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# AN INVESTIGATION OF SILICON AND GERMANIUM COMPOUNDS OF GROUP-VI ELEMENTS.

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Dedicated to my mother and to the memory of my father

# AN INVESTIGATION OF SILICON AND GERMANIUM COMPOUNDS OF GROUP VI ELEMENTS

by

Boris M. Glavinčevski

A Dissertation
submitted to the Faculty of Graduate Studies through the
Department of Chemistry in partial fulfillment of the
requirements for the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario, Canada

1978

## FOREWORD

The work described in this thesis was undertaken in the Chemistry Department of the University of Windsor, Ontario, Canada, between July 1973 and November 1977 under the supervision of Dr. John E. Drake.

First of all the author would like to express his sincere gratitude to his supervisor for his willing guidance and encouragement throughout this work. Special thanks are extended to Drs. R. T. Hemmings and C. G. Riddle for earlier direction in the ways of chemical research and to his colleagues, namely Dr. H. E. Henderson, Mr. A. J. F. Clark and Mrs. L. Khasrou for many helpful discussions and much needed stimulation. Very special thanks are due to his mother and relatives for their encouragement and understanding. Additional thanks also go to June Tilson for her inspiration and to Mrs. D. Gadoury for her help with the preparation of this manuscript. Warm thoughts are held in memory for his deceased father who offered much support and encouragement in his earlier studies.

The author would also like to acknowledge the Board of Education and Culture, Bitola and Electronic Industry-Niš, Yugoslavia for the financial support of his B.Sc. studies, the National Research Council of Canada for financial support, the Faculty of Graduate Studies for a University of Windsor postgraduate award, and the Department of Chemistry for their generosity in granting teaching assistantships.

Finally, the author wishes to express his appreciation to the members of the University of Windsor technical and secretarial staffs for their valuable assistance in instances too numerous to mention.

Boris M Glavinčevski

WINDSOR, ONTARIO

March, 1978

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List of abbreviations used:

Me, methyl; Et, ethyl; Bu, butyl; Ph, phenyl

n.m.r., nuclear magnetic resonance; i.r., infrared

PES, photoelectron spectroscopy; XPS, X-ray photoelectron spectroscopy (spectra); R, Raman

X, halogen; E, chalcogen ; M, a Group IV element

TMS, tetramethylsilane

p.p.m., parts per million

$\nu$, stretch; $\delta$, deformation; $\rho$, rock

# ABSTRACT

Comparative reactions of some halogenosilanes, disilazanes, bis(silyl)- and bis(germyl)-carbodiimides with Group VI species; and metathesis reactions of some halogeno-silanes and -germanes with complex aluminates, mercury (II), lead (II), silver (II), lithium (I) and silicon (IV) species are investigated, leading to the efficient syntheses of the chalcosilanes and -germanes of the formula $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M=Si, Ge; E=O,S,Se,Te; n=0→3. These compounds are identified by their $^1H$ n.m.r., vibrational and mass spectra with further characterization coming from X-ray photoelectron spectroscopic studies. The vibrational assignments of the mono- and dimethylated germyl and silyl chalcogenides are based on comparisons with the parent species and related monohalogeno- and pseudohalogeno-germanes and -silanes. The chemical characterization of the series of compounds containing the M–E bond involves: a) cleavage reactions with known quantities of gaseous hydrogen halides; b) self-condensation processes; c) co-condensation with group VI hydrides; d) elimination of the chalcogen atom and subsequent formation of binuclear species; e) redistribution of germyl and silyl groups on the chalcogen atom with formation of mixed germyl, silyl and germyl-silyl chalcogenides of the type $H_3MEMMe_3$ where M=Ge,Si; E=S,Se,Te; and f) fast exchange reactions between halogenogermanes and digermoxanes.

The reactivity of the M-E bond is investigated with assorted species. Thus, the germoxane linkage (Ge-O-Ge) is susceptible to protic reagents including $H_2E$ and REH yielding chalcogermanes, viz. - $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$, $Me_{\underline{n}}H_{3-\underline{n}}GeER$ where E=S,Se; R=H, Me, Et; n=0 $\rightarrow$ 3. The Si-E-Si linkage, unlike the Ge-E-Ge linkage where E=S,Se is readily cleaved by hydroxylic reagents (ROH) leading to $Me_{\underline{n}}H_{3-\underline{n}}SiOR$ compounds where R=Me, Et, $CH_2CF_3$ or $CH_2CCl_3$ and n=0 $\rightarrow$ 3. An alternate synthetic route to the methoxy-silanes and -germanes involves exchange reactions between methoxystannanes and halogeno-silanes and germanes. A further demonstration that the germoxy species are convenient intermediates comes from their conversion to heterocyclic compounds including $(Me_2GeS)_3$, $(MeGe)_4S_6$ and $(MeGe)_4Se_6$.

The exchange reactions involving complex aluminates, $Li[Al(ER)_4]$, and the appropriate Group IV halide are extended to prepare the compounds $Me_{\underline{n}}H_{3-\underline{n}}MER$ and $Me_{\underline{n}}M(ER)_{4-\underline{n}}$ where M=Si, Ge; E=S,Se; R=Me,Et and n=0 $\rightarrow$ 3. In all cases the compounds are examined spectroscopically.

# CHAPTER I

# EXPERIMENTAL TECHNIQUES

The main group hydrides, halides and organometallic derivatives are volatile, hydrolyzable, flammable, or explosive and frequently all four. Hence, the manipulation of these and related species requires moisture - and oxygen-free conditions and this, combined with the disagreeable odour, makes the vacuum method highly desirable. Where certain off line procedures were required, the chemicals and equipment were handled in a nitrogen-filled glove bag.

Vacuum line techniques are well documented[1-4] and have many advantages. In a 'closed' vacuum system, contamination from the atmosphere is minimized and small scale preparations may be employed. The volatile nature of the species permits a wide range of rapid, non-destructive characterization procedures as well as maximum protection against toxicosis. A wide range of techniques can be suited to this system, i.e. $^{1}H$ n.m.r., infrared, Raman, mass and X-ray photoelectron spectroscopy.

## I.1 THE VACUUM LINE

The vacuum line (Fig. I.1) was constructed from Pyrex glass and consisted of two manifolds (2,3) (volume ca. 150 ml each) interconnected by four U-traps and a central manifold (1) leading to pumping system. The pumping system was composed of a rotary oil pump (R), a mercury diffusion pump (D) and two liquid nitrogen 'backing' traps (T). Pressure readings between 1-760 Torr (0.13 - 101.33 kPa) were monitored (± 0.5 Torr) by mercury manometers (M) whilst a Pirani vacuum gauge (P) recorded pressures below 1 Torr (0.13 kPa) (normal

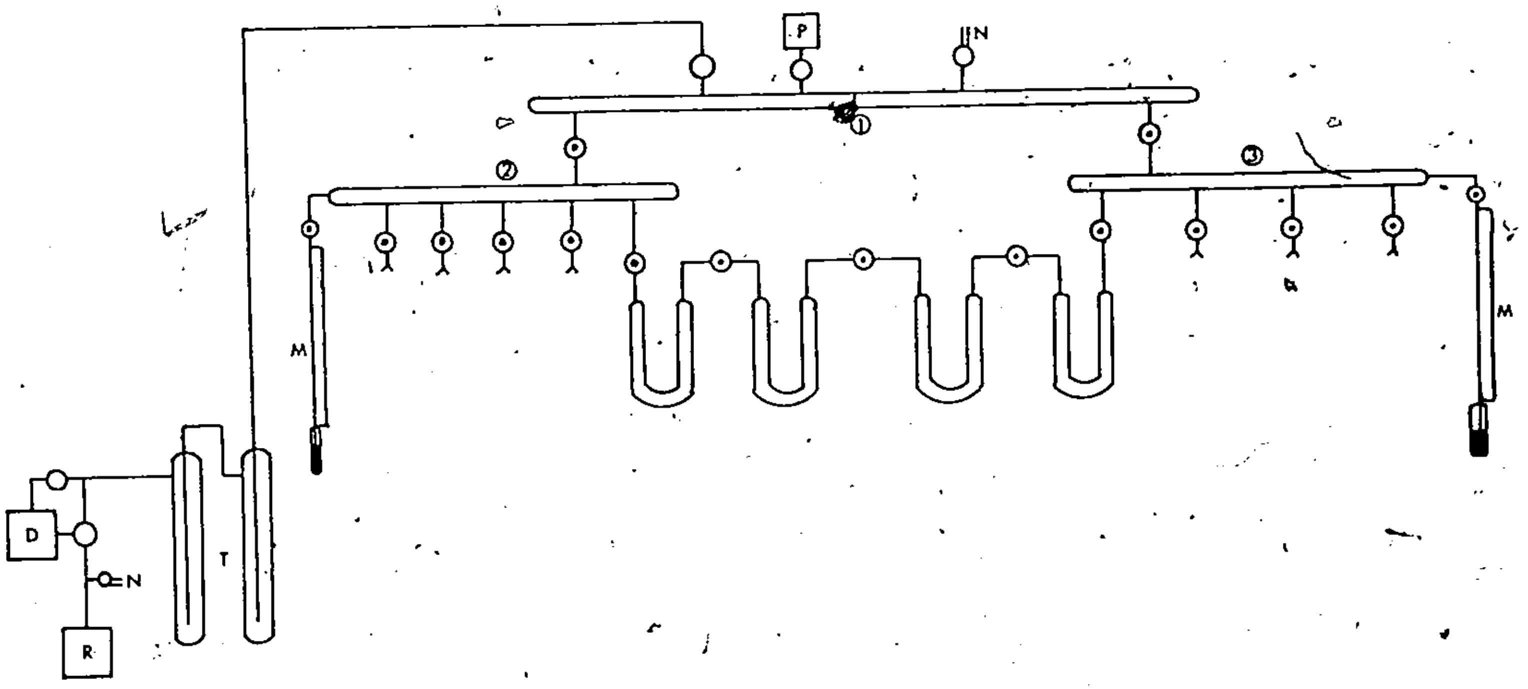

Figure I.1 The vacuum line

M mercury manometer
N dry nitrogen inlet
P Pirani gauge
R rotary pump

L liquid nitrogen traps
○ greased stopcock
⊙ teflon stopcock
⅄ FS19 ball joint

pressure was 1.5 x $10^{-2}$ Torr or 2 x $10^{-3}$ kPa). High-vacuum Teflon-in-glass valves and silicone-greased ground glass joints were preferred because of the marked solubility of the materials in hydrocarbon grease.

## I.2 THE SEPARATION OF VOLATILE MATERIALS

The simplest method of separating the compounds of a volatile mixture was trap to trap distillation using low temperature slush baths[2,4]. These cold baths are listed in Table I.1. The efficiency of separation varied considerably with quantity and relative composition of the mixture, the rate of distillation, condensation surface, and efficiency of the vacuum system. After satisfactorily representative samples were obtained, their purity was verified by spectroscopic analysis.

Table I.1. Low temperature slush baths*

| Slush bath | Temperature (°C) |
|---|---|
| ice/water | 0 |
| ice/salt water | 0 to -15 |
| carbon tetrachloride/liquid $N_2$ | -23 |
| chlorobenzene/liquid $N_2$ | -45 |
| chloroform/liquid $N_2$ | -63 |
| 'dry-ice'/acetone (or methanol) | -78 |
| toluene/liquid $N_2$ | -96 |
| 1 - bromobutane/liquid $N_2$ | -112 |
| methyl cyclohexane/liquid $N_2$ | -126 |
| n-pentane/liquid $N_2$ | -132 |
| iso-pentane/liquid $N_2$ | -160 |
| liquid $N_2$ | -196 |

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*All slush bath temperatures are estimated to ±5°C. Attention is drawn to the toxicity of all organic materials.

## I.3 STORAGE AND REACTION VESSELS

These were constructed of Pyrex-glass and their shapes were determined by the volatility, stability and quantity of the compound in question. The choice of taps for storage and reaction vessels was governed by the nature of the compounds involved and the particular experimental conditions. The following schematic (Fig.I.2) provides a suitable description of the various types of storage and reaction vessel used in this work. The simple hydrides and those compounds that were stable gases at room temperature (e.g. HCl, $GeH_4$, $MeGeH_3$, $SiH_4$) were stored in vessels 'A' (100-2000 ml capacity) fitted with either greased or greaseless stopcocks and a MS19 ball-joint for attachment to the vacuum line. Low volatile compounds, which attacked or dissolved in grease (e.g. $BBr_3$, $GeH_3Br$) or were generally unstable (e.g. $GeH_3I$) were stored in the liquid/solid phase in vessels 'B' (10-100 ml capacity) fitted with Teflon-in-glass stopcocks either at room temperature, -78° or -196° depending upon the compound. In some cases, vessels 'B' were modified to vessels 'I' for low volatile species such as $(Me_3Ge)_2Te$. These vessels were also used in reactions where the internal pressure did not exceed 1 atmosphere. Break-seal ampoules were used for the storage of small quantities of compounds and these were usually held at 25°, -78°, or -196°. Dry solvents (e.g. $C_4H_4O$, $Et_2O$) were stored, under vacuum, in contact with drying agents (i.e. $Li[AlH_4]$) in vessels 'F' equipped with Teflon-in-glass stopcocks.

The design of the reaction vessels was dictated by both the quantity of reactants and the phase in which reaction occurred. For gas phase reactions (e.g. HI/$AlI_3$ reactions) a vessel 'D' (150-1000 ml) was used. For smaller scale reactions at low pressures or in the condensed phase a reaction finger 'C' (5-100 ml) fitted with a MS19 ball joint and Teflon-in-glass stopcock was used. For surface-area dependent reactions, such as those where a gas reacts with a low-volatile liquid (e.g. HI/$Me_2GeBr_2$) vessel 'F' was used. Reactions involving passage of a gas through a solid were conducted in vessels of type 'E'; e.g. the preparation of $H_3GeF$ by passage of $H_3GeI$ over $PbF_2$; the volume of the vessel was ca 150 ml. For exothermic reactions, where the product is susceptible to decomposition or hydrolysis (e.g. $H_3SiI$ passed over HgS) vessel 'L' was used. The column was equipped with two U-traps, 2 MS19 ball joints, a constriction and a \$24/40 joint for packing and cleaning purposes. For sealed tube reactions (e.g. $(H_3Ge)_2Se/H_2Se$) n.m.r. capillaries (1-4 mm o.d.) drawn from the MS19 joint 'G' were utilized. These were filled and sealed off on the vacuum line. For sealing, an appropriate torch was used to give a sharp hot flame, so that the time required to soften the glass was short and the heating was localized in a narrow area. Sometimes it was advantageous to use a standard n.m.r. tube (5 mm o.d.) attached to a MS19 joint with a constriction at the neck 'H', so that the sealing could be completed quickly at the constriction. Opening of

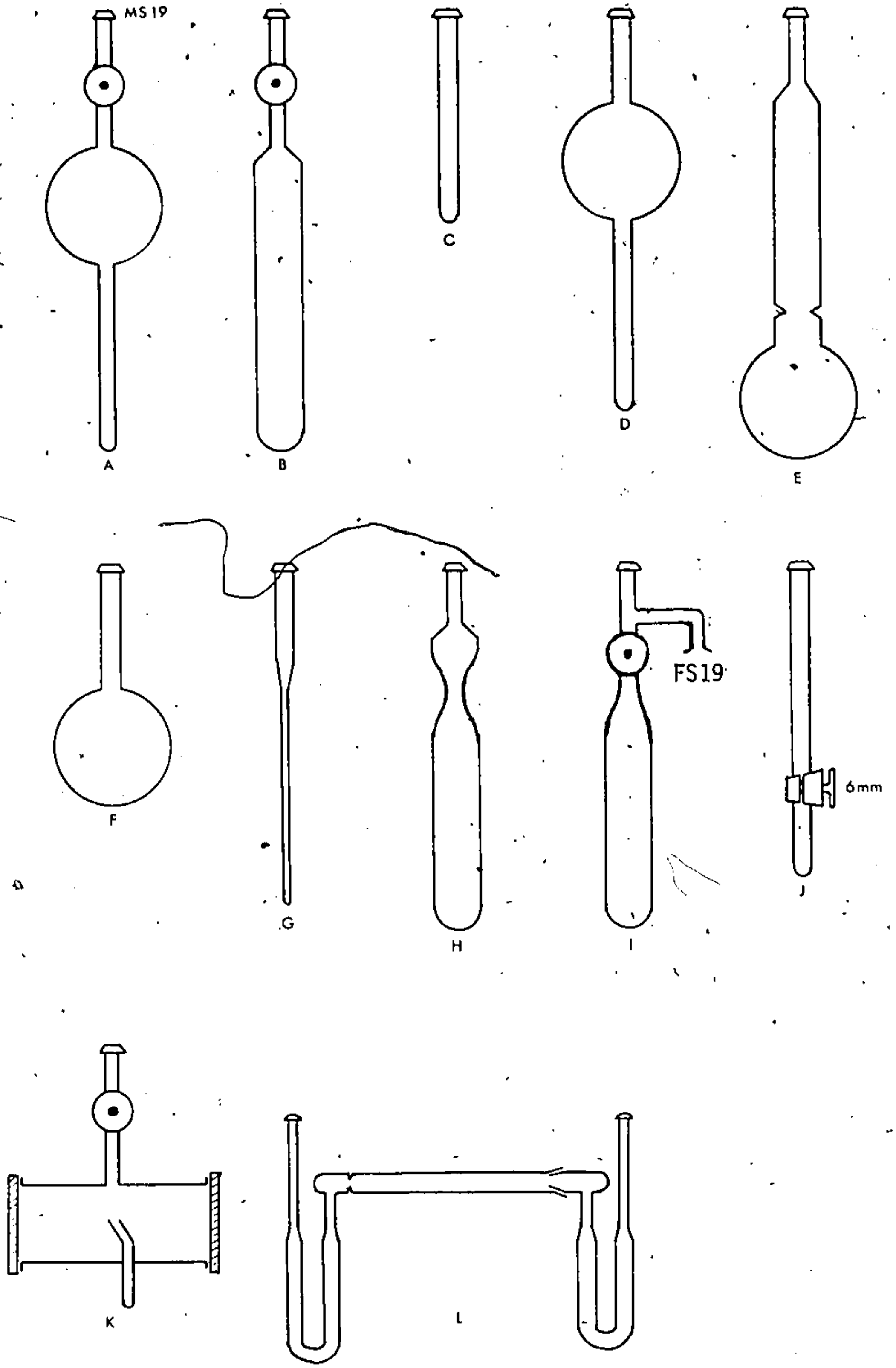

Figure I.2 Storage and reaction vessels

such tubes on the vacuum line was effected by the tube breaker 'J', equipped with a MS19 ball joint and a greased (6 mm) tap.

## I.4 CLEANING OF RE-USABLE GLASSWARE

The cleaning of re-usable glassware is one of the important aspects in successful experimentation. This faotor was considered when the apparatus and the species were selected for the experiment. Different methods were employed in cleaning glassware, with respect to both reagents and processes. The following cleaning fluids were most common: water, dilute or concentrated acids (e.g. 10% HF, HCl/$HNO_3$ 3:1), sodium hydroxide/ethanolic solution, organic solvents detergents, etc. The techniques included soaking, washing with a brush and in some cases washing by ultrasonic devices. In many cases, the cleaning required several steps in a certain sequence. After cleaning, the glassware was dried in an oven at 100°C.

## I.5 INSTRUMENTATION AND PHYSICAL METHODS

(a) Infrared spectroscopy: A gas cell 'K' of 50 mm or 90 mm path length, fitted with KBr plates (4000-350 $cm^{-1}$) was used for volatile samples. A small finger permitted distillation of small quantities of material into the cell. In general, gas pressures ranging from 1 to 15 mmHg were employed. Low volatile liquids were recorded as smears between CsI plates (4000-200 $cm^{-1}$) in an air-tight device. A Beckman I.R. 12 (4000-200 $cm^{-1}$) spectrometer was used. The positions of sharp peaks were accurate to ± 1 $cm^{-1}$.

(b) Raman spectroscopy: Liquid and solid samples were sealed under vacuum in Pyrex glass capillaries (*ca*. 2 mm o.d., *ca*. 50-100 mm long) and placed it in a Spectra Physics/Beckman 700 laser-Raman spectrometer with an argon laser source. Accuracies of ± 2 $cm^{-1}$ were routinely available on sharp peaks.

(c) Nuclear magnetic resonance spectroscopy ($^1H$ n.m.r.): Samples were sealed in Pyrex glass capillaries (*ca*. 2 mm o.d.) which were placed inside standard n.m.r. tubes with $CCl_4$ to ensure good sample spinning. Samples were run neat or in presence of a solvent ($CCl_4$, $C_6H_{12}$) and a reference (TMS, $C_6H_{12}$). A Jeolco C-60HL spectrometer equipped with a standard variable temperature probe and electronic integrator was used for $^1H$ analysis and structural determination.

(d) Mass spectrometry: Mass spectra were obtained using a Varian MAT CH5 Double Focusing spectrometer equipped with an INCOS 2000 computer system; at an electron energy of 70 eV. Samples were admitted to the spectrometer from a small finger with a 3 mm Teflon-in-glass stopcock. Sealed tubes were broken using a tube breaker 'J' on a small vacuum line connected to the inlet system of the spectrometer.

