 The i.r. and Raman spectra (cm\(^{-1}\)) of the bis(vinylidimethylsilyl) chaloconides.\(^*\)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>((\text{CH}_2=\text{CHSiMe}_2)_2\text{S})</th>
<th>((\text{CH}_2=\text{CHSiMe}_2)_2\text{Se})</th>
<th>((\text{CH}_2=\text{CHSiMe}_2)_2\text{Te})</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.r. Raman</td>
<td>i.r. Raman</td>
<td>i.r. Raman</td>
<td>i.r. Raman</td>
</tr>
<tr>
<td>(\nu(\text{CH}_2=))</td>
<td>3045m</td>
<td>3054m</td>
<td>3042m</td>
</tr>
<tr>
<td>(\nu(=\text{CH}))</td>
<td>2980w</td>
<td>3000w</td>
<td>2956v</td>
</tr>
<tr>
<td>(\delta(\text{CH}_2))</td>
<td>2869w</td>
<td>2897w</td>
<td>2888w</td>
</tr>
<tr>
<td>(\gamma(\text{CH}_3))</td>
<td>1585m</td>
<td>1583m</td>
<td>1580m</td>
</tr>
<tr>
<td>(\delta(\text{CH}_3))</td>
<td>1404m</td>
<td>1404m</td>
<td>1391m</td>
</tr>
<tr>
<td>(\rho(=\text{CH}))</td>
<td>1400s</td>
<td>1393s</td>
<td>1393s</td>
</tr>
<tr>
<td>(\gamma(\text{Si-O}))</td>
<td>783v</td>
<td>783v</td>
<td>784v</td>
</tr>
<tr>
<td>(\gamma(\text{Si-Si}))</td>
<td>775vs</td>
<td>775vs</td>
<td>775vs</td>
</tr>
<tr>
<td>(\gamma(\text{Si-Si}))</td>
<td>693vs</td>
<td>693vs</td>
<td>693vs</td>
</tr>
<tr>
<td>(\gamma(\text{Si-Si}))</td>
<td>610vw</td>
<td>610vw</td>
<td>610vw</td>
</tr>
<tr>
<td>(\gamma(=\text{CH}))</td>
<td>510m</td>
<td>512m</td>
<td>515m</td>
</tr>
<tr>
<td>(\gamma(=\text{Si-Si}))</td>
<td>478m</td>
<td>410m</td>
<td>410m</td>
</tr>
<tr>
<td>(\gamma(=\text{Si-Si}))</td>
<td>400m</td>
<td>400m</td>
<td>400m</td>
</tr>
<tr>
<td>Skeletal def.</td>
<td>73w</td>
<td>73w</td>
<td>73w</td>
</tr>
<tr>
<td>(\nu(=\text{CH}))</td>
<td>3045m</td>
<td>3054m</td>
<td>3042m</td>
</tr>
<tr>
<td>(\nu(=\text{CH}))</td>
<td>2980w</td>
<td>3000w</td>
<td>2956v</td>
</tr>
<tr>
<td>(\delta(\text{CH}_2))</td>
<td>2869w</td>
<td>2897w</td>
<td>2888w</td>
</tr>
<tr>
<td>(\gamma(\text{CH}_3))</td>
<td>1585m</td>
<td>1583m</td>
<td>1580m</td>
</tr>
<tr>
<td>(\delta(\text{CH}_3))</td>
<td>1404m</td>
<td>1404m</td>
<td>1391m</td>
</tr>
<tr>
<td>(\rho(=\text{CH}))</td>
<td>1400s</td>
<td>1393s</td>
<td>1393s</td>
</tr>
<tr>
<td>(\gamma(\text{Si-O}))</td>
<td>783v</td>
<td>783v</td>
<td>784v</td>
</tr>
<tr>
<td>(\gamma(\text{Si-Si}))</td>
<td>775vs</td>
<td>775vs</td>
<td>775vs</td>
</tr>
<tr>
<td>(\gamma(\text{Si-Si}))</td>
<td>693vs</td>
<td>693vs</td>
<td>693vs</td>
</tr>
<tr>
<td>(\gamma(=\text{CH}))</td>
<td>510m</td>
<td>512m</td>
<td>515m</td>
</tr>
<tr>
<td>(\gamma(=\text{Si-Si}))</td>
<td>478m</td>
<td>410m</td>
<td>410m</td>
</tr>
<tr>
<td>(\gamma(=\text{Si-Si}))</td>
<td>400m</td>
<td>400m</td>
<td>400m</td>
</tr>
<tr>
<td>Skeletal def.</td>
<td>73w</td>
<td>73w</td>
<td>73w</td>
</tr>
</tbody>
</table>

* Spectra recorded at R.T.

Abbreviations used: v, very; b, broad; sh, shoulder; s, strong; m, medium; ms, moderately strong; w, weak;
p, polarized; dp, depolarized.

† Incidental with (Si-O).
reports presented elsewhere\textsuperscript{18, 43, 68, 69, 70}.

The stretching vibration attributed to the presence of the C=C bond in the molecules has a wave-number of about 1592 cm\(^{-1}\) in the Raman effect with a corresponding i.r. counterpart. The stretching vibrations arising from the C\(_2\)Si skeleton contribute to a number of features between ca. 787 and ca. 574 cm\(^{-1}\). These have been assigned by analogy with previous assignments in the literature for vinyl\textsuperscript{18, 43, 68} and related compounds\textsuperscript{50}. As the Si-E-Si bond stretching vibrations are the most characteristic of the new chalcogenides, their positions fall at 1049 vs and 542 sp (O); 448 vsp (S); 398 vsp (Se); and 297 cm\(^{-1}\) (Te). The lowering of \(\nu\)(Si-E) arises because of the increased mass of the chalcogen, and may also reflect weakening of the Si-E bond. Similar trends of decreasing Si-E stretching frequencies have been observed in the stretching frequencies occurring in related silyl species\textsuperscript{50}, \((\text{Me}_n\text{H}_{3-n}\text{Si})_2\text{E}\). The remaining vibrational degrees of freedom involve only the deformations of the C=C-Si-E-Si=C skeletal frame and they appear in the low-frequency region.

The frequency of the Si-E-Si deformations decrease, as expected, less rapidly than the frequency of the skeletal stretching. The resulting trend of decreasing deformation frequencies for Si-E-Si along the series
confirmed that the heavy atom skeletons are bent at the central atom as are the related species.

The force constants of the Si-E bonds were calculated by making the naïve assumption that in the 1,3-divinyl-tetramethyldisilyl chalcogenides the Si-E bond can be treated as a diatomic molecule, the average values of the Si-E asymmetric and symmetric stretch-es were taken as the stretching vibrations of the assumed diatomics. The Si-E (E=O,S,Se,Te) bond force constants so calculated give the values listed in Table IV.5. Despite the fact of the exaggerated approximation, the values of the force constants disclose the expected trend where the force constant of Si-O is very much greater than the other Si-chalcogen bonds, which suggests a much greater rigidity of the Si-O bond compared to the remaining Si-chalcogen bonds. This, is of course in keeping with the general stability of compounds containing Si-O bonds where a degree of Si-O π-bonding has been invoked. Given the gross approximation, the calculated values still suggest a bond of similar rigidity in the case of Si-S and Si-Se but a weaker bond for Si-Te. This is consistent with the observation that tellurium metal was usually deposited during the course of recording an i.r. spectrum.
(a) Force constant calculations

\[ \Delta \varepsilon = \hbar / 2 \pi \sqrt{k/\mu} \]

Thus

\[ k = 4\pi^2 \mu \Delta \varepsilon^2 / \hbar^2 \]

\[ \Delta \varepsilon = h\nu \]
\[ \nu = c/\lambda \]
\[ \nu = c\nu \]

Therefore

\[ \Delta \varepsilon = h c \nu \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N} \]

where

\( \Delta \varepsilon \) = The energy of a quantum of radiation in erg.

\( h \) = Planck's constant \( 6.62 \times 10^{-27} \) erg-sec.

\( \mu \) = The reduced mass of a diatomic molecule.

\( c \) = Velocity of light \( 3.00 \times 10^{10} \) cm/sec.

\( N \) = Avogadro’s number \( 6.023 \times 10^{23} \).

\( \lambda \) = The wavelength of radiation.

\( \nu \) = Frequency in cycles per second.

\( \nu \) = The wave number in reciprocal centimeters.

\( m_1 \) and \( m_2 \) = The atomic mass of atom one and the atomic mass of atom two in a diatomic molecule.

\( k \) = The force constant of the bond of a diatomic molecule.