(e) X-ray photoelectron spectroscopy: Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer, using magnesium K$\alpha$ X-radiation (1253.6 eV or 200.8 aJ) for photoelectron excitation. Samples were introduced in the vapour phase at pressures close to 5 x $10^{-2}$ Torr (6.67 x $10^{-3}$ kPa). Argon gas was bled in to form 20% of the total sample. Binding energies in excess of

120 eV were referenced to the argon $2p_{3/2}$ level at 248.63 eV. All other binding energies were referenced indirectly, via Ar $2p_{3/2}$, to the neon 2s level at 48.47 eV.[5]

(f) Vapour pressures: The compound under investigation was distilled into a small finger, immersed in various slush baths, and allowed to expand against a mercury manometer.

# CHAPTER II

# THE PREPARATION AND PURIFICATION OF STARTING MATERIALS

The compounds listed below were either commercially available or had well established preparative routes. They are considered 'starting materials' as the interest was not primarily associated with their preparation. Their purity was checked by infrared/Raman spectroscopy (i.r./R), $^1$H n.m.r. spectroscopy (n.m.r.) and/or vapour pressure measurements (v.p.) where appropriate.

ALUMINUM, Al: commercial;[d] used as obtained.

ALUMINUM TRIIODIDE, $AlI_3$: commercial;[b] stored at r.t. under $N_2$; resublimed and dried under vacuum.

AMMONIA, $NH_3$: commercial;[i] pumped off under vacuum through a trap held at -78° and dried over sodium or lithium.

ANTIMONY TRIFLUORIDE, $SbF_3$: commercial;[k] dried in a 65° oven for five hours or longer prior to use.

BORON TRIBROMIDE, $BBr_3$: commercial;[b] degassed at -78° prior to use. Stored at r.t. in vessel 'B' fitted with a Teflon-in-glass stopcock; i.r.[6]

BORON TRICHLORIDE, $BCl_3$: commercial;[i] degassed at -112° prior to use and stored at r.t. as for $BBr_3$; i.r.[6]

BROMOTRIMETHYLGERMANE, $Me_3GeBr$: commercially available;[b] degassed at -78° and stored in vessel 'B' at r.t.; i.r.[7]; n.m.r.[8]

BROMOTRIMETYLSILANE, $Me_3SiBr$: commercial;[l,m] degassed at -78° prior to use and stored at r.t. in vessel 'B'; i.r.,[9,10] n.m.r.[11]

CHLORODIMETHYLSILANE, $Me_2HSiCl$: commercially available;[b] degassed at -78° and stored in vessel 'B' at r.t.; i.r.[12], n.m.r.[11]

CHLOROTRIMETHYLGERMANE, $Me_3GeCl$: commercial[b]; degassed at -78° and stored in vessel 'B' at r.t.; i.r.[8], n.m.r.[8]

CHLOROTRIMETHYLSILANE, $Me_3SiCl$: commercial;[b] distilled through traps held at -45°, -78°, and -196°. The pure $Me_3SiCl$ was retained in the -78° trap and stored at r.t. in vessel 'B'; i.r.[13], n.m.r.[11], v.p.[2]

DICHLORODIMETHYLGERMANE, $Me_2GeCl_2$: commercially available;[b] degassed at -78° and stored at r.t. in vessel 'B'; i.r./R,[14] n.m.r.[14]

DICHLORODIMETHYLSILANE, $Me_2SiCl_2$: commercial;[b] degassed at -78° prior to use. Stored at r.t. in vessel 'B'; n.m.r.,[15] v.p.[2]

DICHLOROMETHYLSILANE, $MeHSiCl_2$: commercial;[b] degassed at -78° and stored in vessel 'B' at r.t.; n.m.r.,[11] v.p.[2]

DIMETHYLGERMANE, $Me_2GeH_2$: prepared[16] by the reduction of $Me_2GeCl_2$ with $Li[AlH_4]$ in $n$-$Bu_2O$. Stored at r.t. in vessel 'A'; i.r./R,[17,18] n.m.r.,[19] v.p.[2]

DIMETHYLSILANE, $Me_2SiH_2$: prepared[20,21] by the reduction of $Me_2SiCl_2$ of $Me_2HSiCl$ with $Li[AlH_4]$ in $n$-$Bu_2O$ . Stored in vessel 'A' at r.t. i.r.,[22] v.p.[2]

ETHANETHIOL, $CH_3CH_2SH$: commercial;[a] degassed at -78° before use; i.r.,[23] v.p.[2]

ETHANOL, $CH_3CH_2OH$: commercial;[a] degassed at -78° prior to use; i.r.,[23] v.p.[2]

FLUOROGERMANES, $Me_nH_{3-n}GeF$ ($n = 0 \rightarrow 3$): prepared[24-27] by passage of $Me_nH_{3-n}GeX$ ($X$ = Br, I; $n$ = 0,1,2) through a loosely packed column of $PbF_2$ and glass wool. Stored at -78° or -196° in vessel 'B'. $Me_3GeF$ was also prepared from $(Me_3Ge)_2O$ with $AsF_3$,[28] and stored at r.t. in vessel 'B'. The purity was checked by i.r.[24,25,29-31] n.m.r.[24,25,27,31,32]

GERMANE, $GeH_4$: commercially available;[i] purified by passage through traps held at -126° and degassed at -196°. Stored at r.t. in vessel 'A'; i.r.,[33] n.m.r.,[32] v.p.[2]

HEXABUTYLDISTANNOXANE, $(n-Bu_3Sn)_2O$: commercially available,[b] used as ~~obtained~~.

HYDROGEN BROMIDE, HBr: commercial;[i] degassed at -196° and stored in vessel 'A' at r.t.; i.r.[34]

HYDROGEN CHLORIDE, HCl: commercial;[i] degassed at -196° and stored in vessel 'A' at r.t.; i.r.[34]

HYDROGEN IODIDE, HI: Although HI may be obtained by pumping on hydroiodic acid[b] through a trap held at -78°, it was quickly and efficiently prepared as follows.[35] A reaction vessel 'F' (250 ml; containing a stirring bar and fitted with a dropping funnel) was charged with red phosphorus (10 g) or with phosphorus pentoxide ( 40 g). The adapter to the vacuum line was plugged with glass wool to reduce contamination of the line by iodine vapour. The system was evacuated and a solution consisting of iodine (4 g) and hydroiodic acid (80 g or ca. 50 ml) was added dropwise. The reaction was carried out at room temperature and HI was collected in a pure state at -196°, after first passing through traps held at -23° and -78°. Stored at r.t. in vessel 'B'; i.r.[34]

HYDROGEN SELENIDE, $H_2Se$: prepared.[36] Typically, a strip of burning magnesium ribbon[d] was plunged into a finely powdered mixture of aluminum[d] (3.3 g) and selenium (5.6 g) contained in a small cruicible to produce $Al_2Se_3$. The cruicible and alloy were placed, when cooled, into a reaction vessel equipped with a dropping funnel and an attachment to the vacuum system. The contents were evacuated. Distilled water was then slowly added to the alloy. Rapid formation of $H_2Se$ resulted and it was collected in a trap held at -196°; after first being passed through a trap at -78°, and then stored at r.t. in vessel 'A'.

HYDROGEN SULFIDE, $H_2S$: prepared[37] in an analogous manner to that for $H_2Se$, and stored at r.t. in vessel 'A'.

IODINE, $I_2$: commercially available;[d] resublimed and degassed from -78° prior to use.

IODOETHANE, $CH_3CH_2I$: commercial;[f] degassed at -78° prior to use.

IODOGERMANES, $Me_{\underline{n}}H_{3-\underline{n}}GeI$ ($\underline{n}$ = 0,1, 2): prepared[24,26,27,38] by the reaction of $Me_{\underline{n}}GeH_{4-\underline{n}}$ ($\underline{n}$ = 0,1, 2) with $I_2$, stored at -78° or 196° in vessel 'B'.

IODOMETHANE, $CH_3I$: commercial;[f] degassed prior to use.

IODOSILANES, $Me_{\underline{n}}H_{3-\underline{n}}SiI$ ($\underline{n}$ = 0,1, 2): prepared[39-43] by the reaction of $Me_{\underline{n}}SiH_{4-\underline{n}}$ ($\underline{n}$ = 0 → 3) with HI in the presence of catalytic amounts of $AlI_3$. Stored at r.t. in vessel 'B'; i.r.[42,44-46], n.m.r.[11,47,48]

LEAD (II) CYANAMIDE, $PbCN_2$: commercial;[g,n] dried under vacuum conditions before use.

LEAD (II) DIFLUORIDE, $PbF_2$: commercial;[g,n] dried under vacuum conditions before use.

LEAD (II) OXIDE, PbO: commercial;[b] used as obtained.

LEAD (II) SULFIDE, PbS: commercial;[b] use as obtained.

LITHIUM, Li: commercial;[b] cleaned with petrolium ether prior to use.

LITHIUM ALUMINUM HYDRIDE, $Li[AlH_4]$: commercial;[b] used as supplied.

LITHIUM OXIDE, $Li_2O$: commercial;[b] used as supplied.

LITHIUM SULFIDE, $Li_2S$: commercial;[b] used as supplied.

MERCURY OXIDE, HgO: commercial;[b] used as supplied.

MERCURY SULFIDE, HgS: commercial;[b] used as supplied.

METHANETHIOL, $CH_3SH$: kindly donated by Dr. J. M. McIntosh. Commercially available;[a] stored in vessel 'B' at r.t.; i.r.[34]

METHANOL, $CH_3OH$: commercial;[a] degassed at -78° before use; i.r.,[23] n.m.r.;[49] v.p.[2]

METHOXYTRIBUTHYSTANNANE, $Bu_3SnOMe$: commercially available;[b] and used as supplied.

METHYLGERMANE, $MeGeH_3$: prepared[50] by the reaction of germyl potassium with iodomethane in 1,2 - dimethoxyethane. The volatile products were fractionated through traps at -126°, -160° and -196°. The pure $MeGeH_3$ collected in the -160° trap was stored at r.t. in vessel 'A'; i.r./R,[17,18] n.m.r.[19]

METHYLSILANE, $MeSiH_3$: prepared[20,51] by reduction of $MeHSiCl_2$ or $MeSiCl_3$ with $Li[AlH_4]$ in n-butyl ether. The pure product was collected at -196° after passage through a trap at -78° Stored at r.t. in vessel 'A'; i.r./R.,[52] n.m.r.,[47] v.p.[2]

SELENIUM POWDER, $Se_8$: commercial;[d] used as supplied.

SILANE, $SiH_4$: commercially available;[i] degassed at -196° and stored at r.t. in vessel 'A'; i.r.,[33] n.m.r.[48]

SILVER (II) OXIDE, AgO: commercial;[b] used as supplied.

SOLVENTS: dimethyl ether[i] was used as supplied. Diethyl ether,[f] n-butyl ether,[a] monoglyme,[e] diglyme,[e] benzene[f] and tetrahydrofuran[e] were dried and stored over $Li[AlH_4]$ in vessel 'F' at r.t. prior to use. Spectral-grade[c,j] carbon tetrachloride and cyclohexane were vacuum distilled and stored in vessel 'B' at r.t.

TELLURIUM POWDER, Te: commercial;[d] used as supplied.

TETRAMETHYLSILANE, $Me_4Si$: commercial;[h] stored at r.t. in vessel 'B'; n.m.r.[19]

TRICHLOROMETHANETHIOL, $CCl_3SH$: commercial;[a] degassed prior to use.

2,2,2, - TRICHLOROETHANOL, $CCl_3CH_2OH$: commercial;[a] degassed before use.

TRIBROMOMETHYLGERMANE, $MeGeBr_3$: commercial[b]; degassed at -78° and stored in vessel 'B' at r.t.; i.r./R[7]

2,2,2, - TRIFLUOROETHANOL, $CF_3CH_2OH$: commercial;[a] degassed at -78° before use.

TRIFLUOROMETHANESULFENYL CHLORIDE, $CF_3SCl$: commercial;[o] degassed at -196° and stored in vessel 'B' at r.t.; i.r.,[53] n.m.r.[54]

COMMERCIAL SUPPLIES

a. Aldrich Chemical Co., Milwaukee, Wisc.
b. Alfa Inorganics Inc., Beverly, Mass.
c. Anachemia Chemicals Ltd., Montreal
d. The British Drug Houses Ltd., Poole, Dorset, Eng.
e. Eastman Organic Chemicals, Rochester, N.Y.
f. Fisher Scientific Co., Fair Lawn, N.J.
g. ICN Life Sciences Group (K & K), Plainview, N.Y.
h. Laramie Chemical Co., Laramie, Wy.
i. Matheson Gas Products, East Rutherford, N.J.
j. NMR Specialities Inc., New Kensington, Pa.
k. Ozark-Mahoning Co., Tulsa, Okla.
l. PCR Inc., Gainesville, Fla.
m. Petrarch Systems, Levittown, Pa.
n. Research Organic/Inorganic Chem. Corp., Sun Valley, Calif.
o. Columbia Organic Chemicals, Co., Inc., Columbia, S.C.

# CHAPTER III

## SOME PRELIMINARY CONSIDERATIONS

Although the novelty of silyl and germyl species has long passed, the fact that they feature in an increasingly large number of compounds reflects a continuing research interest. Several excellent review articles outline the synthesis and properties of the silanes and their derivatives.[55-61] The chemistry of the germanes and of germyl derivatives was developed more slowly because of thermal instability problems and the scarcity of synthetic procedures. However, at this time, a large number of these compounds have been prepared and studied and many of the interesting comparisons made between simple carbon and silicon compounds can now be extended to include the analogous germanium compounds. The synthesis and properties of the germanes and their derivatives have been summarized in several recent reviews[60,62-65]. A quick comparison of the series of $R_3C-$, $R_3Si-$ and $R_3Ge-$ derivatives, where R = H or organic residue, is essential in assessing the bonding and chemical characteristics of a particular linkage as one proceeds from $C \longrightarrow Si \longrightarrow Ge$.

Along the series $C \longrightarrow Si \longrightarrow Ge \longrightarrow Sn \longrightarrow Pb$ there is (i) an increase in atomic size and hence effectively a decrease in steric shielding by substituents, (ii) an increase in polarity of bonds to the more electronegative substituents and (iii) a more extensive electron cloud and an increase in polarizability[66]. Although these properties may not be rigorously related to chemical activity, certain general trends are clear.

Thus, the Si-X bond of $R_3SiX$, where X=halogen, is usually more reactive and more labile than the analogous C-X bond, while the Ge-X bond is more labile than the Si-X bond, but reacts rather less readily with oxidizing reagents. The Si-O-Si linkage, which results from oxidation of the Si-X bond, is the most important inorganic one while the C-C bond is the most important organic linkage. The C-C bond is more stable than the Si-Si bond but the Si-O-Si bond sequence is more stable than C-O-C. The electron-withdrawal resulting from increasing halogenation in $CH_3SiH_3$ decreases the stability of the C-Si bond to hydrolysis so that water cleaves $CCl_3SiCl_3$[67] and $CF_3SiF_3$[68] whereas base leaves $CH_3SiH_3$ intact[1]. The non-polar nature of the C-Si bond reduces attack by polar reagents so that $(CH_3)_4Si$ is stable in water whereas the more polar $SiBr_4$ reacts vigorously.

The M-H bond energies of the tetrahydrides, $MH_4$, decrease along the series C ⟶ Pb, as apparently do those of the two $H_3M\text{-}MH_3$ and $H_3M\text{-}M'H_3$ series[69], where M = Si, Ge and M' = a Group IV element. Consequently whilst the M-H bond is thermodynamically able to undergo many reactions as compared with the C-H bond, the heavy atom bonding in the system C-M-H is relatively inert. The course of the reactions is greatly affected by the polarity of the M-H bond, which is actually similar to the C-Br link rather than the C-H (Table III.1) and therefore, many reactions of the silanes and germanes are similar to the reactions of alkyl halides.

Table III.1.

| Bond | $\overset{\delta+}{Si}$-$\overset{\delta-}{H}$ | $\overset{\delta+}{Ge}$-$\overset{\delta-}{H}$ | $\overset{\delta-}{C}$-$\overset{\delta+}{H}$ | $\overset{\delta+}{C}$-$\overset{\delta-}{Br}$ |
|---|---|---|---|---|
| Electronegativity | 1.8 2.1 | 1.9 2.1 | 2.5 2.1 | 2.5 2.8 |
| Electronegativity difference | +0.3 | +0.2 | -0.4 | +0.3 |

The effect of the silicon atom and its subgroup is not limited to bonds by which it is directly attached to carbon or other elements but extends to more remote bonds. The C-Cl bond is more reactive toward nucleophilic reagents[70] in $Me_3SiCH_2Cl$ than it is in $Me_3CCH_2Cl$, presumably because of the lower steric hinderance. However, $Me_3SiCH_2Cl$ is less reactive toward $AgNO_3$ than $Me_3CCH_2Cl$, due to the high electronegativity of the group which hampers electrophilic attack on the halogen. An interesting feature is the so called $\beta$- effect, i.e. the tendency of silicon and germanium compounds with a halogen at a $\beta$- carbon, e.g. $Me_3SiCH_2CH_2Cl$ to decompose with formation of $Me_3SiCl$ and $CH_2 = CH_2$, while the carbon analog can be obtained by condensation of $Me_3CCl$ and $CH_2 = CH_2$[71]. Among these effects it is worth noting the addition of bromine at the triple bond of vinylethynylsilanes in contrast to the addition at the double bond of vinylacetylene analogs[72].

These differences and similarities based on comparisons of bond polarities are limited by assessments of the extent and effect of $\pi$-type interactions. Unlike carbon, silicon and germanium may both be considered to have low lying d-orbitals suitable for $(p\rightarrow d)\pi$ bonding with ligand orbitals of correct symmetry.[56,69]. There has been much speculation about the role of d-orbitals in chemical bonding since the classic work of Pauling on orbital hybridization[73]. The formation of $(p\longrightarrow d)\pi$ bond was considered theoretically by Craig[74-77], Jaffe[78], Moffitt[79] and Cruickshank[80,81], and it appears that the extent of this type of bonding is considerable when the central atom carries a formal positive charge in the singly bonded structure and is surrounded by atoms or groups more electronegative than itself. The effect of the formal positive charge on the central atom is to increase the electron affinity and to contract its d-orbitals making them less diffuse. This should then increase the overlap integral between the d-orbitals making them less diffuse. This should then increase the overlap integral between the d-orbitals of the central atom and the p-orbitals of the atoms or groups attached to it. As a result of these theoretical considerations, the role of d-orbitals in the bonding of silicon and germanium compounds has been widely discussed in the literature. The reviews by Stone[82], Burger[83], Ebsworth[69] and Attridge[84] deal with the problems of obtaining significant experimental evidence for $(p\longrightarrow d)\pi$ interactions involving elements of the silicon subgroup. It is generally thought that $\pi$-interactions involving germanium are less important than silicon and to a lesser extent with donor atoms of second-and lower-row elements. The reasons for the differences in π-electron ecceptor capability of silicon and germanium have not been established conclusively. It may be related in part to the presence of a radial node in the 4d-orbitals of germanium but not silicon[85]. The most frequently quoted evidence for (p⟶d)π bonding is discussed in Chapter VI where only those aspects relevant to my research project will be mentioned.

This research project has been concerned with three studies of the lower Group IV elements and is a continuation of work started by Dr. J. E. Drake and his research group. The first study involved the synthesis of new Main-Group Organometallic and Hydride derivatives as well as the improved synthesis of known compounds containing a silicon or germanium atom bound to a Group VI element. The second study stemmed from the realization that these species, with relatively simple structures, were ideal for spectroscopic investigation. $^1$H n.m.r., Raman, infrared and X-ray photoelectron spectroscopic studies, as well as mass spectrometry were used as essential analytical tools for the characterization of these hydrides and organometalloids. This was particularly the case because conventional analytical procedures are inappropriate when dealing with these compounds which typically are highly air and moisture sensitive.

The interest in the third study was centered around the reactivity of the M-E (M=Si, Ge; E=O,S,Se,Te) bond with selected reagents. The thermal instability of the M-E species produced interesting results. The modes of decomposition were studied and compared with those of related systems.

A search into the background of these series of analogous compounds of silicon and germanium reveals that although a great deal of intriguing work has been done with the parent Silyl- and Germyl- Group VI Species, much work of interest remained to be done on these and Related Species and this is reported in this thesis. A brief review of the previous preparative and related studies of the simple Silyl- and Germyl-Group VI Species provides a base for the present investigation. Where possible, the studies of the Silyl- and Germyl- Group VI Species are dealt with together but frequently it is more convenient to treat them separately.

## III.1. SILYL- GROUP VI SPECIES

The tendency for silicon to favor the formation of the siloxane bond (Si-O) was first recognized by Stock[1] through his pioneering work with boron and silicon hydrides. He isolated $(H_3Si)_2O$ and $(H_5Si_2)_2O$ via the hydrolysis of the Si-X bond where X = Cl, Br, I and he coined their name siloxanes. $(H_3Si)_2O$ and its methyl analogs can also be formed by hydrolysis of many other silyl compounds including: silylphosphines[86,87] and -arsines[87]; disilyl-sulfides,[88,89] -selenide[88] and -telluride[90]. The last three compounds have been prepared by the interaction of halogenosilanes with mercuric sulfide, silver selenide[88,91] and lithium sulfide,[92] selenide[99] and telluride[90,99], seleno and telluro Grignard reagents[93], Table III.2. A conversion series for the reaction of silyl and organosilyl compounds with silver salts has been formulated which indicates how certain bonds attached to silicon may be interconverted.[94-96] The order of the series is as follows:

$$(R_3Si)_2Te \longrightarrow R_3SiI \longrightarrow (R_3Si)_2Se \longrightarrow (R_3Si)_2S \longrightarrow R_3SiBr \longrightarrow$$

$$R_3SiNCN \longrightarrow R_3SiCl \longrightarrow R_3SiNCSe \longrightarrow (R_3SiN)_2C \longrightarrow R_3SiNCS \longrightarrow$$

$$R_3SiCNO \longrightarrow R_3SiN_3 \longrightarrow (R_3Si)_2O \longrightarrow R_3SiF$$

The R groups in the above compounds may be hydrogen, aliphatic or aromatic groups, or combinations of these. Conversions in this series may be carried out satisfactorily by the reaction of any compound earlier in the series with the appropriate silver salt. For example, the desired disilyl sulfide can be obtained from the reaction of disilyl selenide with silver sulfide, e.g. $(R_3Si)_2Se + Ag_2S \longrightarrow (R_3Si)_2S + Ag_2Se$ [1]. The direct production of $R_3M\text{-}E\text{-}MR_3$ species, where E = S,Se,Te, by the reaction of $R_3SiX$ where X = Cl,Br,I with HgS, $Li[Al(EH)_4]$ where E = S,Se and $Li_2Te$ will be described in the following chapter and provides a general method for application to organosilicon and hydride chemistry.

Studies on the Si-E systems have centered around the nature of the heavy atom bonding. In general, Lewis acids[97] (e.g. $AlI_3$) cleave the Si-O bond while Lewis bases[98] (e.g. $NH_3$) encourage condensation. Van Dyke has shown that the amphoteric phosphorus(III) halides cleave $H_3SiOMe$ but not $(H_3Si)_2O$,[173] indicating a reduction in Lewis basicity with additional silyl substitution as is also found for the series $Me_3N$ through to $(H_3Si)_3N$.[100] With $B_2H_6$[101] and $Me_3Ga$[102] as reference acids, $(H_3Si)_2O$ is a weaker nucleophile than $Me_2O$ but stronger than $(H_3Si)_3N$. This is expected since the result of several investigations indicate that the skeletal Si-O-Si angle is ca.144[103], Table III.3. A marked degree of $(p \longrightarrow d)\pi$ bonding is implied by such a wide angle when carbon is replaced by silicon. The discovery of the effect of skeletal angle widening in siloxanes aroused interest in related germyl species.

## III.2. GERMYL- GROUP VI SPECIES

These are known for the sequence $(R_3Ge)_2E$ where $E = O,S,Se,Te$ and $R = H,Me$. The preparative routes involve reactions of germyl carbodiimides[104,105], germylphosphine or arsine[106,107] with Group VI hydrides; exchange reactions of halogenogermanes with metal salts (PbO,[108] HgS,[109] $Li_2S$,[110] $Na_2Se$ or $Na_2Te$[111]) and disilyl chalcogenides[99], and silent electrical discharge reactions of germane with $H_2S$ and $H_2Se$[112], Table III.2. The former routes were reexamined and subsequently improved upon, as will be described in the following chapter. The speculation as to the Ge-E-Ge bond angles for $E = O,S$ from calculations based on the i.r. spectra[113,114] have been

Table III.2. Preparative and reaction routes for disilyl- and digermyl-Group VI species

| Reactants | | Product chalcogenide | Reference |
|---|---|---|---|
| $H_3SiAsH_2$ | $H_2O$ | $(H_3Si)_2O$ | 87 |
| $H_3SiPH_2$ | $H_2O$ | $(H_3Si)_2O$ | 87 |
| $(H_3Si)_2PH$ | $H_2O$ | $(H_3Si)_2O$ | 86 |
| $(H_3Si)_2S,Se$ | $H_2O$ | $(H_3Si)_2O$ | 88 |
| $(H_3Si)_2Te$ | $1/2O_2$ | $(H_3Si)_2O$ | 90 |
| $(MeH_2Si)_2S$ | $H_2O$ | $(MeH_2Si)_2O$ | 42 |
| $MeH_2SiI$ | $H_2O$ | $(MeH_2Si)_2O$ | 42 |
| $Me_2HSiI$ | $Ag_2CO_3$ | $(Me_2HSi)_2O$ | 89 |
| $Me_2HSiI$ | HgS | $(Me_2HSi)_2S$ | 89 |
| $MeH_2SiI$ | HgS | $(MeH_2Si)_2S$ | 42 |
| $H_3SiI$ | HgS | $(H_3Si)_2S$ | 88 |
| $H_3SiBr$ | $Li_2S$ | $(H_3Si)_2S$ | 92, 129 |
| $H_3SiBr$ | $Li_2E$ | $(H_3Si)_2E$ E=Se,Te | 99 |
| $H_3SiI$ | $Li_2Te$ | $(H_3Si)_2Te$ | 90 |
| $Me_3SiCl$ | $Li_2Te$ | $(Me_3Si)_2Te$ | 90 |
| $H_3SiI$ | $Ag_2Se$ | $(H_3Si)_2Se$ | 91, 88 |
| $Me_3SiCl$ | PhEMgBr | $(Me_3Si)_2E$ E=Se,Te | 93 |
| $(H_3GeN)_2C$ | $H_2Se$ | $(H_3Ge)_2Se$ | 104 |
| $(Me_{\underline{n}}H_{3-\underline{n}}GeN)_2C$ | $H_2E$ | $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$ E=O⟶Te | 105, 125 |
| $H_3GeAsH_2$ | $H_2E$ | $(H_3Ge)_2E$ E=S,Se | 106, 107 |
| $H_3GePH_2$ | $H_2E$ | $(H_3Ge)_2E$ E=S,Se | 106, 107 |
| $H_3GeBr$ | PbO | $(H_3Ge)_2O$ | 108 |
| $H_3GeI$ | HgS | $(H_3Ge)_2O$ | 109 |
| $H_3GeBr$ | $Li_2S$ | $(H_3Ge)_2S$ | 110 |
| $Me_3GeCl$ | $Na_2E$ | $(Me_3Ge)_2E$ E=Se,Te | 111 |
| $H_3GeBr$ | $(H_3Si)_2E$ | $(H_3Ge)_2E$ E=Se,Te | 99 |
| $H_3GeF$ | $(H_3Si)_2S$ | $(H_3Ge)_2S$ | 174 |
| $H_4M$ | $H_2E$ | $(H_3M)_2E$ M=Si,Ge; E=S,Se | 112 |

clarified by an electron diffraction examination which places the Ge-O-Ge angle at 126° and that of Ge-S-Ge at 99°,[115,116] Table III.3. The former angle has been cited as evidence for $\pi$-bond character but of a lesser degree than occurs for the silicon analogue.

Table III.3. Comparison of bond angles in analogous Group IV compounds*

| Molecule | ∠M-O-M (deg) | ∠M-S-M (deg) | ∠M-Se-M (deg) |
|---|---|---|---|
| $(H_3C)_2E$[a] | 111.5 ±1.5 | 98.9 ±0.2 | 96.2 ±0.2 |
| $(H_3Si)_2E$[a] | 144.1 ±0.9 | 97.4 ±0.7 | 96.6 ±0.7 |
| $(H_3Ge)_2E$[a] | 125.6 ±0.4 | 98.9 ±0.3 | 94.6 ±0.5 |
| $(Me_3Si)_2E$[a,c] | 148.0 ±3.0 | 122.0 | |
| $(Me_3Ge)_2E$[a,c] | 141.0 ±0.5 | 123.0 | |
| $(Me_3Sn)_2E$[a,c] | 141.0 ±0.5 | 124.0 | |
| $(F_3Si)_2O$[b] | 155.7 ±2.0 | | |
| $(H_2SiO)_4$[b] | 148.6 ±1.2 | | |
| $(Me_2SiE)_3$[b,d] | 131.6 ±0.4 | 110.0 | |
| $(Me_2SiO)_4$[b] | 144.8 ±1.2 | | |
| $(Me_2SiS)_2$[d] | | 75.0 | |
| $(MeSi)_4S_6$[e] | | 104.5 ±0.1 | |
| $(MeGe)_4S_6$[f] | | 104.6 ±2.0 | |

*Quoted from: [a]B. Rozsondai and I. hargittai, Acta Chim. Acad. Sci. Hung., 90(2),157 (1976); L. V. Vilkov and L. S. Khaikin, Topics in Current Chemistry, 53, Springer, Berlin (1975). [b]B. Csakvari, Zs. Wagner, P. Gomory, F. C. Mijlhoff, B. Rozsondai, and I. Hargittai, J. Organometal. Chem., 107, 287 (1976). [c]S. Sorrio, A. Foffani, A. Ricci, and R. Danieli, J. Organometal. Chem., 67, 369 (1974). [d]Ref.195. [e]J. C. J. Bart and J. J. Daly, Chem. Comm., 1207 (1968). [f]R. H. Benno and C. J. Fritchie, J. Chem. Soc. (Dalton), 543 (1973).

# CHAPTER IV

## THE SYNTHESIS OF BIS(SILYL)- AND BIS(GERMYL)- CHALCOGENIDES

## $(Me_nH_{3-n}M)_2E$ WHERE M=Si,Ge,E=O,S,Se,Te AND $n=0\rightarrow 3$

## IV.1. INTRODUCTION

This chapter is primarily concerned with the synthesis of bis(silyl) - and bis(germyl) - chalcogenides of the formula $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M=Si,Ge; E=O,S,Se,Te and $\underline{n}$= 0 → 3. The synthetic routes include comparative reactions of some halogenosilanes, disilazanes, bis(silyl) - and bis(germyl) - carbodiimides with Group VI species; and metathesis reactions of some halogeno-silanes and -germanes with complex aluminates, mercury (II), lead (II), silver (II), lithium (I) and silicon (IV) species. For the preparation of the fully substituted species, $(Me_3M)_2E$, commercially available halides, $Me_3MX$ where X = Cl, Br were used for the most part. In the case of the hydridic species, $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where $\underline{n}$ = 0,1,2, the use of previously prepared $Me_{\underline{n}}H_{3-\underline{n}}MX$ halides prevailed. The preparative routes are well-defined and include the reactions of silanes with hydrogen iodide in the presence of catalytic amounts of aluminum triiodide[43] [1], the cleavage of phenylsilane with hydrogen iodide or bromide[43] [2], the halogenation of germanes with iodine[43] [3], boron trichloride[43] [4] and exchange reactions of chloro-, or bromo- germanes with hydrogen bromide or iodide[43] [5].

$$Me_{\underline{n}}SiH_{4-\underline{n}} + HI \xrightarrow{AlI_3} Me_{\underline{n}}H_{3-\underline{n}}SiI + H_2 \qquad [1]$$

$$PhSiH_3 + HBr \longrightarrow H_3SiBr + PhH \qquad [2]$$

$$Me_{\underline{n}}GeH_{4-\underline{n}} + I_2 \longrightarrow Me_{\underline{n}}H_{3-\underline{n}}GeI + HI \qquad [3]$$

$$6Me_{\underline{n}}GeH_{4-\underline{n}} + 2BCl_3 \longrightarrow 6Me_{\underline{n}}H_{3-\underline{n}}GeCl + B_2H_6 \qquad [4]$$

$$Me_{\underline{n}}H_{3-\underline{n}}GeCl + HBr \longrightarrow Me_{n}H_{3-\underline{n}}GeBr + HCl \qquad [5]$$

The fluorogermanes used in the exchange reactions with bis(silyl) - carbodiimides and -chalcogenides were prepared by the interaction of an iodogermane with lead (II) fluoride[27] [6] or by the action of $SbF_3$ on $(Me_3Ge)_2O$ [7], i.e.

$$2Me_{\underline{n}}H_{3-\underline{n}}GeI + PbF_2 \longrightarrow 2Me_{\underline{n}}H_{3-\underline{n}}GeF + PbI_2 \qquad [6]$$

$$3(Me_3Ge)_2O + 2SbF_3 \longrightarrow 6Me_3GeF + Sb_2O_3 \qquad [7]$$

## IV.2. EXPERIMENTAL

### (a) Reactions of halogenosilanes with water

$$2Me_{\underline{n}}H_{3-\underline{n}}SiX + H_2O \longrightarrow (Me_{\underline{n}}H_{3-\underline{n}}Si)_2O + 2HX \qquad [8]$$

In a typical experiment, $MeH_2SiI$ (4.06 mmol) was condensed, under vacuum conditions, into a reaction vessel (ca. 70 ml, type 'B') containing 8 ml of degassed distilled water. The stopcock was closed and the contents allowed to react at room temperature with some shaking. After ca. 15-20 minutes a small amount of hydrogen was pumped off while the vessel was held at -196°. The volatile material was then allowed to distill through a series of U-traps held at -45°, -78° and -196°C. The trap at -45° retained the excess $H_2O$ while that at -196° retained hydrogen iodide. The fraction at -78° was passed again through traps held at -45°, -78° and -196°. The trap at -45°

contained a small amount of water while pure $(MeH_2Si)_2O$ (1.80 mmol, 89%) was retained at -78°, as identified spectroscopically[44]. Traces of $(MeH_2Si)_2O$ were also collected in the trap at -196° and the amount increased with longer fractionation time and back pumping. By a similar procedure $Me_2HSiI$ (2.92 mmol) was reacted with $H_2O$ (ca. 6 ml) to give $(Me_2HSi)_2O$ (1.39 mmol, 95%; identified initially by its $^1H$ n.m.r. parameters[11]). The analogous reaction of $Me_3SiBr$ (2.67 mmol) with $H_2O$ (ca. 6 ml) was allowed to occur for 35 minutes. Upon fractionation through traps held at -23°, -78° and -196°, the excess water was collected at -23° while the trap at -196° retained hydrogen bromide.[34] The fraction at -78° was refractionated through traps held at -23° and -78°. The former trap retained traces of $H_2O$ and the latter pure $(Me_3Si)_2O$ (1.20 mmol, 90%). The infrared spectrum[117] showed prominant features at: 2959 (ms), 2899 (m), 1410(m), 1252(vs), 1055(vs), 843(vs), 823(m), 756(m), 688(m), 620(m), 522(w), 330(vs) $cm^{-1}$. Analogously, $H_3SiBr$ (2.64 mmol) and $H_2O$ (ca. 5 ml) were allowed to react for 15 minutes with shaking to give $(H_3Si)_2O$ (1.07 mmol, 81%) retained at -126°, HBr at -196° and $H_2O$ at -78°C. Features in the infrared spectrum of $(H_3Si)_2O$[117] assignable to the silyl group were at 2183(s), 2169(s), 1105(s), 957(vs), 764(m) $cm^{-1}$.

## (b) Reactions of disilazanes with $H_2O$, $H_2S$ and $H_2Se$

$$(Me_2HSi)_2NH + H_2O \longrightarrow (Me_2HSi)_2O + NH_3 \qquad [9]$$

$$(Me_3Si)_2NH + H_2S \longrightarrow [Me_3SiS]^-NH_4^+ \xrightarrow{Me_3SiCl} (Me_3Si)_2S + NH_4Cl \quad [10]$$

Typically, $(Me_2HSi)_2NH$ (3.48 mmol) was condensed under vacuum conditions into a reaction vessel (ca. 70 ml, type 'B') containing 4 ml of degassed distilled water. The stopcock was closed and the contents were allowed to react at room temperature for 20 minutes with some shaking of the vessel. Fractionation of the products through a series of traps held at -45°, -78° and -196°C gave the pure $(Me_2HSi)_2O$ (3.39 mmol) in a 97% yield as condensate in the -78° trap. The excess water was retained at -45° while $NH_3$ was collected in the -196° trap. The analogous reaction of $(Me_3Si)_2NH$ (2.77 mmol) with a slight excess of $H_2O$ for 25 minutes at room temperature gave $(Me_3Si)_2O$ (2.70 mmol) at -78°, $NH_3$ at -196° and traces of water at -23°.

In another experiment $(Me_3Si)_2NH$ (2.58 mmol) was combined with excess $H_2S$ as above. On warming to room temperature a white solid adduct was formed immediately. After 25 minutes the vessel was immersed in a -45° bath and the volatile material was collected in a trap held at -196°. Spectroscopic investigation showed that the contents of the -196° trap consisted of $H_2S$, traces of $Me_3SiSH$ and $[Me_3SiS]^-NH_4^+$. The reaction vessel was then held at -196° and $Me_3SiCl$ (1.08 mmol) added. The mixture was brought to room temperature ~~and~~ allowed to react for 4 hours. Fractionation of the volatile products gave $(Me_3Si)_2S$ (0.18 g, 1.01 mmol) in a trap held at -23° and traces of $Me_3SiCl$ and a white solid at -196°. The white solid in the vessel was shown to be $NH_4Cl$ and unreacted $[Me_3SiS]^-NH_4^+$. By a similar procedure $(Me_3Si)_2NH$ (2.03 mmol) was reacted with excess $H_2Se$. Subsequent reaction of $Me_3SiCl$ (1.19 mmol) with $[Me_3SiSe]^-NH_4^+$ gave $(Me_3Si)_2Se$ (0.22g, 0.98 mmol). Contamination of the vacuum system with the solid adduct made this synthetic route inconvenient. The purity of the products was initially checked by their infrared spectra[117]: $(Me_3Si)_2S$ - 2950(s), 2890(m), 1452(w), 1406(m), 1252(s), 865(s), 845(vs), 828(vs), 755(m), 692(m), 628(s), 493(vs), 441(m), 243(s), 225 $cm^{-1}$; $(Me_3Si)_2Se$ - 2960(s), 2900(m), 1406(m), 1257(vs), 843(vs), 823(vs), 747(s), 686(s), 623(s), 369(vs), 363(sh), 215(s), 232 $cm^{-1}$.

### (c) Reactions of bis(silyl)- and bis(germyl)- carbodiimides with $H_2E$ where E=O,S,Se

$$(Me_3MN)_2C + H_2O \longrightarrow (Me_3M)_2O + 1/2(H_2NCN)_2 \qquad [11]$$

$$M = Si,Ge$$

Bis(silyl)- and bis(germyl)- carbodiimides were prepared in high yields by the direct reaction of iodomethyl-silanes and -germanes or bromotrimethyl-silane and -germane with lead (II) cyanamide. Typically, $Me_2HSiI$ (5.83 mmol) was passed back and forth through a column (type 'L') of fresh anhydrous lead (II) cyanamide (25g; packed in alternating layers with glass wool). After four double passes the volatile material was fractionated through traps held at -45° and -196°C. Pure $(Me_2HSiN)_2C$, in

89% yield, was retained at −45° and identified spectroscopically.[105] Similar conditions were employed to synthesize $(MeH_2SiN)_2C$ and the corresponding germyl carbodiimides in overall yields of 86%. For the reaction involving $H_3SiI$ or $H_3GeI$ the column was cooled with ice because of the exothermic nature of the reaction and the thermal instability of the reaction contents. Some hydrogen was evolved during the reaction, but was removed by pumping as it formed. After three double passes fractionation of the volatile material through traps held at −78° and −196° revealed $(H_3SiN)_2C$ in 84% yield or $(H_3GeN)_2C$ in 80% yield in the former trap with some traces of $SiH_4$[33] or $GeH_4$[33] in the latter. By contrast, the high thermal stability of $Me_3SiBr$ and $Me_3GeBr$ allowed the reactions with $PbCN_2$ to be carried out at high temperatures. Typically $Me_3SiBr$ (5.21 mmol) was condensed into a vessel (ca. 25 ml, type 'B') charged with $PbCN_2$. The stopcock was closed, the bath at −196° removed and the vessel was placed through the top hole of an oven set at ca. 100°C. After 85 hours the vessel was reattached to the vacuum line, the system evacuated and the volatile material collected at −196°. This material was passed further through traps held at −23°, −78° and −196°C. The trap at −23° retained pure $(Me_3SiN)_2C$ in 82% yield, while the trap at −78° contained some traces of $(Me_3Si)_2O$.[117] Similarly, $(Me_3GeN)_2C$ was obtained in 80% yield, and its purity was confirmed by spectroscopic analysis.[105] Bis(germyl)carbodiimides were also prepared by the reaction between bis(silyl)carbodiimides and fluorogermanes.

Typically, $(Me_3SiN)_2C$ (0.40g, 2.15 mmol) was distilled into a reaction vessel (10 ml, type 'B') held at -196° containing a slight excess of $Me_3GeF$ (6.00 mmol). The mixture was allowed to react at room temperature for ca. 45 minutes, with shaking, and then vacuum fractionated. A pure sample of $(Me_3GeN)_2C$ (0.54g, 1.96 mmol) was retained in a trap at -23°; the excess of $Me_3GeF$ in a trap at -78°, and $Me_3SiF$ (4.09 mmol) at -196°. The analogous reactions using $Me_{\underline{n}}H_{3-\underline{n}}GeF$ ($\underline{n}$=0,1,2) with $(Me_3SiN)_2C$ gave $(Me_{\underline{n}}H_{3-\underline{n}}GeN)_2C$ in 95% yields and their purity was checked spectroscopically.[105]

In the experiments involving the reactions of hydrogen chalcogenide with bis(silyl)carbodiimide only water was found to react leading to the formation of the corresponding disiloxane in high yield. The analogous reactions involving bis(germyl)-carbodiimides lead readily to germyl-Group VI species and dicyanodiamide. Typically, $(Me_2HGeN)_2C$ (0.26g, 1.05 mmol) was condensed, in vacuo, into a previously evacuated 35 ml reaction vessel (type 'B') held at -196°. An excess of $H_2S$ (1.50 mmol) was then distilled into the vessel. The mixture was allowed to react at room temperature with shaking. After 20 minutes, vacuum fractionation of the products at -78° and -196° was carried out. The -78° trap retained $(Me_2HGe)_2S$ (0.23g, 0.96 mmol, 91%), while the -196° trap retained $H_2S$ (0.40 mmol) identified by its vapour pressure.[37] White, polymeric dicyano-diamide was retained in the reaction vessel. The same procedure was used to produce $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$ where E = O,S,Se and $\underline{n} = 0 \longrightarrow 3$ in ca. 94% overall yields.