Atomic mass of silicon = 28.086

" o oxygen = 15.999"
Average of $\nu(i.r.)$ and $\nu(Ra漫)$ of Oxygen

$\nu = 1049 + 542 / 2$

$= 796 \text{ cm}^{-1}$ for oxygen

$\Delta \epsilon = 6.62 \times 10^{-27} \times 3.00 \times 10^{10} \times 796$

$= 15808.56 \times 10^{-17}$

$= 1.58 \times 10^{-13} \text{ erg}$

$\mu = \frac{28.09 \times 16.00}{28.09 + 16.00} \times \frac{1}{6.02 \times 10^{23}}$

$= \frac{449.44}{255.42} \times 10^{-23}$

$= 1.71 \times 10^{-23} \text{ gm}$

$\kappa = \frac{(3.14)^2 \times 1.69 \times 10^{-23} \times (1.58 \times 10^{-13})^2}{(6.62 \times 10^{-27})^2}$

$= \frac{166.32}{43.82} \times 10^5$

$= 3.8 \times 10^5 \text{ dyne/cm}$

The force constant of the remaining Si-$E$ ($E=S, Se, Te$) bonds were calculated in an analogous manner.
Table IV.5 The force constants of the Si-E (E=O,S,Se,Te) bonds *

<table>
<thead>
<tr>
<th>( \nu ) cm(^{-1} )</th>
<th>( \Delta \varepsilon ) (10^{-13})</th>
<th>( \mu ) (10^{-23})</th>
<th>( \kappa ) (10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>796</td>
<td>1.58</td>
<td>1.69</td>
<td>3.8 \times 10^5</td>
</tr>
<tr>
<td>463</td>
<td>9.20 \times 10^{-14}</td>
<td>2.48 \times 10^{-23}</td>
<td>1.9 \times 10^5</td>
</tr>
<tr>
<td>394</td>
<td>7.82 \times 10^{-14}</td>
<td>3.44 \times 10^{-23}</td>
<td>1.9 \times 10^5</td>
</tr>
<tr>
<td>297</td>
<td>5.90 \times 10^{-14}</td>
<td>3.82 \times 10^{-23}</td>
<td>1.2 \times 10^5</td>
</tr>
</tbody>
</table>

*The trend of the force constants\(^72\) of Si-halide bonds (Si-F 5.3 \times 10^5; Si-Cl 2.3 \times 10^5; and Si-Br 1.8 \times 10^5 dyne/cm) is similar to those of Si-chalcogen bonds.*
IV.3 THE MASS SPECTRUM OF \((\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\)

The field ionization and electron impact mass spectra of 1,3-divinyl-tetramethyldisiloxane were recorded with the aim of molecular weight confirmation and structural elucidation. The mass spectra of the heavier analogues were not recorded because of their extreme sensitivity to hydrolysis. The molecular ion, \((\text{C}_8\text{H}_{18}\text{Si}_2\text{O})^+\) was present in both spectra but of very low abundance m/e 186, <1.0%. The most abundant ion is that formed by the elimination of a methyl group, \(\text{M}^+-\text{CH}_3\) m/e 171 (100%). Further analysis of the electron impact spectrum disclosed that the fragmentation pattern is very similar to that published by Tamas et al.\(^7\), thus the fragmentation will not be discussed here.

IV.4 THE REACTIVITY OF 1,3-DIVINYL-TETRAMETHYLDISILYL CHALCOGENIDES

The reactions of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{E}\) with some simple species including anhydrous \(\text{HX}\) (X=Cl,Br), aqueous HCN, SO\(_2\)F\(_2\), CCl\(_3\)SCL, CH\(_3\)SH, H\(_2\)S and H\(_2\)Se are described. The reactions were carried out in sealed tubes at various temperatures and the identification of the products was achieved by \(^1\text{H}\) n.m.r. spectroscopy.
IV.5 EXPERIMENTAL

(a) Reaction of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{E}\) with anhydrous HX (X=Cl, Br)

The reaction of the Si–E bond where E=S, Se, Te with HX is described in chapter III.2(3), p. 28. The analogous reaction of \((\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\) (0.0289 g, 0.1554 mmol) was carried out with an excess of anhydrous HCl (0.700 mmol) and trace amounts of cyclohexane. Initial observation of the \(^1\text{H}\) n.m.r. spectrum revealed proton resonances of only the starting material \((\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\), \(^1\text{H}\delta\text{(Me)}\) 0.12 p.p.m. After longer reaction times, weak proton resonances attributable to \(\text{CH}_2=\text{CHSiMe}_2\text{Cl}\) were observed at \(^1\text{H}\delta\text{(Me)}\) 0.43 p.p.m.