### (d) Reactions of halogeno-silanes and -germanes with $Li[Al(SH)_4]$ and $Li[Al(SeH)_4]$

In a typical experiment, fresh $Li[AlH_4]$ (0.05g, 1.32 mmol) was placed in a reaction vessel (ca. 70 ml, type 'B', equipped with a Teflon-in-glass stopcock) which was attached to the vacuum line and thoroughly evacuated. The connector was packed with glass wool to prevent contamination of the vacuum line with $Li[AlH_4]$. Methyl ether (ca. 10 ml) was then condensed in at -196° followed by an excess hydrogen selenide, $H_2Se$ (6.82 mmol). The reactants were allowed to react, with cautious warming while monitoring the pressure of the volatile species. A vigorous effervescence, with evolution of hydrogen, was immediately apparent as soon as the two phases mixed. The vessel was then held at -196°, the stopcock closed and the noncondensable gas, $H_2$, pumped off. When the system was thoroughly evacuated the manifold was closed and the stopcock of the vessel was reopened allowing the noncondensable gas to expand against the mercury manometer. The stopcock was closed again and the hydrogen gas pumped off. When the system was thoroughly re-evacuated the procedure was repeated with occasional quenching at -78° or -196° (because the reaction became too vigorous) until no hydrogen was liberated. The contents were then isolated again, by closing the stopcock, and brought to room temperature for

20 minutes, with occasional shaking. After this time, the vessel was held at -196° and the stopcock was reopened and some traces of hydrogen were pumped off. In this manner, over a relatively short time (*ca*. 40 minutes) 5.2 mmol of hydrogen were evolved. A similar procedure was also used to prepare $Li[Al(SH)_4]$.

Several experiments were carried out in an attempt to determine the conditions for a maximum yield of bis(silyl)- and bis(germyl)- chalcogenides. The experimental details given here represent the optimum conditions found for the reaction. Typically, $H_3SiI$ (2.39 mmol) was condensed at -196° into the reaction vessel containing the selenoaluminate and allowed to react at -45° for *ca*. 2 hours with occasional shaking. Fractionation of ~~the~~ volatile material through U-traps held at -78° and -196° gave pure $(H_3Si)_2Se$ (0.14g, 0.99 mmol, 83%) at -78° and $Me_2O$ and $H_3SiSeH$ (identified by its $^1H$ n.m.r. parameters[118]) at -196°. In a similar set of experiments using $H_3MI$ (M=Si,Ge) and $Li[Al(EH)_4]$ E=S,Se gave similar yield of bis(silyl)- and bis(germyl)- chalcogenides which were identified spectroscopically. The analogous reactions involving halogenomethylsilanes and -germanes were carried out in the absence of solvent at room temperature for *ca*. 2-3 hours with constant shaking. Lower yields of fully methylated chalco-silanes and -germanes were obtained due to the higher thermal stability of the $Me_3MEH$ species as compared with the hydridic chalcogenols. Details of the preparations are collected in Table IV.1.

Table IV.1. Reactions of halogeno-silanes and -germanes with $Li[Al(EH)_4]$*

$$\underset{\text{I}}{4H_3SiI} + \text{"}Li[Al(EH)_4]\text{"} \longrightarrow \underset{\text{II}}{2(H_3Si)_2Se} + 2H_2Se + LiI + AlI_3$$

| $Me_nH_{3-n}MX$ | E=S<br>I<br>(mmol) | E=Se<br>I<br>(mmol) | Product | E=S<br>II<br>(mmol) | E=Se<br>II<br>(mmol) | Yield %<br>E=S | Yield %<br>E=Se |
|---|---|---|---|---|---|---|---|
| $H_3SiI^+$ | 4.08 | 2.39 | $(H_3Si)_2E$ | 1.88 | 0.99 | 92 | 83 |
| MeH SiI | 3.76 | 3.04 | $(MeH_2Si)_2E$ | 1.70 | 1.42 | 90 | 93 |
| $Me_2HSiI$ | 2.43 | 3.68 | $(Me_2HSi)_2E$ | 1.07 | 1.60 | 88 | 87 |
| $Me_3SiBr$ | 3.66 | 2.89 | $(Me_3Si)_2E$ | 1.12 | 0.80 | 61 | 55 |
| $H_3GeI^+$ | 4.28 | 3.15 | $(H_3Ge)_2E$ | 2.00 | 1.43 | 94 | 91 |
| $MeH_2GeI$ | 3.93 | 2.90 | $(MeH_2Ge)_2E$ | 1.79 | 1.28 | 91 | 88 |
| $Me_2HGeI$ | 2.87 | 3.06 | $(Me_2HGe)_2E$ | 1.32 | 1.38 | 92 | 90 |
| $Me_3GeBr$ | 3.21 | 2.34 | $(Me_3Ge)_2E$ | 1.20 | 0.80 | 75 | 68 |

*In all reactions an excess of "$Li[Al(EH)_4]$" was used.

+The reactions were allowed to occur in presence of $Me_2O$ at -45°.

## (e) Reactions of halogeno-silanes and -germanes with heavy metal salts

### (1) - $Me_{\underline{n}}H_{3-\underline{n}}SiI$ with HgS

The reactor was a horizontal tube (ca. 25 mm i.d. X 350 mm long, type 'L') equipped with U-traps at either end (one end had a constriction and the other end was detachable via a B-24 joint to facilitate packing). The tube was packed alternately with glass wool and anhydrous red mercuric sulfide (ca.20g). The tube was attached to the vacuum line and thoroughly evacuated for ca. 1 hour, through the constricted end to avoid contamination of the vacuum line with the packing material. Iodosilane ($H_3SiI$; 0.4307 g; 2.73 mmoles) was then allowed to pass through the column from one U-trap to the other. Typically after two double passes, the volatile products were fractionated on the vacuum line using cold traps at -45°, -95°, and -196°. No volatile species were present in the -45° trap, except when disproportionation occurred. The second trap retained bis(silyl)-sulfide ['disilathiane' $(H_3Si)_2S$; 0.1164 g, 1.24 mmol] while the -196° following trap contained only traces of disiloxane (identified by its infrared spectrum[117]). No hydrogen was formed. The yield of disilathiane, based on the iodosilane consumed, was 91%. Optimum yields were achieved by minimizing the amount of moisture in the system. The infrared spectrum[119] showed prominent bands at 2180(vs), 962 and 951(vs,B), 907(vs,A), 675(ms), 635(s,C), 610(s), 517(s) and 480(ms) $cm^{-1}$.

In the same manner, the iodosilane ($MeH_2SiI$, 2.38 mmol; $Me_2HSiI$, 1.01 mmol; $Me_3SiI$, 1.94 mmol) was passed through the tube four times. The volatile products were collected and fractionated, using cold traps at -45° and -196°. The former trap retained the corresponding methyldisilathiane, viz. - $(MeH_2Si)_2S$, 97%; $(Me_2HSi)_2S$, 92%; $(Me_3Si)_2S$, 95%. Any unreacted iodide or siloxane was collected in the -196° trap. The formation of siloxanes was again minimized by carefully removing moisture from the system by thorough evacuation.

(2) - $H_3GeI$ with HgS

The reactor and conditions were identical to those described in part (1). Typically, $H_3GeI$ (2.83 mmol) was allowed to pass back and forth over the anhydrous mercuric sulfide. After two double passes, $^1H$ n.m.r. spectroscopic examination revealed considerable amounts of residual iodide. A further four double passes, followed by fractional distillation and spectroscopic examination, revealed ca. 35% conversion of $H_3GeI$ into $(H_3Ge)_2S$ and some disproportionation, involatile, by-product in the U-traps.

(3) - $MeH_2GeI$ and $Me_3GeI$ with PbS

Because the conversion of $H_3GeI$ to $(H_3Ge)_2S$ was poor and tedious, the direct synthesis of germyl sulfides and oxides from iodo- and bromo-germanes and lead (II) salts was investigated.

In a typical reaction, $MeH_2GeI$ (1.03 mmol) was allowed to react with excess of PbS at 25° for ca. 30 minutes. Fractionation of the volatile materials through traps held at -78° and -196° gave a mixture of $(MeH_2Ge)_2S$ and $MeH_2GeI$ in the former, and a small amount of $MeGeH_3$ in the latter. The conversion of $MeH_2GeI$ into $(MeH_2Ge)_2S$ was ca. 39% as estimated by their respective peak ratios in the $^1H$ n.m.r. spectrum. $Me_3GeI$ (2.40 mmol) at 80° for 2 hours gave $(Me_3Ge)_2S$ (0.90 mmol, 75.0%).

(4) - $MeH_2GeBr$ and $Me_3GeBr$ with PbS

A mixture of $MeH_2GeBr$ (1.89 mmol) and excess of PbS was allowed to react at 25° for ca. 25 minutes as in (3). Fractionation of the volatile material gave unchanged $MeH_2GeBr$ (1.80 mmol). No reaction occurred even when the mixture of $Me_3GeBr$ (2.96 mmol) and excess of PbS was heated at 85° for ca. 2 hours.

(5) - $Me_nH_{3-n}GeBr$ with PbO

$$2H_3GeBr + PbO \longrightarrow (H_3Ge)_2O + PbBr_2 \qquad [12]$$

Typically, lead (II) oxide (ca. 10-15g) was placed in a reaction vessel (ca. 45 ml, equipped with a Teflon-in-glass valve and MS19 ball joint, type 'B'), attached to the vacuum line. (glass wool was packed in above the vessel to prevent contamination of the vacuum line by PbO) and degassed. Upon evacuation, bromogermane ($H_3GeBr$; 0.92 mmol) was condensed into the vessel held at -196°. The valve was closed and the reactants allowed to warm to room temperature. The reaction proceeded for ca. 8 minutes with constant shaking. Separation of the volatile materials at -126° and -196° gave digermoxane [$(H_3Ge)_2O$; 0.42 mmol] condensing in the -126° trap and traces of germane (identified spectroscopically) in the -196° trap. The yield (low yields may result due to the rapid decomposition of bromogermane in contact with silicone-grease) of digermoxane, based on the bromogermane consumed, was 91%, and the purity was confirmed by its infrared spectrum[114] giving prominent absorptions at 2112(s), 928, 882, 798(vs), 784(vs), 674 and 452 $cm^{-1}$.

By a similar procedure, the bromogermane ($MeH_2GeBr$, 1.56 mmol; $Me_2HGeBr$, 2.98 mmol; $Me_3GeBr$, 3.67 mmol) was allowed to react with a large excess of PbO at room temperature for 20-45 minutes. After this time the volatile products were collected and fractionated, using cold traps at -78° and -196°. The former trap retained the corresponding methyldigermoxane, viz. - $(MeH_2Ge)_2O$, 0.76 mmol, 97.4%; $(Me_2HGe)_2O$, 1.47 mmol, 98.7% and $(Me_3Ge)_2O$, 1.83 mmol, 99.5%. Traces of methyl- and dimethyl-germane were found in the -196° trap.

However, when gaseous $MeH_2GeBr$ (1.41 mmol) was allowed to pass back and forth six times at room temperature over a mixture of PbO (ca. 20g) and a small amount of powdered glass held in a column (type 'L') on glass wool, the recovery of $MeH_2GeBr$ (1.39 mmol) was almost quantitative.

(6) - $Me_{\underline{n}}H_{3-\underline{n}}GeI$ with PbO

Typically, $Me_2HGeI$ (1.46 mmol) was condensed onto excess of PbO in an analogous manner to (5). After *ca*. 15 minutes at 25°, fractionation of the volatile materials at -78° and -196° gave $(Me_2HGe)_2O$ (0.45 mmol, 61.7%) in the former and $Me_2GeH_2$[17,18] (0.20 mmol) in the latter. Similarly, $H_3GeI$ (0.86 mmol), $MeH_2GeI$ (1.22 mmol) and $Me_3GeI$ (3.67 mmol) were converted by PbO to the corresponding oxides, viz. - $(H_3Ge)_2O$ (0.15 mmol, 34.9%), $(MeH_2Ge)_2O$ (0.28 mmol; 45.2%) and $(Me_3Ge)_2O$ (1.82 mmol, 98.9%).

In the alternative preparation, when $Me_{\underline{n}}H_{3-\underline{n}}GeI$ (n=0,1,2) was streamed as a gas over a previously evacuated column of PbO as in (1), very little formation of germoxanes (5-15%) was achieved as verified by the relative intensity of the stretching vibrations, $\nu_s$(Ge-O) and $\nu_s$(Ge-I) in the Raman spectra.

(7) - $Me_3GeX$ (X=F,Cl,Br) and $Me_2GeBr_2$ with AgO

The reactions of halogenogermanes with heavy metal salts were extended to include the use of AgO. Because of the exothermic nature of the reactions only selected halogenogermanes were used.

In a typical experiment, $Me_3GeCl$ (0.1840g 1.22 mmol) was condensed at -196° into a reaction vessel (ca. 10 ml, type 'B', equipped with a Teflon-in-glass stopcock) containing AgO (0.9g). When the mixture was allowed to react the vessel became warm and a gas was evolved. The vessel was then shaken and left at room temperature for 5 minutes. Fractionation of the volatile material through U-traps held at -78° and -196° gave pure $(Me_3Ge)_2O$ (0.1408 g, 0.56 mmol) in the former and chlorine in the latter trap. The yield of hexamethyldigermoxane based on $Me_3GeCl$ consumed, was 92%. Its purity was confirmed by the Raman spectrum. In another experiment small amount of mercury was added to the reaction mixture and there was no reaction between mercury and chlorine nor between the hexamethyldigermoxane and chlorine.

In a similar manner, $Me_3GeBr$ (0.3251 g, 1.65 mmol) was completely consumed in an exothermic reaction with AgO (1.0 g) with formation of $(Me_3Ge)_2O$ and bromine, retained at -45°, and a small amount of non-condensable gas. Subsequent Raman spectroscopic examination of the mixture revealed the presence of a typical Ge-O stretching vibration, $\nu_s$(Ge-O), at 452 and $\nu$(Br-Br) at 286 $cm^{-1}$ but not $\nu_s$(Ge-Br) at <u>ca</u>. 263 $cm^{-1}$. The removal of bromine was effected by mixing the mixture with a small amount of mercury for 10 minutes, and fractionating the volatile material through traps held at -45° and -196°. The former trap retained pure $(Me_3Ge)_2O$ while $HgBr_2$ remained in the vessel. Thus the reactions appeared to be:

$$2Me_3GeX + AgO \longrightarrow (Me_3Ge)_2O + AgX_2 \qquad [13]$$

$$AgX_2 \longrightarrow AgX + 1/2X_2 \quad (X=Cl,Br) \qquad [14]$$

$$(Me_3Ge)_2O + X_2 \longrightarrow \text{no reaction} \qquad [15]$$

$$Cl_2 + Hg \longrightarrow \text{no reaction} \qquad [16]$$

$$Br_2 + Hg \longrightarrow HgBr_2 \qquad [17]$$

The reactions of chlorotrimethyl-, or bromotrimethylgermanes with AgO may proceed with explosive violence and should be carried out on a small scale. $Me_2GeBr_2$ (0.6298 g, 2.40 mmol) reacted explosively with AgO (1.0 g) when an attempt was made to prepare heterocyclic germoxy species. By contrast when $Me_3GeF$ (0.1151 g, 0.87 mmol) was allowed to react with AgO (1.0 g) no reaction occurred and $Me_3GeF$ was recovered quantitatively.

### (f) Reactions of some halogeno-germanes and -silanes with lithium salts

#### (1)- $Me_{\underline{n}}H_{3-\underline{n}}GeX$ with lithium oxide

Despite the amount of research by several workers on the use of alkaline salts as synthetic reagents, there had been no report in the literature on the use of $Li_2O$ before the commencement of this study. Several experiments were carried out in an attempt to determine the conditions of exchange reactions between halogenogermanes and $Li_2O$.

Typically, $Me_2HGeI$ (0.80 g, 3.48 mmol) was condensed at -196° into a reaction vessel (*ca.* 60 ml, type 'B', equipped with a Teflon-in-glass stopcock) containing $Li_2O$ (0.060 g, 2.00 mmol), followed by $Me_2O$ (*ca.* 10-15 ml). The reaction vessel was isolated and warmed to -78° with occasional shaking. After *ca.* 96 hours, the reaction vessel was opened and fractionation of the volatile materials gave a 1:1 mixture of $(Me_2HGe)_2O$ and $Me_2HGeI$ (ca. 0.39 g) as well as small amounts of immiscible droplets of water retained in the trap at -78° (as identified spectroscopically) and $Me_2O$ in the -196° trap. Attempts to separate the $(Me_2HGe)_2O$ from $Me_2HGeI$ by trap to trap fractional distillation were unsuccessful. Longer reaction times and appreciable excesses of $Li_2O$ had little effect on the product mixture. In a similar manner a mixture of $(MeH_2Ge)_2O$ and $MeH_2GeI$ was isolated. By contrast, bromotrimethylgermane, $Me_3GeBr$ (0.58 g, 2.91 mmol) and $Li_2O$ (0.04 g, ca. 6 mmol) in $Et_2O$ left at 25° with continuous stirring for ca. 80 hours gave $(Me_3Ge)_2O$ (0.3570 g, 1.42 mmol, 98%). The purity of $(Me_3Ge)_2O$ was confirmed by the absence of the stretching vibration, $\nu_s$(Ge-Br), at ca. 263 $cm^{-1}$ in the Raman spectrum.

(2) - $Me_{\underline{n}}H_{3-\underline{n}}GeX$ and $Me_{\underline{n}}H_{3-\underline{n}}SiX$ with lithium sulfide, selenide and telluride

Comparatively few of these reactions were known. Disproportionation of initially formed $Me_3SiEPh$ (E=Se,Te) probably accounts for the unexpected formation of $(Me_3Si)_2E$ in the reaction of $Me_3SiCl$ with PhEMgBr.[93] The compounds $(Me_3Si)_2E$ have been obtained more directly via $Li_2E$ species.[90,120] Digermyl sulfide[110] and selenide,[121] $(H_3Ge)_2E$ (E=S,Se) have been obtained by the exchange of bromogermane with $Li_2E$ and $(H_3Si)_2Te$ from bromo-,[99] or iodo-[90]silane and lithium telluride. Following the preparative procedure of the latter three compounds a very poor conversion of the halogenomethyl-germanes and -silanes into the corresponding chalcogen compounds was achieved. Disproportionation and the thermal instability of the reaction products was a major problem in the preliminary studies and therefore attention was centered on the preparation of the lithium salts. Thus, I describe the preparation of $Li_2E$ (E=Se,Te) and their metathesis reactions with some halogeno-germanes and -silanes.

Typically, powdered selenium (0.403 g, 5.10 mmol) and clean lithium wire (0.069 g, 10.00 mmol) were allowed to react in dry ammonia (*ca.* 10-15 ml) at -78° in a reaction vessel (*ca.* 70 ml, type 'B') attached to the vacuum system via a Teflon-in-glass stopcock. The reaction was accelerated by occasional removal of the -78° bath accompanied by shaking and cautious warming while monitoring the $NH_3$ pressure until the blue color of dissolved lithium is discharged (this was slower if lithium had an oxide coating). After typically 12 hours the $NH_3$ was pumped off. Glass wool was placed in such a way as to prevent the contamination of the vacuum line by $Li_2Se$ powder resulting from the sudden expansion of the $NH_3$. The light grey salt was heated at 140°-160° for 6 hours in vacuo and stored under nitrogen at room temperature. Lithium telluride was prepared in the same way and it is characteristically a darker grey than the selenide. Hydrolysis gave typically 98% of the Se content required for $Li_2Se$ as $H_2Se$, whilst ca. 80% resulted for the release of $H_2Te$ from $Li_2Te$.