(b) Reaction of \((\text{VinSiMe}_2)_2\text{O}\) with aqueous HCN

Hydrogen cyanide was prepared by the addition of aqueous solution of NaCN onto \(\text{H}_2\text{SO}_4\) containing some FeSO\(_4\). The reaction is exothermic and HCN was collected in a storage vessel as it was formed. Excess of hydrogen cyanide containing some moisture was sealed with \((\text{VinSiMe}_2)_2\text{O}\) (0.0412 g, 0.2215 mmol) and traces of TMS. When the tube was shaken immiscible droplets were formed. The \(^1\text{H}\) n.m.r. spectrum disclosed resonances of only the starting materials:
(VinSiMe₂)₂O ¹H δ(Me) 0.13 p.p.m.; δ(HCN) 2.62 p.p.m.
and δ(H₂O) 4.10 p.p.m. The tube was placed in an
oven set at 120° and after three days there was no
change in the ¹H n.m.r. spectrum.

(c) Reaction of (CH₂=CHSiMe₂)₂O with SO₂F₂

In a typical run 0.3670 mmol of (CH₂=CHSiMe₂)₂O
was sealed with an excess of SO₂F₂ (0.900 mmol) and
trace amounts of TMS. The ¹H n.m.r. spectrum showed
the resonances of only the oxide.

(d) Reaction of (CH₂=CHSiMe₂)₂O with CCl₃Cl

Typically, (CH₂=CHSiMe₂)₂O (0.4023 mmol) and
and CCl₃Cl (0.3132 mmol) with trace amounts of TMS
were sealed into a semimicro n.m.r. tube. After 16
hours the ¹H n.m.r. spectrum was recorded and re-
vealed the proton resonances of only the oxide.

(e) Reaction of (CH₂=CHSiMe₂)₂O with CH₂SH

Typically, (VinSiMe₂)₂O (0.0138 g, 0.0742
mmol) and methane thiol, CH₂SH, (0.1637 mmol)
were sealed with trace amounts of TMS in a semi-
micro n.m.r. tube. The ¹H n.m.r. spectrum of the
reaction at R.T. disclosed the resonances of only
the starting materials. The sealed tube was then
placed in an oven at 120°. After 24 hours there was
a definite change of the colour from colourless to
yellow. The proton n.m.r. spectrum revealed additional weak resonances at 2.70, 2.33 and 0.31 p.p.m. indicating a slight addition of CH₃SH to the vinyl group with the formation of (CH₃SCH₂CH₂SiMe₂)₂O.

(f) Reaction of (VinSiMe₂)₂S with H₂S

The sulphide, (VinSiMe₂)₂S (0.0306 g, 0.1515 mmol) and an excess of anhydrous H₂S (0.500 mmol) were sealed in a semimicro n.m.r. tube with some TMS. The ¹H n.m.r. spectrum of the reaction was recorded after 10 minutes and disclosed only the resonances of the starting materials (VinSiMe₂)₂S ¹H ₅(Me) 0.38 and ₆(H₂S) 0.82 p.p.m. After longer reaction time (ca. 14 days) there was essentially no change in the reaction.

(g) Reaction of (CH₂=CHSiMe₂)₂Se with H₂Se

Typically, (CH₂=CHSiMe₂)₂Se (0.0831 g, 0.3382 mmol) and an excess of H₂Se (1.1230 mmol) were sealed in a semimicro n.m.r. tube. The ¹H n.m.r. spectrum of the reaction was recorded after 16 hours and revealed resonances centred at ca. 2.68, ca. 1.50, ca. 1.29, ca. 0.48, ca. -0.83 and a very weak peak at ca. -2.82 p.p.m. assignable to (HSeCH₂CH₂SiMe₂)₂Se and presumably traces of HSeCH₂CH₂SiMe₂SeH, Figure IV.14.
IV.6 DISCUSSION

The Si-E (E=S,Se,Te) bond is generally less stable than the Si-O bond, this trend was also seen in the force constants of the Si-E bonds. As mentioned earlier, compounds containing the Si-E bonds are almost all unstable to air and moisture. Their thermal stability generally decreases with increasing atomic weight of E. As an extension of previous work, the cleavage of the Si-E-Si linkage with anhydrous HX (X=Cl,Br) was conducted for observation of reactivity and structural confirmation. Aside from the siloxane linkage Si-O-Si, these bonds are readily cleaved by HX followed by the formation of CH2=CHSiMe2X and the respective H2E, i.e.,

\[(\text{VinSiMe}_2)_2\text{Se} + 2\text{HCl} \rightarrow \text{2VinSiMe}_2\text{Cl} + \text{H}_2\text{Se} \]  (1)