In a typical reaction, the vessel containing $Li_2Se$ (ca. 0.46 g, 5.00 mmol) was attached to the vacuum line and thoroughly evacuated. Then, dimethyl ether (ca. 10-15 ml) followed by $Me_2HGeI$ (8.80 mmol) was condensed in at -196°. The reaction vessel was isolated and warmed to -78° with occasional shaking. After ca. 96 hours, the reaction vessel was opened and the volatile materials fractionated at -78° and -196°. The latter trap retained $Me_2O$ and traces of $Me_2GeH_2$ and $Me_2Se$, which were identified spectroscopically. The material at -78° was further fractionated through traps held at -45° and -78°. The -45° trap contained pure bis(dimethyl germyl) selenide, [$(Me_2HGe)_2Se$, 3.90 mmol, 88%; P m/e 279-294 $(Me_4H_nGe_2Se)^+$]. No $Me_2HGeI$ was recovered. The analogous reactions of iodosilanes ($H_3SiI$, 6.65 mmol and $MeH_2SiI$, 7.96 mmol) with slight excess of $Li_2Te$ were carried out in the same way and gave $(H_3Si)_2Te$[90] (2.98 mmol, 90%) and $(MeH_2Si)_2Te$ (3.52 mmol, 88%), respectively. The reactions involving bromotrimethylgermane and chlorotrimethylsilane were allowed to occur at room temperature in $Me_2O$ or $Et_2O$ with continuous stirring. The purity of the compounds was confirmed spectroscopically. The S-, Se- and Te- residues in the reaction vessel were handled in an efficient fume hood. Smell contamination was considerably reduced by treatment of the residues with a strong bleach solution followed by an acid wash. Details of other preparations are collected in Table IV.2.

Table IV.2. Exchange reactions of iodogermanes and chlorosilanes with $Li_2E$

$$2Me_{\underline{n}}H_{3-\underline{n}}MX + Li_2E \longrightarrow (Me_{\underline{n}}H_{3-\underline{n}}M)_2E + 2LiX$$

$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

| | E = S | | | E = Se | | | E = Te | | |
|---|---|---|---|---|---|---|---|---|---|
| $Me_{\underline{n}}H_{3-\underline{n}}M$ | I (mmol) | II (mmol) | Yield (%) | I (mmol) | II (mmol) | Yield (%) | I (mmol) | II (mmol) | Yield (%) |
| $H_3Ge$ | 2.76 | 0.92 | 67 | 4.16 | 1.61 | 77 | 8.45 | 3.52 | 83 |
| $MeH_2Ge$ | 4.32 | 1.80 | 83 | 3.56 | 1.43 | 80 | 7.14 | 3.17 | 89 |
| $Me_2HGe$ | 1.71 | 0.70 | 82 | 8.80 | 3.90 | 89 | 9.88 | 4.20 | 85 |
| $Me_3Ge$* | 3.16 | 1.43 | 91 | 12.25 | 5.23 | 85 | 5.78 | 2.49 | 86 |
| $Me_2HSi$ | 9.96 | 4.72 | 95 | 8.02 | 3.60 | 90 | 11.38 | 5.25 | 92 |
| $Me_3Si$ | 7.00 | 3.20 | 91 | 8.34 | 4.00 | 96 | 10.36 | 4.95 | 93 |

* X = Br

When E = O, incomplete conversion of the iodogermanes afforded 1:1 mixture of $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2O$ and $Me_{\underline{n}}H_{3-\underline{n}}GeI$ ($\underline{n}$=1,2).

## (g) Reactions of fluorogermanes with bis(silyl)chalcogenides

The experimental details given below represent the conditions whereby a high yield of chalcogermanes were produced, in a relatively short reaction time.

The reactor was a glass ampule (ca. 10 ml) fitted with a high vacuum Teflon-in-glass valve and glass MS19 joint for attachment to the vacuum line. The ampule was evacuated and cooled to -196° and $H_3GeF$ (0.61 mmol) and a slight deficit of $(Me_3Si)_2S$ (0.24 mmol) were distilled in. The mixture was allowed to react at room temperature for 5 - 10 minutes. The volatile materials were then fractionated in vacuo using traps held at -45° and -196°. Unreacted $H_3GeF$[11] (0.10 mmol), $Me_3SiF$[122] (0.47 mmol) and traces of $GeH_4$[32] were identified by analysis of the $^1H$ n.m.r. spectrum of the contents of the trap which was held at -196°. The trap held at -45° retained pure digermyl sulfide, $(H_3Ge)_2S$ (0.23 mmol, 96%). Similar experiments using excess $MeH_2GeF$ and $Me_2HGeF$ gave $(MeH_2Ge)_2S$ (95%) and $(Me_2HGe)_2S$ (100%). The analogous reaction of $(Me_3Si)_2S$ (3.28 mmol) with excess $Me_3GeF$ (8.15 mmol) for 45 minutes at room temperature gave a mixture of $(Me_3Ge)_2S$, $(Me_3Si)_2S$ and the mixed sulfide $Me_3SiSGeMe_3$ at -23°, and $Me_3SiF$ and $Me_3GeF$ at -196°. All species were identified by their $^1H$ n.m.r. parameters[8,11,123]. Similar product distribution was obtained with longer reaction times. However, when $(Me_3Si)_2S$ (0.14 mmol) and $Me_3GeF$ (0.41 mmol) were allowed to react in a sealed tube at high temperature (ca.80°C) and left overnight, then $(Me_3Ge)_2S$ (0.14 mmol) was formed quantitatively. Details of all preparations are collected in Table IV.3.

Table IV.3. Exchange reactions of $(Me_3Si)_2E$ species with fluorogermanes

$$\underset{(I)}{(Me_3Si)_2E} + 2Me_{\underline{n}}H_{3-\underline{n}}GeF \longrightarrow \underset{(II)}{(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E} + 2Me_3SiF$$

E = S,Se,Te; n = 0,1,2,3

| | E = S | | | E = Se | | | E = Te | | |
|---|---|---|---|---|---|---|---|---|---|
| $Me_{\underline{n}}H_{3-\underline{n}}Ge$- | I (mmol) | II (mmol) | Yield (%) | I (mmol) | II (mmol) | Yield (%) | I (mmol) | II (mmol) | Yield (%) |
| $MeH_2Ge$ | 0.43 | 0.43 | 100 | 1.02 | 1.00 | 98 | 1.32 | 1.30 | 98 |
| $Me_2HGe$ | 0.23 | 0.22 | 96 | 0.79 | 0.78 | 99 | 1.22 | 1.22 | 100 |
| $Me_3Ge$ | 0.14 | 0.14 | 100 | 0.85 | 0.85 | 100 | 0.85 | 0.85 | 100 |
| $H_3Ge$ | 0.24 | 0.23 | 96 | 0.23 | 0.23 | 100 | 0.95 | 0.94 | 99 |

## IV.3. PHYSICAL PROPERTIES

Bis(silyl)- and bis(germyl)- chalcogenides are all clear, colorless liquids when pure but the telluro species become readily pale yellow to brownish at room temperature. The sulfur compounds have a well-earned reputation with regard to their bad odor. The selenium and tellurium compounds are worse and the smell has a tendency to stick to the clothes, the hair, and indeed the whole person. I, as a synthetic chemist, became accustomed to it but the other members of the laboratory and other associates did not. The repulsive smell was in itself a good protection against these toxic and noxious gases or liquids, but the adequate fume hood and effective ventilation were indispensible. Of course, one must admit that this noxious factor has certainly delayed the development of M-Se and M-Te chemistry where M = a Group IV element. The current interest in organoselenium research is to a considerable extent due to the possible biological effects and their practical consequences.

The Si-S, Si-Se and Si-Te species are very easily oxidized, e.g. by air, but are otherwise stable. The hydridic species i.e. $(H_3Si)_2E$ (E=Se,Te) and $(H_3Ge)_2E$ (E=S,Se,Te) are stable at room temperature for some time but disproportionation is likely to occur over extended periods of time. Whilst, $(H_3Si)_2E$ (E=O,S) are the most stable of the fully hydridic species, $(H_3Ge)_2O$ is the least stable and it was stored in sealed glass tubes held at -196°. Indeed, all the compounds were best kept in sealed glass tubes and stored in a refrigerator. All of these chalcogen compounds are sufficiently volatile that they could be easily handled under vacuum line conditions, provided contact with silicone-grease was kept to a minimum. Other physical properties are summarized in Table IV.4.

Table IV.4. Physical Properties of some Silyl- and Germyl- Group VI Species

| Compound | M.p. (°C) | | B.p. °C(torr) | | T* | | Ref. | |
|---|---|---|---|---|---|---|---|---|
| | Si | Ge | Si | Ge | Si | Ge | Si | Ge |
| $(H_3M)_2O$ | -144 | | -15 | | | | a | |
| $(MeH_2M)_2O$ | -138 | | 35 | 65 | 22 | | 42 | b |
| $(Me_2HM)_2O$ | | | 73 | 116 | 21 | | 89 | b |
| $(Me_3M)_2O$ | | -61 | 100 | 129 | | 26 | d | c |
| $(H_3M)_2S$ | -70 | -35 | 59 | | 23 | | 88 | |
| $(MeH_2M)_2S$ | -120 | | 105 | | 22 | | 42 | |
| $(Me_2HM)_2S$ | -146 | | 145 | | 16 | | 89 | |
| $(Me_3M)_2S$ | | -22 | 162 | 40/1 | | | 95 | 192 |
| $(H_3M)_2Se$ | -68 | -41 | 85 | | 23 | | 88 | 99 |
| $(Me_3M)_2Se$ | -7 | | 58 | | | | 117 | |
| $(H_3M)_2Te$ | | -75 | 49 | | | | 90 | 99 |
| $(Me_3M)_2Te$ | 14 | | 74 | | | | 117 | |

*T=Trouton's constant, (cal mole$^{-1}$ deg$^{-1}$)

[a] R.C.Lord, D.W.Robinson, and W.C.Schumb, J. Am. Chem. Soc., 78, 1327 (1956).

[b] Ref. 169. [c] J.E.Griffiths and M.Onyszchuk, Can. J. Chem., 39, 339 (1961).

[d] R.O.Sauer, J. Am. Chem. Soc., 66, 1707 (1944).

## IV.4. DISCUSSION

The Si-O bond is the ultimate product of oxidation or hydrolysis of almost all silicon compounds. The hydrolysis of monohalogenosilanes gives disiloxane and not silanol[124] though it is presumably formed as an intermediate, e.g.

$$H_3SiBr + H_2O \longrightarrow "H_3SiOH" + HBr \qquad [18]$$

$$2"H_3SiOH" \longrightarrow (H_3Si)_2O + H_2O \qquad [19]$$

The fact that halogenosilanes react with fission of the Si-X bond in preference to the Si-H bond can be rationalized in their terms which take into account the greater polarity of the Si-X linkages. Thus, the process SiH $\longrightarrow$ $Si^+ + H^-$ requires 250 kcal·mol$^{-1}$ (1046 kJ·mol$^{-1}$) whereas the process SiBr $\longrightarrow$ $Si^+ + Br^-$ requires only 179 kcal·mol$^{-1}$ (748.9 kJ·mol$^{-1}$)[94]. Also, the greater tendency for chloro-, bromo-, or iodo-silanes compared with fluorosilanes to react with nucleophilic reagents can be explained in part in terms of the greater degree of $(p \rightarrow d)\pi$ bonding in the Si-X bond when X is F, an effect which not only gives a very strong Si-F bond but also renders the silicon d-orbitals less available for use in forming a low energy transition state with five bonds from silicon of the $sp^3d$ type.[94]

In view of this, the comparative experiments indicate the preferential formation of the Si-O bond [20] over the Si-S bond [21] and the latter over the Si-N bond [22] relative to the Ge-N bond [23], i.e.

$H_3SiNCNSiH_3 + H_2O \longrightarrow H_3SiOSiH_3 + 1/2(H_2NCN)$ [20]

$H_3SiNCNSiH_3 + H_2S \longrightarrow$ no reaction [21]

$Me_3SiNHSiMe_3 + 2H_2S \longrightarrow Me_3SiS^-NH_4^+ + Me_3SiSH$ [22]

$H_3GeNCNGeH_3 + H_2S \longrightarrow H_3GeSGeH_3 + 1/2(H_2NCN)$ [23]

Thus, the interaction of bis(germyl)carbodiimides, $(Me_{\underline{n}}H_{3-\underline{n}}GeN)_2C$ with Group VI species[125] represents a convenient small-scale synthetic route to the corresponding chalcogenides, $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$ where E = O,S,Se and $\underline{n} = 0 \rightarrow 3$. Proponents of the importance of $(p \rightarrow d)\pi$ bonding in the Si-N system[56,69] relative to the Ge-N, would no doubt accept this as further evidence of the 'extra' stability of the Si-N bond or of the decreased polarity of the bond making the silicon less open to nucleophilic attack. It seems improbable that the supposed relative weakness of the Ge-N bond could completely account for the quantitative cleavage of the Ge-N bond to form the Ge-O,-S and -Se bonds. However, the ready cleavage of the Si-N bond by $H_2O$ is probably associated with the formation of the strong Si-O bond.[126,127]

For this reason, very few methods were available that lead to thio- and seleno-silanes, and consequently convenient synthetic routes were sought. In recent years, interest has been focused on the partial reduction of Group V and VI species with $Li[AlH_4]$.[128,129] Analogously, the thio- and seleno-aluminates, "$Li[Al(EH)_4]$" were produced and used to further attack by halogeno-silanes and germanes leading to the formation in high yield, of $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M = Si,Ge; E = S,Se and n = 0,1,2, in a relatively short time. The formation of these species is likely to occur via intermolecular condensation of the intermediate silane- and germane-chalcogenols, $Me_{\underline{n}}H_{3-\underline{n}}MEH$. The results of the experiments are listed in Table IV.1.

The metathesis reactions that halogeno-silanes and -germanes undergo with heavy metal salts are analogous to the 'halogen exchange' reactions in organic chemistry.[130] The halogen on silicon and germanium which exchanges with the heavy metal salt, PbO, AgO and HgS is usually bromide or iodide, where presumably the soft bromine or iodine, in the Pearson sense,[131] has a greater affinity for the soft metal than does the hard chalcogen, e.g.

$$2\overset{h}{\mathrm{Ge}}\text{-}\overset{s}{\mathrm{Br}} + \overset{s}{\mathrm{Pb}}\overset{h}{\mathrm{O}} \longrightarrow \overset{h}{\mathrm{Ge}}_2\overset{h}{\mathrm{O}} + \overset{s}{\mathrm{Pb}}\overset{s}{\mathrm{Br}}_2 \qquad [24]$$

where h=hard, s=soft

Various authors have formulated conversion series for the reactions between silyl and germyl species with metal salts.[95,96,132] The series more or less follow the order of bond and lattice energies and the ease with which conversion may be brought about at room temperature shows that the activation energies in the systems are probably low. Thus, at ambient temperature without the use of solvent, lead (II) oxide[133] and mercury (II) sulfide[16] provide facile conversion of $Me_{\underline{n}}H_{3-\underline{n}}GeBr$ and $Me_{\underline{n}}H_{3-\underline{n}}SiI$ into $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2O$ and $(Me_{\underline{n}}H_{3-\underline{n}}Si)_2S$ series, respectively. The corresponding reactions using $Me_{\underline{n}}H_{3-\underline{n}}GeI$ give lower yields (ca. 35-60%) and appreciable amounts of decomposition by-product, germane, $Me_{\underline{n}}GeH_{4-n}$ where n = 0,1,2. By contrast, when iodo- and bromo-germanes were passed as gases over lead(II) oxide there were essentially no reactions.[133] Similarly, dibromodimethylgermane does not react with lead(II) oxide even under forcing conditions, in contrast to the highly exothermic reaction with silver(II) oxide. Whilst bromogermanes do not react with PbS, $Ag_2S$ and HgS (in accord with the conversion principle[95,96,132]) there is partial conversion of iodogermanes into the corresponding sulfides. This can be compared with the reaction of iodosilanes with HgS. Nevertheless, the lower reactivity of iodogermanes toward PbS relative to $Li_2S$ is also shown in the reactions with PbSe contrasted with $Li_2Se$. However, while iodo- and bromogermanes react with lithium sulfide, selenide and telluride in ether to give high yields of chalcogermanes, Table IV.2, the corresponding reactions of iodomethyl- and iododimethyl-germane with lithium oxide do not go to completion at -78°, but iodo- and bromo-trimethylgermane afford high yields of hexamethyldigermoxane at room temperature.[133] An important contribution to the reactions must be the high lattice energy of $Li_2O$ with other possible contributions coming from the specific reaction conditions and the novel rapid exchange (on the n.m.r. time scale) between the halogenogermanes and the corresponding oxides, i.e. $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2O/Me_{\underline{n}}H_{3-\underline{n}}GeX$ where X = Br,I and $n = 0 \longrightarrow 3$. This observation places some doubt on the reported conversions of

$H_3GeI$ to $(H_3Ge)_2O$ with HgO and of $(H_3Ge)_2O$ to $H_3GeI$ with $HgI_2$[113].

The quantitative conversions to chalcogermanes, $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$, were obtained by treating the $(Me_{\underline{n}}H_{3-\underline{n}}Si)_2E$ species in absence of solvent with the appropriate fluorogermane according to the following reaction:

$$(Me_3Si)_2E + 2Me_{\underline{n}}H_{3-\underline{n}}GeF \longrightarrow (Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E + 2Me_3SiF \qquad [25]$$

$$E = S, Se, Te;\ n = 0 \rightarrow 3$$

In contrast to the"heavy metal" salt conversions, this type of conversion may be explained in terms of the greater ability of the harder moiety[131] to be attached to silicon, i.e.

$$\overset{h}{Si} - \overset{s}{E} + \overset{s}{Ge} - \overset{h}{F} \longrightarrow \overset{s}{Ge} - \overset{s}{E} + \overset{h}{Si} - \overset{h}{F} \qquad [26]$$

Some time ago Eaborn[95] suggested that in discussing reactions of organosilicon compounds with heavy metal salts more meaningful prediction regarding to the favoured direction of reactions obtained by using "ionic bond energies" rather than usual bond energies. The "ionic bond energies" indicate the energy necessary to break bonds heterolytically (i.e. $SiX \rightarrow Si^+ + X^-$) rather than into atoms. Accordingly, the attempts to prepare chalcogermanes by this method using the more readily available chlorides were unsuccessful because mixed species of the type $Me_3SiEGeMe_3$ were obtained, i.e.

$$(Me_3Si)_2S + Me_3GeCl \longrightarrow Me_3SiSGeMe_3 + Me_3SiCl \qquad [27]$$

The equilibrium position of the reaction appears to be related to "ionic bond energy" differences in the reactants and products rather than by simple bond energies.[95] Thus, the "ionic bond energies" of the Si-S and the Si-Cl bond are very close and suggest an equilibrium situation, Table V.5.

Table V.5. Selected bond energies*

| | Bond energy | | Electron affinity | | "Ionic bond energy" | |
|---|---|---|---|---|---|---|
| Bond | kcal/mole | kJ/mole | kcal/mole | kJ/mole | kcal/mole | kJ/mole |
| Si-S | *ca.* 70.0 | 292.9 | 61 | 255.2 | 197.0 | 824.2 |
| Si-Cl | 96.0 | 401.7 | 86 | 359.8 | 198.0 | 828.4 |
| Si-Br | 75.6 | 316.3 | 84 | 351.5 | 179.6 | 751.4 |
| Si-I | 56.0 | 234.3 | 76 | 318.0 | 168.0 | 702.9 |
| Si-F | 142.0 | 594.1 | 95 | 397.5 | 235.0 | 983.2 |
| Si-O | 108.0 | 451.9 | 48 | 200.8 | 248.0 | 1037.6 |
| Ge-F | 113.0 | 472.8 | | | 200.2 | 837.6 |
| Ge-O | 82.0 | 343.1 | | | 216.2 | 904.6 |
| Ge-Cl | 81.0 | 338.9 | | | 177.2 | 741.4 |
| Ge-S | *ca.* 58.0 | 242.7 | | | 179.2 | 749.8 |
| Ge-Br | 68.0 | 284.5 | | | 166.2 | 695.4 |
| Ge-I | 51.0 | 213.4 | | | 157.2 | 657.7 |

*Taken in part from ref: 69,95,134,143 and 145 and converted to kJ/mole.

Clearly, by using a fluorogermane the bond energy and also the "ionic bond energy" in the products will be greater and so the formation of the Ge-S, Ge-Se and Ge-Te bonds is thermodynamically favoured product.

# CHAPTER V

## THE CHARACTERIZATION OF BIS(SILYL)- AND BIS(GERMYL)- CHALCOGENIDES

## $(Me_nH_{3-n}M)_2E$ where M=Si,Ge; E=O,S,Se,Te and $n=0 \longrightarrow 3$

The study of silyl and germyl species containing a Group VI element presents a number of interesting problems to the spectroscopist. The primary complications are the handling, sampling and the most significant of all is the interpretation of the spectroscopic parameters. I report herein an attempt of comparative $^1$H n.m.r., infrared, Raman and mass spectroscopic investigation of these species, viz. - $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M=Si, Ge; E=O,S,Se,Te and $\underline{n}=0 \longrightarrow 3$ as well as cleavage reactions of the M-E bonds with anhydrous hydrogen halides.

## V.1. $^1$H NUCLEAR MAGNETIC RESONANCE SPECTRA

The interpretation of nuclear magnetic resonance (n.m.r.) parameters for compounds of the Group IV elements has provoked much discussion and controversy in the literature. Most studies have been concerned with empirical correlations of such parameters as the chemical shift or coupling constant with changes in physical phenomena produced by substituent effects.[11,47,48,69,138] The data are undoubtedly of great significance but it is still uncertain how the measurements are related to the electronic distribution within the molecule.[69]

The $^1$H n.m.r. spectra of the compounds were recorded on a Jeol C60HL high resolution spectrometer at 60 MHz. Because of their malodorous nature and air sensitivity the samples were sealed in Pyrex glass capillaries (<u>ca</u>. 3 mm o.d.) either as neat liquids for obtaining the coupling constants or as solutions for measuring the chemical shifts relative to tetramethylsilane (TMS) or cyclohexane. The solvent used was $CCl_4$ since previous $^1H$ n.m.r. studies of the related silyl and germyl species utilizing $CCl_4$ showed little or no dilution shifts.[27] In some cases, cyclohexane ($\delta CH = 1.44$ p.p.m.) was selected as both solvent and internal standard; it being nonpolar and relatively anisotropic and therefore unlikely to significantly affect the chemical shifts. The capillaries were then placed into standard n.m.r. tubes (ca. 5 mm o.d.) containing $CCl_4$ to ensure good sample spinning. The spectrometer was calibrated to ethylbenzene at a sweep width of 10 p.p.m. The chemical shifts are accurate to ± 0.02 p.p.m. and coupling constants (measured at 5 and 2 p.p.m. sweep width) to ±0.05 Hz for proton coupling, $J^{vic}_{HH}$ , and ± 0.1 Hz for satellite spectra, $J(^{13}CH)$ or $J(^{29}SiH)$ arising from the presence of $^{13}C$ (1.1% natural abundance with $I = 1/2$) or $^{29}Si$ (4.70% natural abundance with $I = 1/2$), Figure V.3. Satellites arising from proton coupling with the magnetic isotope of selenium ($^{77}Se$ 7.58% natural abundance with $I = 1/2$) and tellurium ($^{125}Te$ 6.9% natural abundance with $I = 1/2$) were also observed. The compounds had to be obtained in a high state of purity because small quantities of impurities led to unresolved $^{29}SiH$ and $^{13}CH$ satellites. The redetermined parameters for the parent species, viz. - $(R_3M)_2E$ where E=O,S,Se,Te and R=H, Me are in good agreement with the literature values.

The $^1H$ n.m.r. spectra not only provided the initial characterization for the chalcogen compounds, but also confirmed their purity based on the absence of proton containing impurities. Typical $^1H$ n.m.r. spectra are displayed in Figures V.1 - V.3 and the observed parameters for $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M=Si,Ge; E=O,S,Se,Te and $\underline{n}=0 \rightarrow 3$ are collected in Tables V.1 and V.2. All of the chalcogenides gave first order spectra consistent with the free rotation about the skeletal bonds. For the purposes of discussion the CH and MH protons are denoted as follows, e.g.

$$\underset{\beta}{H_3C}-\underset{\alpha}{H_2Si}-O-\underset{\alpha}{SiH_2}-\underset{\beta}{CH_3}$$

Thus the $(MeH_2M)_2E$ species gave the $\beta$ -proton resonance as a 1:2:1 triplet, intensity 3, to the high field of an associated 1:3:3:1 quartet, intensity 2, attributable to $\alpha(MH_2)$ protons, Figure V.1, while the $(Me_2HM)_2E$ species gave the $\beta$-proton resonance as a 1:1 doublet, intensity 6, to the high field of an associated 1:6:15:20:15:6:1 septet of intensity 1 due to $\alpha(MH)$ protons at lower field, Figures V.2 and V.3. For the parent sequence $(Me_3M)_2E$ the CH proton resonances appeared as a singlet at high field while the MH proton resonances for $(H_3M)_2E$ appeared at lower field, Figures V.4 and V.5.

### (a) $\alpha$ - proton chemical shifts

An examination of the $\alpha$-proton chemical shifts in Table V.1 [$\delta$(SiH)] and Table V.2 [$\delta$(GeH)] shows that the largest consistent trend comes about as the chalcogen changes from O $\rightarrow$ S $\rightarrow$ Se $\rightarrow$ Te in the series $(H_3Si)_2E$ or $(H_3Ge)_2E$. As the less electronegative chalcogen is introduced the $\alpha$-proton resonances

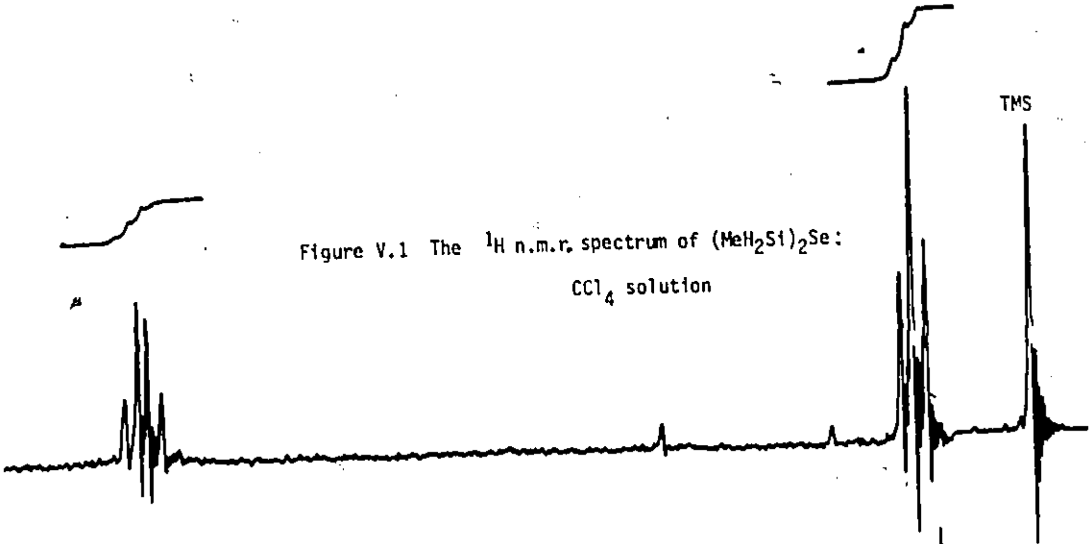

Figure V.1 The $^1H$ n.m.r. spectrum of $(MeH_2Si)_2Se$: $CCl_4$ solution

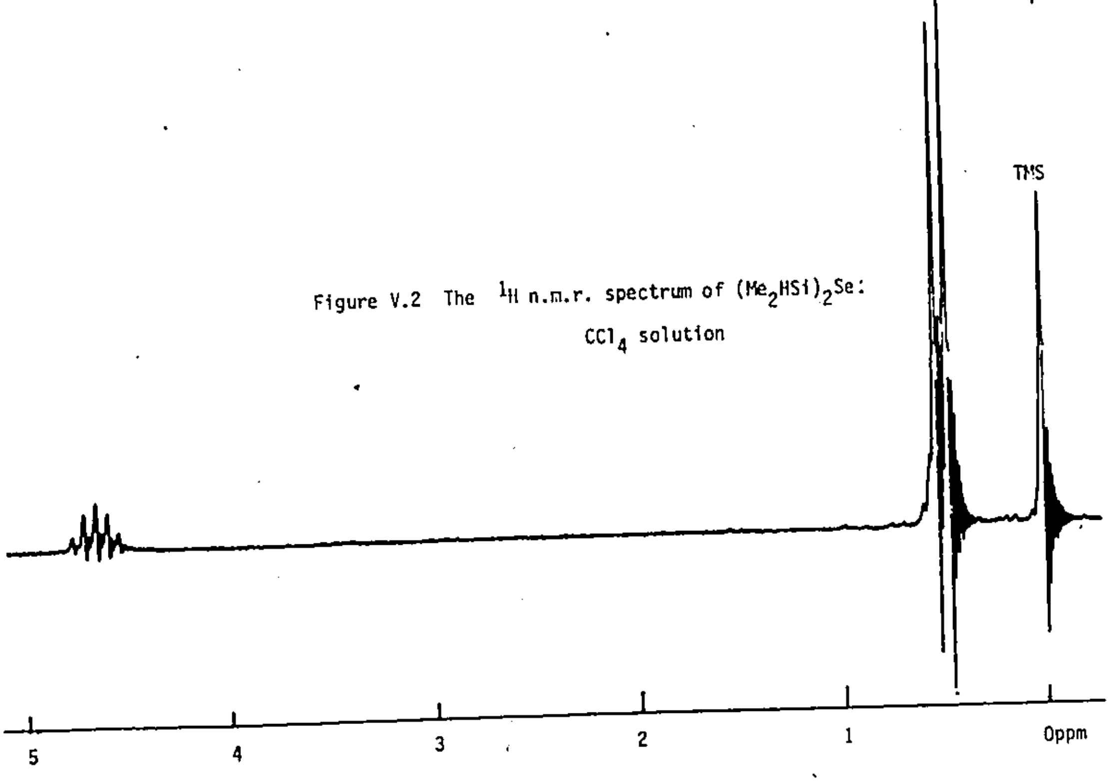

Figure V.2 The $^1H$ n.m.r. spectrum of $(Me_2HSi)_2Se$: $CCl_4$ solution

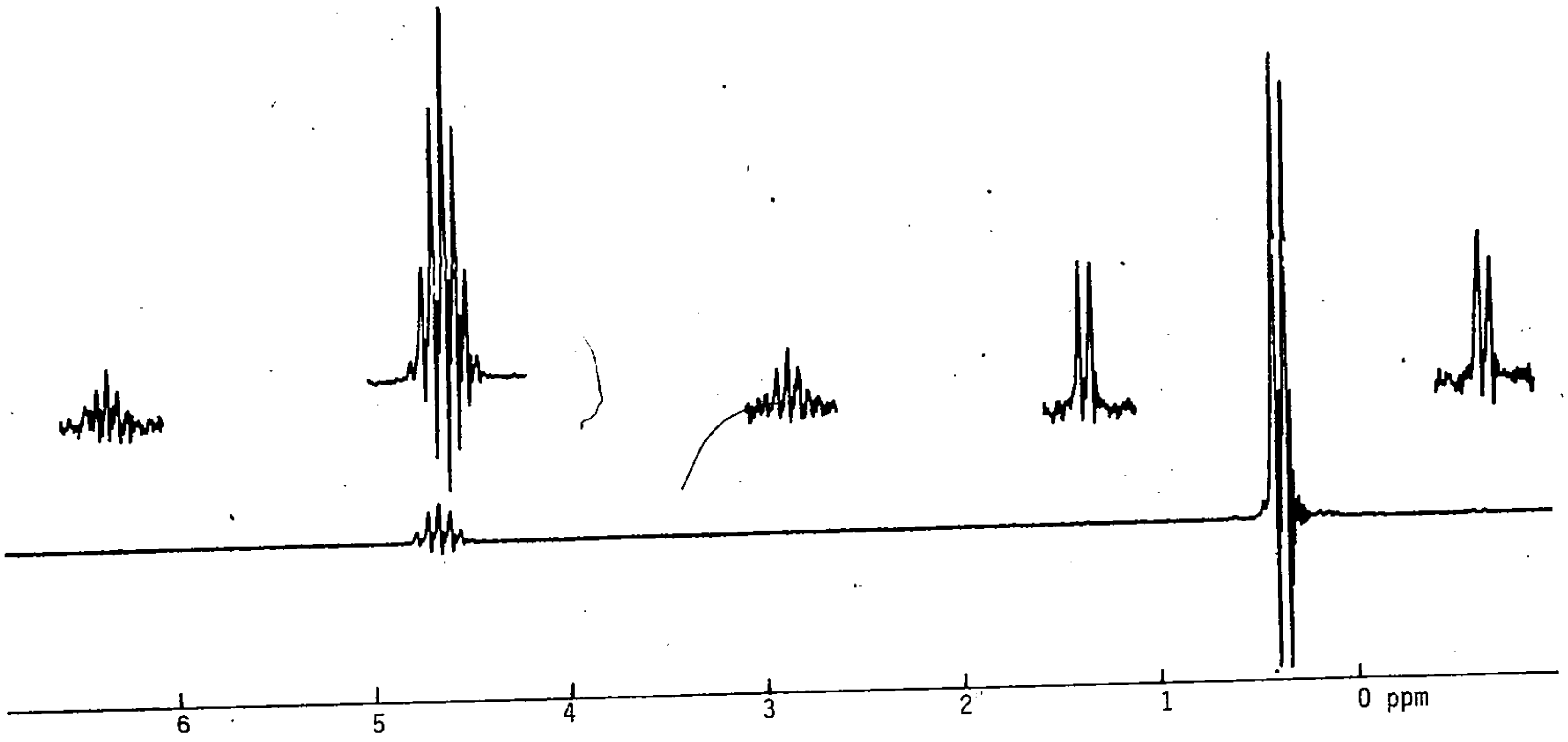

Figure V.3 The $^1H$ n.m.r. spectrum of $(Me_2HSi)_2S$

are shifted to higher field. In other words, the less electron-withdrawing chalcogen leaves the α-proton most shielded which is as might be expected if the inductive effect is the controlling factor. The trend persists equally well for both the $(MeH_2M)_2E$ series and also for the $(Me_2HGe)_2E$ series. In this respect, these trends resemble those observed with regard to α-substitution in the related halogeno-silanes[47] and -germanes,[25,135] $MeH_2MX$ and $Me_2HGeX$ where X=F,Cl,Br,I.

It is interesting to note that as protons are replaced by methyl groups on the M atom the α-proton shift is to lower field. However, the shift is much less for E = O than for E = Te and in general the magnitude of the trend for S and Se fall in between. On the above 'inductive model' this implies firstly, that methyl groups, in this context, are more electronegative than protons, and secondly that they are able to exert a great influence when Si or Ge is attached to Te rather than to O. Indeed, any redistribution of electronic environment of the α-protons brought about by methyl substitution are minimal on oxygen. The net result on the $(Me_2HSi)_2E$ series results in the trends resulting from changing E, being reversed for E = Te,Se and S. This deviation is in contrast to the α-proton shifts of the $Me_2HSiX$ species[11] and related halogeno-[25] and chalco-[105,133] germanes.

### (b) β-proton chemical shifts

The chemical shift of the β-proton resonances in all cases decreases (shifts to higher field) with increasing methyl sub-

Table V.1. The $^1$H.n.m.r. parameters* of $(Me_{\underline{n}}H_{3-\underline{n}}Si)_2E$ species

| Compound | δ(Me) | δ(SiH) | $J^{vic}_{HH}$ | $J^{29}SiH$ | $J^{13}CH$ |
|---|---|---|---|---|---|
| $(H_3Si)_2O$[a] | - | 4.61 | - | 221.5 | - |
| $(MeH_2Si)_2O$[b] | 0.28 | 4.66 | 3.33 | 213.0 | 121.5 |
| $(Me_2HSi)_2O$[c] | 0.14 | 4.69 | 2.85 | 204.9 | 120.0 |
| $(Me_3Si)_2O$[c,d] | 0.06 | - | - | - | 118.0 |
| $(H_3Si)_2S$[a] | - | 4.35 | - | 223.7 | - |
| $(MeH_2Si)_2S$[b] | 0.49 | 4.47 | 3.83 | 214.7 | 123.0 |
| $(Me_2HSi)_2S$[c] | 0.38 | 4.63 | 3.39 | 205.1 | 121.2 |
| $(Me_3Si)_2S$[c,d] | 0.31 | - | - | - | 119.3 |
| $(H_3Si)_2Se$[a] | - | 4.12 | - | 224.0 | - |
| $(MeH_2Si)_2Se$ | 0.59 | 4.43 | 3.98 | 215.8 | 124.5 |
| $(Me_2HSi)_2Se$ | 0.51 | 4.73 | 3.54 | 205.5 | 121.4 |
| $(Me_3Si)_2Se$[d] | 0.42 | - | - | - | 120.6 |
| $(H_3Si)_2Te$[e] | - | 3.71 | - | 224.4 | - |
| $(MeH_2Si)_2Te$ | 0.73 | 4.25 | 4.14 | 216.2 | 125.3 |
| $(Me_2HSi)_2Te$ | 0.63 | 4.82 | 3.74 | 206.0 | 122.7 |
| $(Me_3Si)_2Te$[d,f] | 0.58 | - | - | - | 121.5 |

* The spectra were recorded at ambient temperature. Chemical shifts (δ ±0.02 p.p.m.) are in p.p.m. to low field of $Me_4Si$ as internal standard in $CCl_4$ solution (5% v/v). Chemical shifts of the tellurides were measured relative to cyclohexane. Deviations for coupling constants of neat liquids are J(HH) ±0.05 Hz, J(SiH) ±1 Hz, J(CH) ±0.2 Hz.

[a] Ref. 48; [b] Ref. 47; [c] Ref. 11; [d] Ref. 93; [e] Ref. 90; [f] Ref. 117. Compare with (Me) of $(Me_3Si)_2Te$ ($C_6H_{12}$ solution) of 0.67 ppm in ref.117. and 0.60 ppm ($CCl_4$ solution) in ref.93.

Table V.2. The $^1H$ n.m.r. parameters* of $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$ species

| Compound | δ(Me) | δ(GeH) | $J^{vic}_{HH}$ | $J^{13}CH$ |
|---|---|---|---|---|
| $(H_3Ge)_2O^a$ | - | 5.28 | - | - |
| $(MeH_2Ge)_2O^b$ | 0.59 | 5.28 | 2.91 | 129.1 |
| $(Me_2HGe)_2O^{b,c}$ | 0.40 | 5.40 | 2.43 | 128.2 |
| $(Me_3Ge)_2O^d$ | 0.29 | - | - | 125.9 |
| $(H_3Ge)_2S^e$ | - | 4.62 | - | - |
| $(MeH_2Ge)_2S$ | 0.66 | 4.87 | 3.30 | 129.4 |
| $(Me_2HGe)_2S$ | 0.54 | 4.93 | 2.91 | 129.0 |
| $(Me_3Ge)_2S^d$ | 0.51 | - | - | 127.5 |
| $(H_3Ge)_2Se^a$ | - | 4.23 | - | - |
| $(MeH_2Ge)_2Se$ | 0.77 | 4.55 | 3.38 | 130.1 |
| $(Me_2HGe)_2Se$ | 0.69 | 4.73 | 2.96 | 129.3 |
| $(Me_3Ge)_2Se^d$ | 0.58 | - | - | 128.1 |
| $(H_3Ge)_2Te^a$ | - | 3.59 | - | - |
| $(MeH_2Ge)_2Te^f$ | 0.93 | 4.12 | 3.53 | 132.6 |
| $(Me_2HGe)_2Te^f$ | 0.80 | 4.65 | 3.37 | 131.7 |
| $(Me_3Ge)_2Te^g$ | 0.71 | - | - | 129.1 |

* See footnote to Table V.1.

[a] J(SeGeH) 12.1 Hz, J(TeGeH) 19.4 Hz in ref. 99.

[b] Compare with the values $(MeH_2Ge)_2O$ δ(Me) 0.49, δ(GeH) 5.12 ppm and $(Me_2HGe)_2O$ δ(Me) 0.42, δ(GeH 5.34 ppm in ref.169.

[c] Compare with δ(Me) 0.13, δ(GeH) 5.45 ppm ($Et_2O$ solvent) in A.R.Dahl, C.A.Heil, and D.Norman, Inorg. Chem., 10, 2562 (1975).

[d] Compare with δ(Me) of $(Me_3Ge)_2E$ ($CCl_4$ solution) of 0.31 (O), ).53 (S), 0.66 (Se) ppm in ref.8.

[e] Ref. J.E.Drake and C.Riddle, J.Chem.Soc.(A), 2710 (1968).

[f] Recorded in $C_6H_{12}$ (5% v/v). [g] 0.74 ppm ($C_6H_{12}$ solution) in ref. 111.

stitution but increases as the chalcogen changes from O → S → Se → Te. This is the case for the $\beta$-proton shifts in the corresponding halogenosilanes,[11,47] and related halogeno-[25,135] and chalco-[133] germanes. This general feature appears to be more related to the size of the substituents and hence has been attributed to anisotropy and related effects.[8,136] In this respect the anisotropy contribution of the M–E bond might account for the observed anomaly just mentioned for the $\alpha$-protons. A slight correlation exists between the internal chemical shift [$\delta(SiH_2) - \delta(CH_3)$ and $\delta(SiH) - \delta(CH_3)$] and electronegativity of the substituent. However, with decreasing electronegativity the internal chemical shift of $(Me_2HSi)_2E$ where E=S,Se,Te alters only slightly: $\delta(SiH_2) - \delta(CH_3)E$; O, 4.38 → S, 3.98 → Se, 3.84 → Te, 3.52; $\delta(SiH) - \delta(CH_3)E$; O, 4.54 → S, 4.25 → Se, 4.22 → Te, 4.21. It is unwise to place too much emphasis on the significance of these trends but they are useful as an aid to and confirmation of assignments.