Earlier studies have shown that the M-E-M (M=Si,Ge) skeleton in the related species \((\text{Me}_n\text{H}_3-n\text{M})_2\text{E}^2\) reacts with the corresponding \(\text{H}_2\text{E}^2\) with the formation of chalcogenols \(\text{Me}_n\text{H}_3-n\text{M-EE}^2\). In this study these reactions were attempted not only from the point of view of chemical reactivity of the metalloid-chalcogen bond, but also because they might provide
synthetic pathways to some new vinyl containing silyl species, such as CH₂=CHSiMe₂SeH, according to reaction (2). However, this reaction was

\[(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se} + \text{H}_2\text{Se} \rightarrow 2\text{CH}_2=\text{CHSiMe}_2\text{SeH}\] (2)

not observed but rather there was evidence that H₂Se underwent addition across the double bond according to reaction (3). Thus, in a sealed tube reaction, the selenide reacted with an excess of hydrogen selenide to yield (HSeCH₂CH₂SiMe₂)₂Se i.e.

\[(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se} + \text{H}_2\text{Se} \rightarrow (\text{HSeCH}_2\text{CH}_2\text{SiMe}_2)_2\text{Se}\] (3) (excess)

The reaction was followed by sequential recording of the \(^1\text{H}\) n.m.r. spectrum. The observed \(^1\text{H}\) n.m.r. spectrum of reaction (3) is presented in Figure IV.14. An examination of the spectrum reveals that the reaction of (CH₂=CHSiMe₂)₂Se with H₂Se yields (HSeCH₂CH₂SiMe₂)₂Se with anti-Markownikoff orientation (see chapter III, p. 22). The methylene protons of the -SeCH₂CH₂ fragment form a spin system of AA'XX' type. The corresponding chemical shifts were determined from the centre of each of the multi-
plets, i.e. \((\text{SeCH}_2)\) ca. 2.68 and \((\text{CH}_2\text{Si})\)

\[
\begin{array}{c}
\text{H}_A \text{ H}_X \\
\text{HSe} - \text{C} - \text{C} - \text{Si} = \\
\text{H}_A' \text{ H}_X' \\
\end{array}
\]

c. 1.29 p.p.m.; and that of \((\text{HSe})\) at ca. 1.50 and \((\text{SiMe}_2)\) at 0.48 p.p.m. The values of the proton resonances were determined with respect to the peak appearing at ca. 0.12 p.p.m. assignable to \((\text{CH}_2 = \text{CHSiMe}_2)_2\text{O}\). The appearance of this peak is due to the highly sensitive nature of the Si-Se bond to hydrolysis. The analogous reaction of the sulphide, \((\text{CH}_2 = \text{CHSiMe}_2)_2\text{S}\), with hydrogen sulphide did not disclose the addition of \(\text{H}_2\text{S}\) to the vinyl group or cleavage of the Si-Si linkage. Similarly, the oxide, \((\text{CH}_2 = \text{CHSiMe}_2)_2\text{O}\), with weakly acidic species such as \(\text{HOCN}\) and \(\text{MeSH}\) did not react at R.T. These reactions demonstrate the resistance of the Si-E-Si linkage to chemical attack with increasing electronegativity of the chalcogen atom.
CHAPTER V

PARTIAL HALOGENATION OF SOME

SILANES AND GERMANES
V.1 INTRODUCTION

In this chapter emphasis is placed on the partial halogenation of some silanes and germanes of the general formula $\text{Me}_n\text{H}_{4-n}M$ where $M=\text{Si, Ge}; n=0\rightarrow3$ and $\text{Me}_3\text{SiSiMe}_3$. The halides $\text{Me}_n\text{H}_{3-n}XM\ X=\text{halogen}$ are the most important synthetic intermediates with respect to their conversion to other silyl and germyl species. Most of the synthetic routes leading to halogenosilanes and -germanes are well documented. Nevertheless, the initial interest in the preparation of the halogenosilanes and -germanes stemmed from the growing spectroscopic interest involving both X-ray and u.v. photoelectron spectroscopy of these species.\textsuperscript{74-79} The subsequent concern was directed towards their use in the synthesis of some new silyl and germyl Group VI compounds.

V.2 EXPERIMENTAL

(a) Synthesis of Iodosilane\textsuperscript{80,82-85} $\text{Me}_n\text{H}_{3-n}\text{SiI}$

A flask containing aluminium triiodide (catalytic amount) was attached to the vacuum line and evacuated while being immersed in a $-78^\circ$ slush bath. Glass wool was placed above the vessel in order to minimize contamination of the vacuum line by iodine. After evacuation the $-78^\circ$ slush bath was replaced by one at $-196^\circ$, whereupon silane (4.2 mmol) and hydrogen iodide (6.0 mmol)
were condensed into the reaction vessel. After closing the stopcock the contents of the vessel were allowed to warm to -45°, and allowed to react at this temperature for about four hours, at which time the reaction products were allowed to distill through a series of U-traps at -78°, -95°, and -196° with pumping. The fraction at -78° contained traces of SiH₂I₂. The fraction at -95° contained pure iodosilane, identified by its ¹H n.m.r. and vibrational spectra. The fraction at -196° contained unreacted silane and hydrogen iodide. The yield of iodosilane was 70%.

Diiodosilane and triiodosilane were prepared in an analogous manner as iodosilane. Silane (6 mmol) and hydrogen iodide (12 mmol) were reacted in the presence of catalytic amount of AlI₃. The reaction was allowed to react at R.T. for about 36 hours, whereupon the reaction products were fractionally distilled through traps held in series at -45°, -95°, and -196°. The -196° trap contained unreacted HI, the -95° trap contained no product, and the -45° trap retained the reaction product, the contents of the latter trap was separated into a top and bottom fraction. ¹H n.m.r. analysis indicated the presence of H₂SiI₂ (93%) and HSiI₃ (7%) in the top fraction, while the bottom fraction was composed of H₂SiI₂ (82%) and HSiI₃ (18%).
Both the top and bottom fractions were allowed to distil through traps held at -25° and -78°, the latter trap retained diiodosilane, while triiodosilane was condensed into the former trap.

Trimethylsilane was prepared by the reduction of Me₂SiCl with Li[AlH₄] in n-Bu₂O, it was then utilized as a starting material for obtaining trimethyliodosilane, prepared in an analogous manner as above.

(b) Attempted Preparation of Me₃SiSiMe₂Cl

The recognition of pentamethylchlorodisilane as an important starting material in many reactions, prompted the attempt to prepare it through the following two reactions:

\[ \text{Me}_3\text{SiSiMe}_3 + \text{SbCl}_5 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Me}_3\text{SiSiMe}_2\text{Cl} + \text{ClMe}_2\text{SiSiMe}_2\text{Cl} \] (1)

\[ \text{Me}_3\text{SiSiMe}_3 + \text{H}_2\text{SO}_4 + \text{NH}_4\text{Cl} \rightarrow \text{Me}_3\text{SiSiMe}_2\text{Cl} + \text{ClMe}_2\text{SiSiMe}_2\text{Cl} \] (2)

Reaction (1) was conducted with a reaction vessel (ca. 100 ml) equipped with a finger, a Teflon-in-glass stopcock, and a ball joint. After charging the reaction vessel with SbCl₅ (4.11 mmol), it was degassed at -78°C, whereupon the vessel was cooled to -196°C and dichloromethane was condensed into it, followed by hexamethyldisilane (4.47 mmol). The reaction proceeded immediately when the reactants were brought to R.T. The reaction products were passed through traps held in
series at -45°, -78°, and -196°. The solvent condensed in the latter trap, while the products were collected in the -78° trap. The ¹H n.m.r. spectra of the product revealed the presence of Me₂SiCl₁₁ and Me₂SiCl₂.⁸⁹

Reaction ⁹⁰ (2) was conducted with a reaction vessel (ca. 100 ml) equipped with a finger, a magnetic stirrer, a ball-joint, and a stopcock. The vessel was charged with H₂SO₄ (1.56 g) and NH₄Cl (0.23 g) into the finger. The system was attached to the vacuum line, and thoroughly evacuated after being cooled to -78°. The -78° bath was replaced by a -196° bath, whereupon hexamethyldisilane (3 mmol) was condensed into the reaction vessel. Upon warming the reaction mixture to R.T., effervescence was immediately observed. The reaction mixture was stirred at R.T. for about two hours. Thereafter the reaction vessel was immersed in an ice bath, and within a period of 30 minutes NH₄Cl was added dropwise into the reaction mixture by swinging the side arm (finger). The reactants were stirred at R.T. for an additional half hour, whereupon the products were fractionally distilled through traps held at -45° and -196°. Both traps retained reaction products. The contents in the -196° trap were fractionated again through traps held at -78° and -196°, methane (3.5 mmol) was retained in the latter trap as measured by the
manometer. The $-78^\circ$ trap also retained the reaction product. From the $^1H$ n.m.r. spectra of the products, it was concluded that pentamethylchlorodisilane was not formed, but rather a mixture of products. Possibly chlorinated silanes and -disilanes.