### (c) Coupling constants

The $^{13}C$- and $^{29}Si$-proton coupling constants were obtained from the well resolved satellites equally spaced either side of the $\beta$- and $\alpha$-proton resonances, Figure V.3. Satellites were also observed due to proton coupling with magnetic isotopes of both $^{77}Se$ and $^{125}Te$ so that under the conditions studied there is no exchange of silyl or germyl groups. Proton coupling with the active $^{73}Ge$ nucleus ($^{73}Ge$, 7.8% abundant; $I = 9$[illegible] was not observed but has been reported only in the highly symmetrical molecules $GeH_4$[32] and $GeMe_4$.[149]

The magnitude of the coupling constants for some of the parent species, $(R_3M)_2E$ where R = H,Me and other related silyl and germyl compounds has been discussed in the literature in terms of the s-character in the intervening bonds and hence to the Fermi contact term [8,56,137-141] and to $\pi$-type interactions as well as hyperconjugation of the d-orbitals of the chalcogen atom with the SiH bonds.[56,112,142] ~~At this~~ point, the coupling constants decrease with increasing methyl substitution, but increase as the chalcogen electronegativity decreases (or its bulk increases) which implies that the C-H and M-H bonds increase in s-character from oxygen to tellurium. The larger magnitude of $J(Ge^{13}CH)$ 125.9-132.6 Hz, Table V.2, relative to $J(Si^{13}CH)$ 118.0-125.3 Hz, Table V.1, also conforms to an increasing coupling constant with increasing mass. However, the smaller values of the vicinal interproton coupling, $J^{vic}_{HH}$, as the mass of M (M=Ge > Si) increases could possibly be due to the longer distance in the H-C-Ge-H fragment.[25,150]

Long-range, H-(M-E-M"-)H', coupling has been observed for some Group IV hydrides,[112,142] $H_3M$-E-$M''H'_3$ where M and M" = C,Si,Ge and E=S,Se. For the mixed species (M≠M") such coupling is directly observed in the main, first order $^1H$ n.m.r. spectrum but in the simple hydrides (M=M") may only be observed in the $^{13}C$ and $^{29}Si$ satellites, Figure V.4. Similar coupling is not

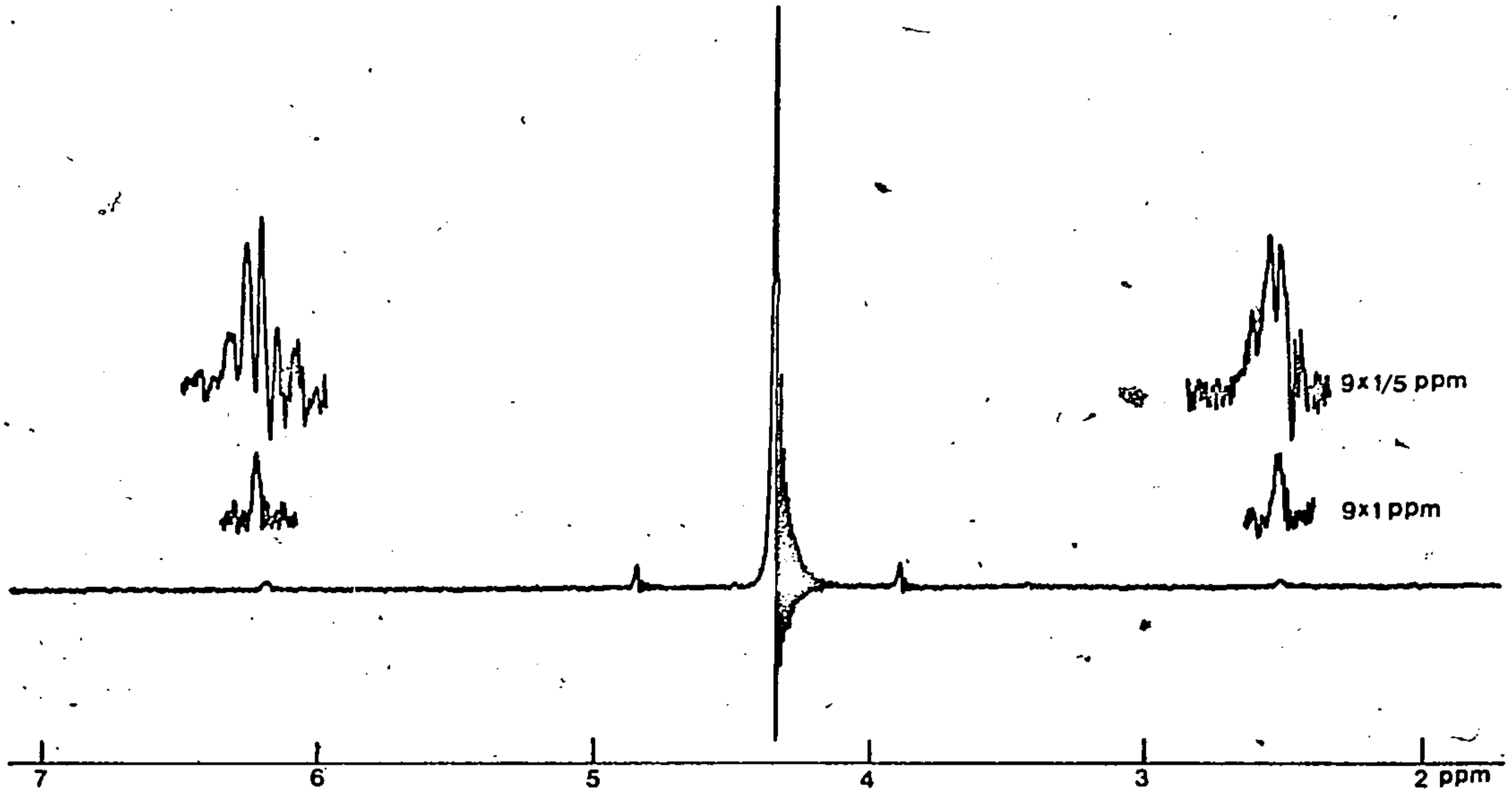

Figure V.4 The $^1$H n.m.r. spectrum of $(H_3Si)_2S$

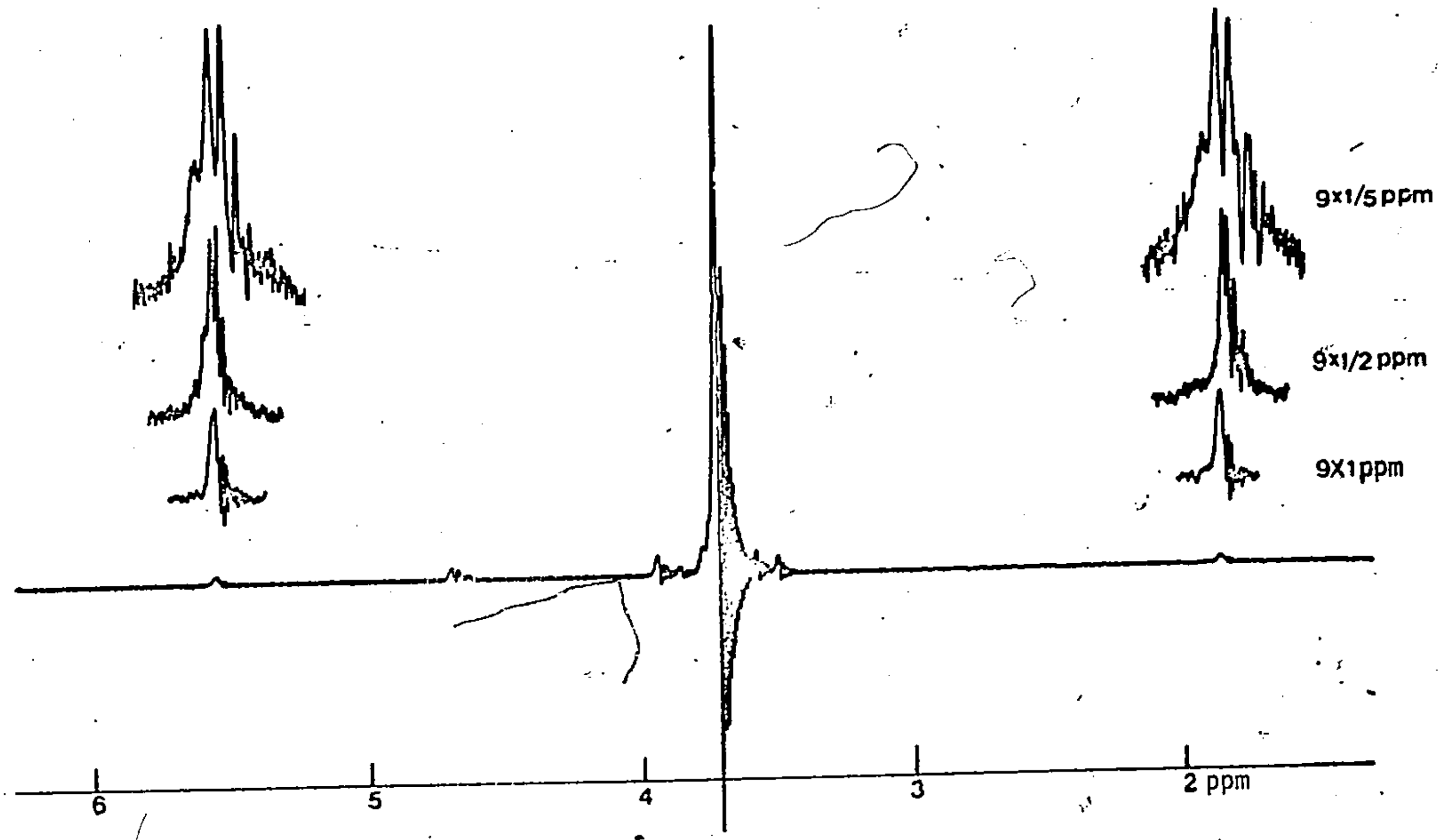

Figure V.5 The $^1H$ n.m.r. spectrum of $(H_3Si)_2Te$

observed in the oxygen analogues, $H_3M{-}O{-}M''H_3'$ indicating that the H-H' distance and the extent of $\pi$-bonding are not of prime importance in determining the value of J(HH'). It has been suggested therefore that the d-orbitals of sulfur and selenium play an important role.[56,112,142] Evidence for this type of coupling was sought in this study for the analogous hydride, $H_3SiTeSiH_3'$. The appearance of the $^{29}$SiH satellites as 1:3:3:1 quartets, Figure V.5, indicates that the d-orbitals of tellurium are also available of involvement in long-range coupling. Thus in the series $H_3SiESiH_3'$ as E changes from S ⟶ Se ⟶ Te, J(HH') decreases: 0.70 ⟶ 0.63 ⟶ 0.59 Hz. The significance of the magnitude of these values and ~~the~~ preponderance of the aforementioned effects in determining the value of the coupling constants are poorly understood but it is important to have comparative data for the series of compounds.

## V.2. VIBRATIONAL SPECTRA

The vibrational (both i.r. and Raman) spectra of $(Me_3M)_2E$[111,117,144,146] and $(H_3M)_2E$[88,99,113,114,119] where M=Si,Ge and E=O,S,Se,Te have appeared in the literature, so only the intermediate species will be discussed. The assignments of the vibrational modes in the spectra of $(MeH_2M)_2E$ and $(Me_2HM)_2E$ are based firstly, on comparisons along the series E=O ⟶ S ⟶ Se ⟶ Te and secondly, on comparisons with the spectra of the aforementioned parent chalcogenides and related monohalogenosilanes[46,147] and -germanes.[25,148] The vibrational spectra of some $(MeH_2M)_2E$ and $(Me_2HM)_2E$ species are displayed in Figures V.6 - V.15 to provide representative examples, while the observed frequencies along with intensities, polarization data, and tentative assignments, are presented in Tables V.3 - V.6.

The general features in the spectra which are characteristic of the heavy-atom skeleton, M-E-M, appear as follows: Si-O stretching (asymmetric and symmetric bands) at ca. 1079 vs (i.r.) and 581-547 vs, p(Raman), compared with $\nu$(Ge-O) at ca. 882 (i.r.) and 501-480 m,p (Raman); $\nu$(Si-S) ca. 489 vs (i.r.) and 473-461 vs, p (Raman), compared with $\nu$(Ge-S) ca. 410 s (i.r.) and ca. 371 vs, p (Raman); $\nu$(Si-Se) ca. 384 ms (i.r.) and ca. 383 vs, p (Raman), compared with $\nu$(Ge-Se) ca. 280 s (i.r.) and ca. 276 vs,p(Raman); and $\nu$(Si-Te) ca. 329 s (i.r.) and ca. 332 va, p (Raman), compared with $\nu$(Ge-Te) ca. 235 m (i.r.) and ca. 229 $cm^{-1}$ vs,p (Raman). A closer inspection of the Raman spectra of the $(Me_2HSi)_2E$ species, where E=S,Se,Te; Figure V.8 , reveals that the $\nu_s$(Si-E) splits in two lines in contrast to the single line 7 of the $\nu_s$(Ge-E). The cause of this splitting, as that of the $\delta$(SiH)- proton shifts, is not clear but the most probable explanation would be that there is a mixture of conformers.

The assignment of the asymmetric Ge-O stretch was complicated by the presence of $\rho(CH_3)$ and $\delta$(GeH) vibrations and examination of the literature suggests that others have also found this vibrational mode difficult to assign for $(H_3Ge)_2O$, $H_3GeOMe$,[114] $MeH_2GeOAc$,[135] $(Me_3Ge)_2O$[151] and related species.[152]

Table V.3. The i.r. and Raman spectra ($cm^{-1}$) of the bis(methylsilyl)chalcogenides*

| Tentative | $(MeH_2Si)_2O$ | | $(MeH_2Si)_2S$ | | $(MeH_2Si)_2Se$ | | $(MeH_2Si)_2Te$ | |
|---|---|---|---|---|---|---|---|---|
| Assignment | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(liq) | Raman(liq) |
| $\nu(CH_3)$ (a) | 2970 mw | 2967 m,dp | 2979 m | 2973 m,dp | 2975 m | 2967 m,dp | 2966 m | 2965 m,dp |
| (s) | 2908 vw | 2908 vs,p | 2912 mw | 2909 vs,p | 2906 w | 2903 vs,p | 2903 mw | 2901 s,p |
| $\nu(SiH_2)$ | 2157 vs | 2159 vs,p | 2159 vs | 2159 vs,p | 2158 vs | 2155 vs,p | 2151 vs | 2147 s,p |
| $\delta(CH_3)$ (a) | 1418 vw | 1422 w,dp | 1417 wbr | 1418 brw,dp | 1418 w | 1418 w,dp | 1413 m | 1411 w,dp |
| (s) | 1265 s | 1259 m,p | 1261 m | 1255 m,p | 1262 m | 1251 m,p | 1246 s | 1249 m,p |
| $\delta(SiH_2)$ (sc) | 970 s | 974 m,dp | 949 s | 944 m,dp | 942 sh | 936 m,dp | 935 s | 931 m,dp |
| $\rho(CH_3)$ (a) | 919 vs | 916 wbr | 909 s | 907 w,p | 900 sh | 896 m,p | 877 vs | 877 s,p |
| (s) | 877 m | 866 mw,dp | 873 vs | 868 mw,dp | 870 vs | 868 brsh,dp | 834 vs | 835 wsh, dp |
| $\nu(SiC)$ | 766 m | 756 s,p | 745 ms | 743 s,p | 737 s | 733 s,p | 720 vs | 721 s,p |
| $\delta(SiH_2)$ (wag) | | 720 vs,p | 699 w | 698 s | | 693 s,p | | 685 s,p |
| (tw) | | 695 sh,dp | | 672 sh,dp | | 657 sh,dp | | 638 br,dp |
| $\rho(SiH_2)$ | 518 w | 519 mw,p | 510 ms | 505 ms,p | 495 w | 493 m,p | 475 mw | 473 w,p |
| $\nu(SiE)$ (a) | 1085 vs | | | 489 sh | 388 m | | 332 s | |
| (s) | ca.575 vw | 581 vs,p | | 461 vs,p | | 380 vs,p | | 328 vs,p |
| $\delta(CSiE)$ (a) | | | | 221 sh,dp | | | | |
| (s) | | 261 sh | | 198 s,p | | 186 s,p | | 173 s,p |
| $\delta(ESiE)$ | | 227 m,p | | 119 w,p | | ca.96 p | | ca.85 vw,p |

* Spectra recorded at room temperature.

m = medium, s = strong, w = weak, v = very, sh = shoulder, br = broad, ms = moderately strong,

p = polarized, dp = depolarized

Table V.4. The i.r. and Raman spectra (cm$^{-1}$) of the bis(dimethylsilyl)chalcogenides*

| Tentative Assignment | $(Me_2HSi)_2O$ |  | $(Me_2HSi)_2S$ |  | $(Me_2HSi)_2Se$ |  | $(Me_2HSi)_2Te$ |  |
|---|---|---|---|---|---|---|---|---|
|  | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(liq) | Raman(liq) | i.r.(liq) | Raman(liq) |
| $\nu(CH_3)$ (a) | 2965 m | 2966 m,dp | 2965 s | 2967 m,dp | 2965 ms | 2962 m,dp | 2959 ms | 2961 m,dp |
| $\nu(CH_3)$ (s) | 2907 w | 2904 vs,p | 2905 m | 2903 vs,p | 2901 m | 2902 vs,p | 2899 m | 2899 vs,p |
| $\nu(SiH)$ | 2125 s | 2129 vs,p | 2130 vs | 2137 s,p | 2136 vs | 2138 s,p | 2130 vs | 2135 s,p |
| $\delta(CH_3)$ (a) | 1425 w | 1425 w,dp | 1425 m | 1425 w,dp | 1426 w | 1423 w,dp | 1421 m | 1416 w,dp |
| $\delta(CH_3)$ | 1393 | 1399 w,dp | 1398 sh[a] | 1396 w,dp | 1394 sh | 1392 w,dp | 1393 sh | 1391 w,dp |
| $\delta(CH_3)$ (s) | 1265 s | 1258 m,p | 1255 vs | 1254 m,p | 1254 vs | 1254 m,p | 1250 vs | 1253 mw,p |
| $\rho(CH_3)$ (a) | 915 s | 907 mw,dp | 896 vs | 894 mw,dp | 893 vs | 885 m,p | 874 vs | 877 m,p |
| $\rho(CH_3)$ (s) | 886 vs | 880 w,dp | 869 vs | 860 w | 854 vs | 862 wsh | 851 vs | 847 vwsh |
| $\rho(CH_3)$ (a,s) | 836 m | 836 mw,p | 833 vs | 841 wsh | 831 vs | 837 wsh | 829 wsh | 835 vwsh |
| $\nu(SiC)$ (a) | 774 m | 764 m,dp | 768 s | 767 m,dp | 765 ms | 765 mw,dp | 758 ms | 762 w,dp |
| $\nu(SiC)$ (s) | 670 w | 670 vs,p | 663 ms | 667 vs,p | 657 ms | 664 s,p | 662 sh | 661 ms,p |
| $\delta(SiH)$ (s) | ca.730 vw | 748 m,p | 716 ms | 715 m,p | 703 ms | 702 m,p | 684 s | 688 m,p |
| $\delta(SiH)$ (a) | 630 w | 626 m,dp | 635 m | 633 m,dp | 632 m | 634 mw,dp | 628 m | 629sh,dp |
| $\nu(SiE)$ (a) | 1074 vs |  | 489 vs |  | 379 vs |  | 326 s |  |
| $\nu(SiE)$ |  |  | 472 sh[a] | 472 vs,p |  | 387 vs,p |  | 335 vs,p |
| $\nu(SiE)$ (s) | ca.565 vw | 547 vs,p | 460 vwsh | 459 sh,p | 372 vwsh[b] | 373 sh,p |  | 323 sh,p |
| $\delta(CSiC)$ |  | 285 sh | 254 w[a] | 255 m,p |  | 250 m,p |  | 240 m,p |
| $\delta(CSiE)$ (s) |  | 259 sh |  | 215 sh |  | 199 sh |  |  |
| $\delta(CSiE)$ (a) |  | 211 sh |  | 188 s,p |  | 184 s,p |  | 177 s,p |
| $\delta(SiESi)$ |  | 193 s,p |  | 103 mw,p |  | 89 wsh |  | ca.78 w |

* See footnote to Table V.3.

[a] liq., [b] gas

Table V.5. The i.r. and Raman spectra ($cm^{-1}$) of the bis(methylgermyl)chalcogenides*

| Tentative Assignment | | $(MeH_2Ge)_2O$ | | $(MeH_2Ge)_2S$ | | $(MeH_2Ge)_2Se$ | | $(MeH_2Ge)_2Te$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(liq) | Raman(liq) |
| $\nu(CH_3)$ | (a) | 2997m | 2990m,dp | 2999m<br>(2970)m | 2988m,dp | 2998m<br>(2967)w | 2987m,dp | 2991m | 2984m,dp |
| | (s) | 2923w | 2920s,p | 2923m | 2919s,p | 2923w | 2916s,p | 2916m | 2915ms,p |
| $\nu(GeH_2)$ | (a) | 2077sh | 2071vs,p | 2082vs | | 2078vs | | 2061vs | |
| | (s) | 2057vs | 2058m,p | 2070vs | 2060vs,p | 2066vs | 2057vs,p | | 2048vs,p |
| $\delta(CH_3)$ | (a) | 1418vw | 1420w,dp | 1420w | 1416w,dp | 1413w | 1414w,dp | 1409m | 1407w,dp |
| | (s) | 1259m | 1248m,p | 1262m | 1243m,p | 1263w | 1240m,p | 1238m | 1238m,p |
| $\delta(GeH_2)$ | (sc) | 876s [a]<br>872vs [b] | 875m,dp | 873sh | 871m,dp | 873s | 868m,dp | 865S | 865m,dp |
| $\rho(CH_3)$ | (a) | 840s | 845wsh | 852s | | 853s | 848sh,p | 832vs | 837w |
| | (s) | 800vs | | 831vs | 823w | 823vs | 820w,dp | 808vs | 815w |
| $\delta(GeH_2)$ | (wag) | 725s | 728w,dp | 709s | 708m,dp | 698s | 695m,dp | 674s | 677m,dp |
| | (tw) | | 661m,dp | | 632sh,dp | | 625sh,dp | | ca.619sh,dp |
| $\nu(GeC)$ | | 610ms | 610vs,p | 605s | 603vs,p | 604s | 602vs,p | 595s | 597s,p |
| $\rho(GeH_2)$ | | 454vw | 453m,p | 445ms | 461m,p | 450w,br | 451m,p | 430m | 429w,p |
| $\nu(Ge-E)$ | (a) | 901sh[a]<br>(883)[b] | 900sh,dp | 409s | 402m,dp | | | 235ms | |
| | (s) | 486m | 501m,p | 378vw | 371vs,p | | 279vs,p | | 226vs,p |
| $\delta(C-Ge-E)$ | | | 236w | | 163ms,p | | 158ms,p | | 147s,p |
| $\delta(Ge-E-Ge)$ | | | 182m,p | | 101ms,p | | 84ms,p | | 77ms,p |

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* Spectra recorded at room temperature.
m = medium, s = strong, w = weak, v = very, sh = shoulder, br = broad, ms = moderately strong, p = polarized, dp = depolarized.