(c) The Preparation of $H_3GeCl$ and $H_2GeCl_2$

The primary purpose of carrying out the following reaction was to obtain dichlorogermaene in high yield, and in addition, using $H_2GeCl_2$ as a starting material, in order to prepare the remaining dihalogermanes for the purpose of obtaining X-ray photoelectron spectra.

In the preparation of monochlorogermaene and dichlorogermaene, a reaction vessel (ca. 250 ml) was thoroughly evacuated on the vacuum line, at which time germane (6 mmol) was condensed in the vessel at a temperature of $-196^\circ$, the reaction vessel was closed and the manifold was thoroughly evacuated, whereasupon $BCl_3$ (4 mmol) was condensed in the above vessel. The reaction mixture was subsequently warmed to $-78^\circ$ and kept at this temperature for 5-6 hours. After this time the reaction products were fractionally distilled through traps held in
series at -78°, -126°, and -196°, nothing was observed in the -78° trap, diborane was retained in the -196° trap, which was removed by condensing it over a large excess of triethylamine. The contents of the -126° trap were redistilled through traps held at -78° and -95°. The products were retained in the latter trap. The 1H n.m.r. spectra indicated that the major product was H₃GeCl, and H₂GeCl₂ was present only in trace amounts.

With the purpose of increasing the yield of H₂GeCl₂, the reaction time was increased to 24 hours, the reaction temperature was increased to R.T., and an excess of BCl₃ was used. All changes failed to increase the yield of dichlorogermane. Furthermore, reacting H₃GeCl with additional amounts of BCl₃ also failed to increase the yield of H₂GeCl₂.

(d) The Preparation of H₃GeBr

Bromogermane was prepared according to reaction (4). A reaction vessel (ca. 250 ml) equipped with a cold finger and a ball-joint was attached to the vacuum line and thoroughly evacuated, whereupon the vessel was cooled to a temperature of -196°, and BBr₃ (1 mmol) was condensed into the reaction
vessel, followed by germane (3.5 mmol). The reactants were warmed to -78°, and the mixture was allowed to react for about 2 hours. After this time, the volatile products were distilled through traps held in series at -45°, -95°, and -196°. The contents of the -95° trap were redistilled through traps at -63°, -95°, and -196°. The -95° trap retained pure monobromogermane which was identified by its i.r. spectrum and its purity further confirmed by 1H n.m.r. The -196° trap retained diborane and some unreacted germane which were discarded.

The Preparation of Me₃GeF and Me₂GeF₂

A reaction vessel (ca. 50 ml) equipped with a greaseless Teflon-in-glass stopcock, and containing PbO/SbF₃ 1:1 (8 g) was thoroughly evacuated on the vacuum line, and Me₃GeBr (3 mmol) was condensed into the above vessel at -196°. The mixture was allowed to react at R.T. for 45 minutes with occasional shaking. After this time the volatile products were distilled through traps held at -23° and -78°. Me₃GeF was retained in the latter trap. Its purity and identity were confirmed by 1H n.m.r. spectroscopy.

Difluorodimethylgermane was prepared by passing Me₂GeBr₂ (2 mmol) through a column (45 cm long,
2.5 cm o.d.) loosely packed with a mixture of glass wool and PbF₂. A pure sample of Me₂GeF₂ was obtained after passing the Me₂GeBr₂ back and forth about twenty times. The identity and purity of Me₂GeF₂ was confirmed by its i.r. and ¹H n.m.r. spectra.

V.3 DISCUSSION

The reactions leading to halogenosilanes and -germanes may be differentiated into those based on the reactivity of silicon and germanium hydrides, and those based on the reactivity of the M-Y bond, where M=Si, Ge; Y=halogen, C, O etc. The parent hydrides SiH₄ and GeH₄ are often used because of their availability, although the tetrahalides have a wide synthetic application. Partially methylated hydrides, MeₙH₃₋ₙM where M=Si, Ge; n=1,2,3 are commonly prepared in high yields by the reduction of the corresponding chloride with LiAlH₄ (MeₙMCl₃₋ₙ) in n-butyl ether.

Methylgermane MeGeH₃ is conveniently prepared by deprotonation of germane with KOH in 1,2-dimethoxyethane with subsequent methylation of the intermediate germyl potassium with MeI at low temperature (-10°).

In general, selective iodination of silanes
$\text{Me}_n\text{H}_{4-n}\text{Si}$ is achieved when they are reacted with a slight deficiency of hydrogen iodide in the presence of catalytic amounts of $\text{AlI}_3$. Since the Si-H bonds are affected selectively, this type of interaction enables one to carry out further halogenation leading to $\text{SiH}_2\text{I}_2$. Silanes containing Si-aryl bonds can be readily halogenated since such bonds are easily ruptured by anhydrous hydrogen halides, as exemplified by reaction (5). While the cleavage of Si-aryl bonds

$$\text{PhSiH}_3 + \text{HI} \rightarrow \text{PhH} + \text{SiH}_3\text{I} \quad (5)$$

is facile, the halogenation of hexamethyldisilane by $\text{SbCl}_5$ or by $\text{NH}_4\text{Cl}$ and $\text{H}_2\text{SO}_4$ proceeds with splitting of the Si-C and Si-Si bonds, hence evoking less interest for the preparation of pentamethylchlorodisilane.

Unlike the silanes, the related iodination of germane with iodine proceeds with good yields of iodogermaine, and is accompanied by the formation of HI. Iodogermaine may also be obtained by halogen exchange reactions either from the chloride or bromide.

Chloro- or bromogermaine are conveniently prepared by reacting germane with $\text{BX}_3$ (where $X=$
Cl-, Br) at low-temperature. However, when further chlorination was attempted only the mono-chlorogermaine was recovered, with small amounts of dichlorogermaine. Nevertheless, the chlorination of germaine with boron trichloride leading to mono-chlorogermaine is facile and clean, while the bromination is somewhat difficult, because of the easy disproportionation of \( \text{H}_3\text{GeBr} \) to \( \text{GeH}_2\text{Br}_2 \) and polygermaine \((\text{GeH}_2)_n\). The lighter halides \((\text{H}_3\text{GeF}, \text{Me}_3\text{GeF}, \text{Me}_2\text{GeF}_2)\) are obtained by metathesis reactions of \( \text{GeH}_3\text{I}, \text{Me}_3\text{GeBr} \) or \( \text{Me}_2\text{GeBr}_2 \) with \( \text{PbF}_2 \). Trimethyl-fluorogermaine is more conveniently prepared by the reaction of \((\text{Me}_3\text{Ge})_2\text{O}\) with \( \text{SbF}_3 \).

\[
3(\text{Me}_3\text{Ge})_2\text{O} + 2\text{SbF}_3 \rightarrow 6\text{Me}_3\text{GeF} + \text{Sb}_2\text{O}_3
\]  

Both halogenosilanes and -germanes are volatile, and were handled by conventional vacuum-line techniques. Their purity was initially confirmed by \(^1\text{H}\) n.m.r. and i.r. spectra. Further confirmation of their purity and structural properties were obtained from their ESCA spectra. The binding energies of all the atoms in these species are discussed elsewhere, and mention is made here only on the general trends of the binding energies within the series \( \text{Me}_n\text{H}_3-n\text{MX}_n \). Halosilanes and methylhalosilanes have been studied
by ESCA 75, 76, 87, some very interesting results have been obtained by these workers, for example, as methyl groups are replaced by halogen atoms, there is a stepwise increase in the binding energy. In the case of the iodides the observed increases of binding energies are less apparent due to a lack of the number of volatile samples available and to sample impurities. In substituting halogens for methyl groups there was a shift of charge from the Me₂M⁺ moiety towards the halogen. This decreased the electron density and increased the binding energy. It has also been found that the hydrogen atom has the ability to behave as a weakly electronegative halogen. X-ray photoelectron spectroscopy may also be utilized as a method for fingerprinting, since each element, except for hydrogen, has a certain energy range by which it may be detected.
REFERENCES


VITA AUCTORIS

Date of birth:
December 10, 1940; Athens, Greece.

Primary school:
A. Agelopoulou Greek and Armenian primary school, Athens, Greece.

Secondary school:
Galt Collegiate Institute And Vocational School, Cambridge (Galt), Ontario.

College:
The Western Ontario Institute Of Technology, Windsor, Ontario.
Chemical Technology Diploma-1964.

University:
Wayne State University, Detroit, Michigan.
B.S. in Chemistry-1972.

Married:
To Armine' Doumbegijian 1971.