[a] Gas. [b] in $CCl_4$ solution

Table V.6. The i.r. and Raman spectra (cm$^{-1}$) of the bis(dimethylgermyl)chalcogenides*

| Tentative Assignment | | $(Me_2HGe)_2O$ | | $(Me_2HGe)_2S$ | | $(Me_2HGe)_2Se$ | | $(MeH_2Ge)_2Te$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | i.r.(gas) | Raman(liq) | i.r.(gas) | Raman(liq) | i.r.(liq) | Raman(liq) | i.r.(liq) | Raman(liq) |
| ν(CH$_3$) | (a) | 2997s | 2987m,dp | 2987m | 2988m,dp | 2983s | 2979m,dp | 2982s | 2978m,dp |
| | (s) | 2926m | 2918vs,p | 2915m | 2917vs,p | 2914s | 2915vs,p | 2912s | 2910s,p |
| ν(GeH) | | 2040vs | 2034vs,p | 2042vs | 2044s,p | 2039vs | 2044s,p | 2036vs | 2038s,p |
| δ(CH$_3$) | (a) | 1422m | 1418m,dp | 1410m | 1412w,dp | 1410m | 1415w,dp | 1408m | 1414w,dp |
| | (s) | 1255s | 1247m,p | 1248m | 1244m,p | 1238s | 1246m,p | 1236s | 1241m,p |
| ρ(CH$_3$) | (a) | 849s | 847m,p | 847s | 852m,p | 846vs | 898w | 839vs | 843m,p |
| | (s) | 805vs | 800w | 824vs | 826w | 820vs | 820sh | 819vs | 820sh |
| | (a,s) | 762m | 758w | 763m | 752w | 758m | 751w | 756m | 752w |
| δ(GeH) | (a) | 702s | 698m,dp | 678s | 683m,dp | 668s | 666m,dp | 650s | 650m,dp |
| | (s) | 664w | 634m,dp | 662w | 630m,dp | 634w | 630m,dp | | 625m,dp |
| ν(GeC) | (a) | 613s | 609m,dp | 607s | 609m,dp | 607vs | 603m,dp | 603s | 601m,dp |
| | (s) | 591s | 593vs,p | 587s | 590vs,p | 583s | 587vs,p | 579s | 581s,p |
| ν(Ge-E) | (a) | 882s | 883w,sh | 410s | 409m,dp | 280s | | 234s | |
| | (s) | 480m | 485m,p | | 379vs,p | | 273vs,p | | 232vs,p |
| δ(C-Ge-C) | | | 250sh | | 198s,p | | 189m,p | | 188m,p |
| δ(C-Ge-E) | (s) | | 214sh | | | | | | |
| | (a) | | 193sh | | 162s,p | | 158s,p | | 152s,p |
| δ(Ge-E-Ge) | | | 169m,p | | 95m,p | | 76m,p | | 63m,p |

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* See footnote to Table V.5.

Table V.7. The i.r. and Raman spectra (cm$^{-1}$) of the digermoxanes*

| Tentative Assignment | $(CD_3H_2Ge)_2O$ i.r.(gas) | $(CD_3H_2Ge)_2O$ Raman(liq) | $(Me_3Ge)_2O$ i.r.(gas) | $(Me_3Ge)_2O$ Raman(liq) | Tentative Assignment |
|---|---|---|---|---|---|
| $\nu(CD_3)$ (a) | 2241 w | 2239 m,dp | 2988 s | 2983 m,dp | (a) $\nu(CH_3)$ |
| (s) | ca.2134 wsh | 2128 vs,p | 2919 m | 2912 vs,p | (s) |
| $\nu(GeH_2)$ | 2062 vs | 2057 vs,p | 1408 mw | 1409 w,dp | (a) $\delta(CH_3)$ |
| $\delta(CD_3)$ (a) | 1037 vw | 1032 w,dp | 1349 w | | |
| (s) | 980 m | 972 s,p | 1245 s | 1246 m,p | (s) |
| $\delta(GeH_2)$ (sc) | 871 s | 879 m,dp | 817 sh | 820 w,p | (a) $\rho(CH_3)$ |
| $\delta(GeH_2)$ | 810 vwsh | 815 mw,dp | 801 vs | 792 wsh | (s) |
| | | 731 m,dp | 757 m | 758 w,dp(a,s) | |
| | 660 s | 655 w,dp | 609 s | 607 s,dp | (a) $\nu(GeC)$ |
| $\rho(CD_3)$ (a) | 770 vs | 778 sh | 569 m | 575 vs,p | (s) |
| (s) | 610 wsh | 604 w,dp | 882 vs | ca.868 w | (a) $\nu(GeO)$ |
| $\nu(GeC)$ | 555 m | 554 vs,p | 460 w | 470 ms,p | (s) |
| $\nu(GeO)$ (a) | 905 vs | | | 245 sh | (a) $\delta(GeC_3)$ |
| (s) | 460 vw | 473 s,p | | 196 s,dp | (s) |
| $\rho(GeH_2)$ | 425 vw | 426 m,p | | 160 s,p | $\delta(GeOGe)$ |
| $\delta(CGeO)$ | | ca.204 vwsh | | | |
| $\delta(GeOGe)$ | | 167 m,p | | | |

*See footnote to Table V.5.

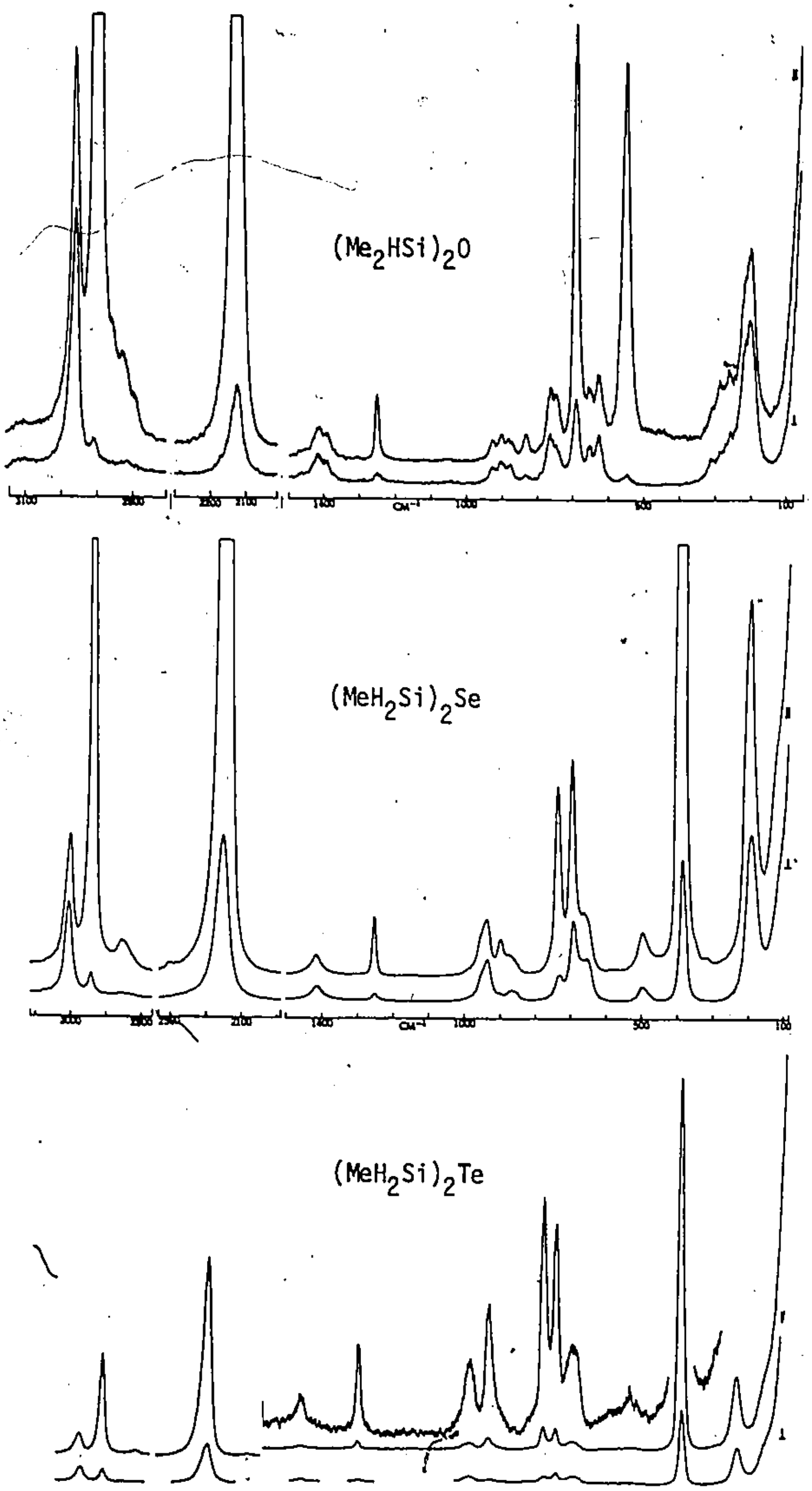


Figure V.6 The Raman spectra of methyldisilyl chalcogenides

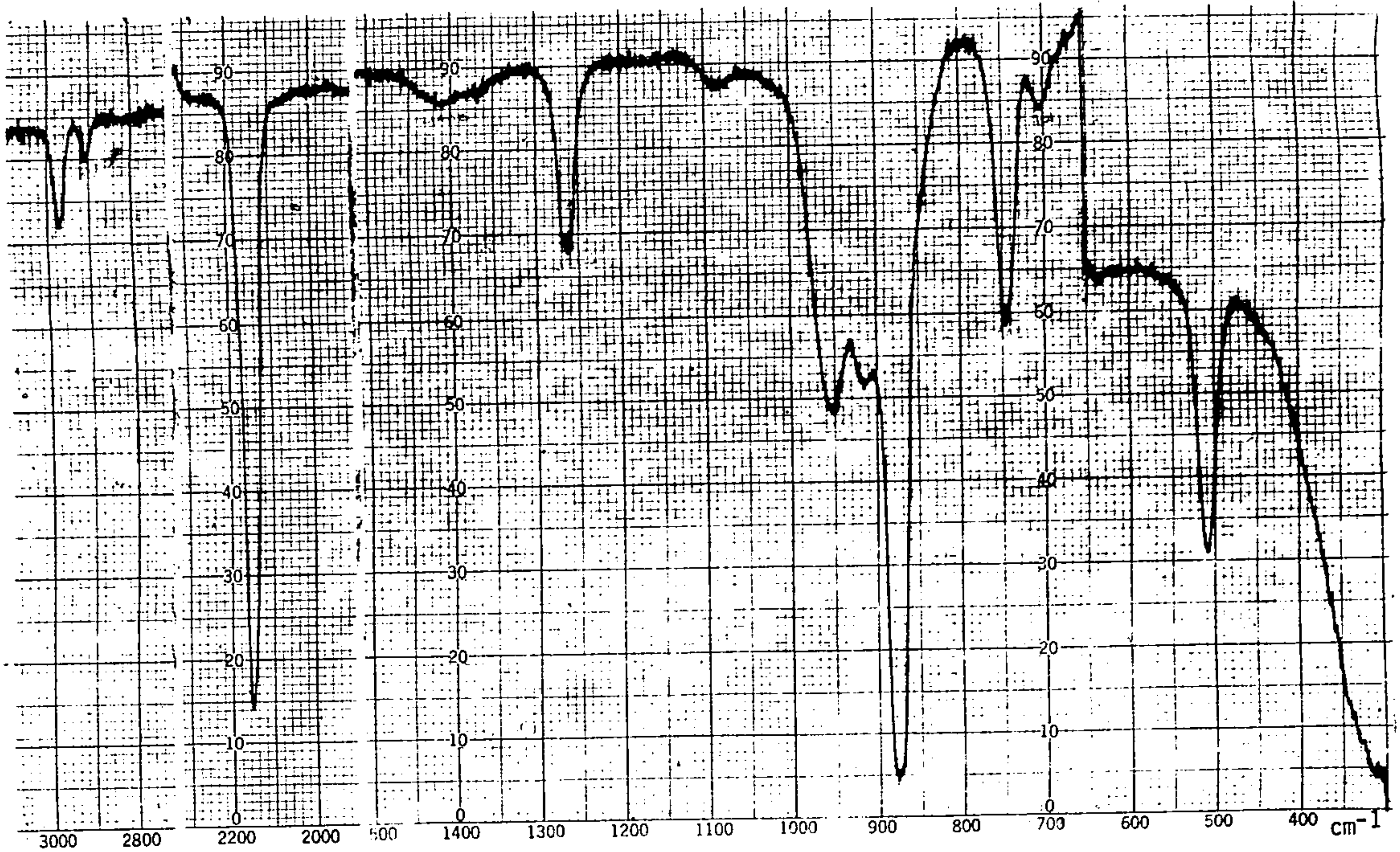
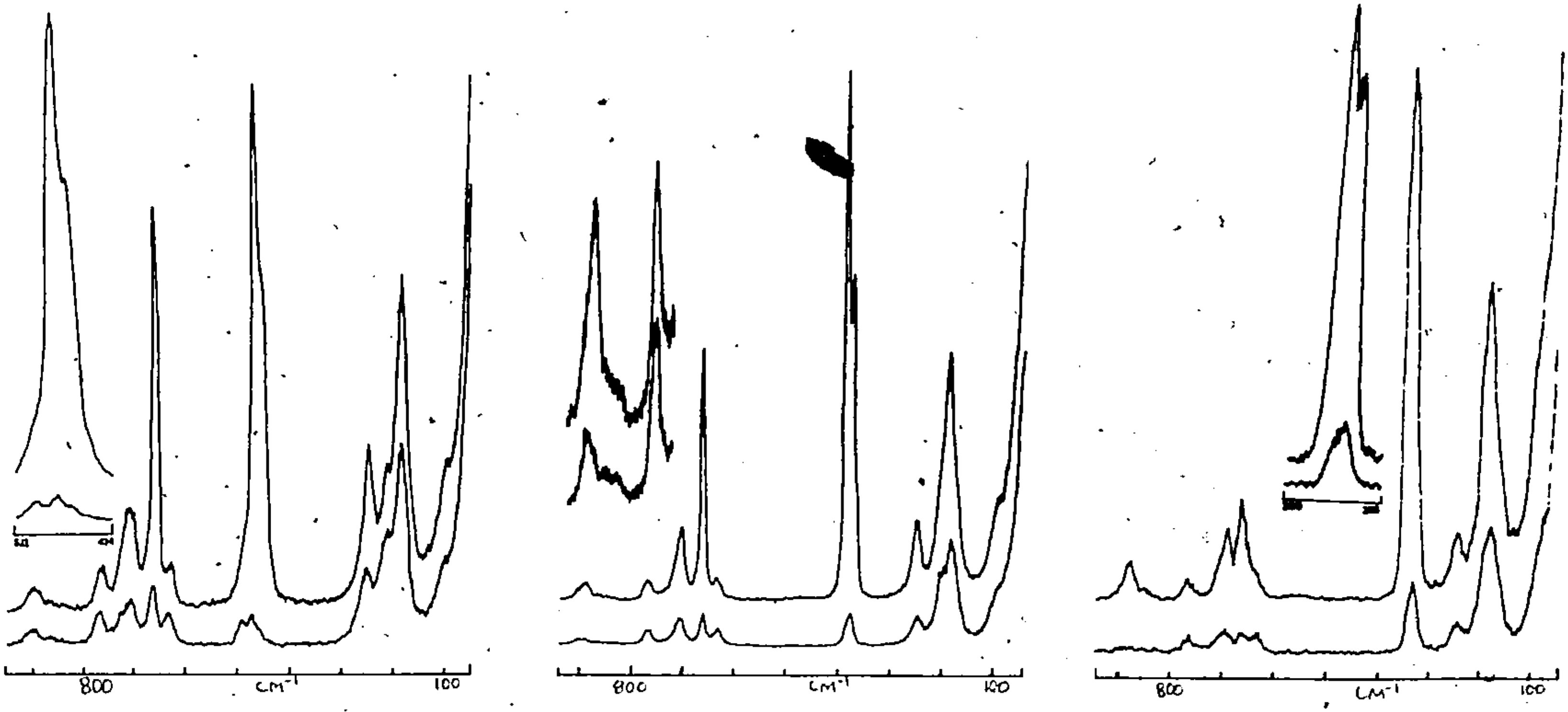


Figure V.7 The gas phase infrared spectrum of $(MeH_2Si)_2S$

Figure V.8 The liquid phase Raman spectra of $(Me_2HSi)_2E$



$(Me_2HSi)_2S$ $(Me_2HSi)_2Se$ $(Me_2HSi)_2Te$

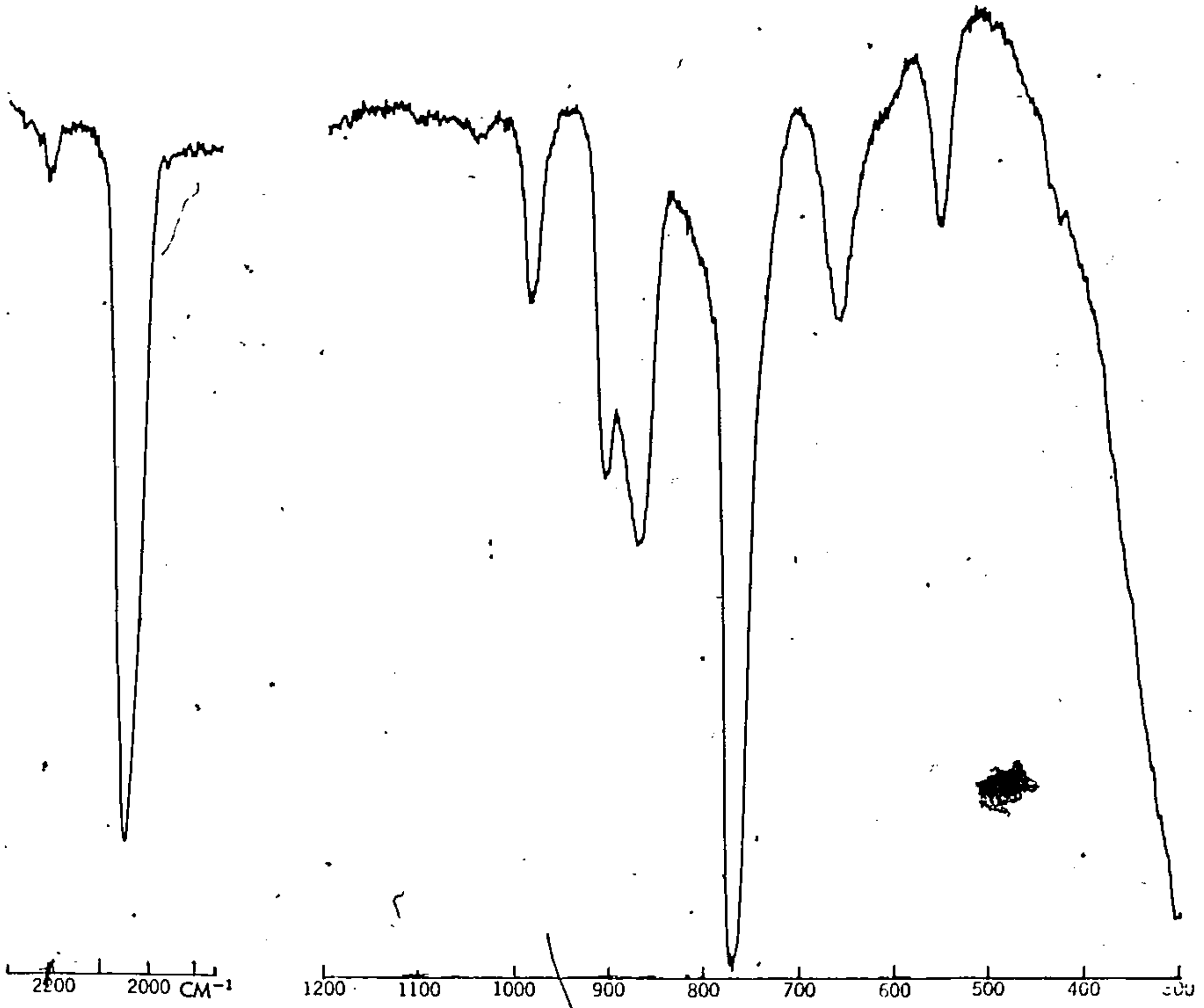


Figure V.9. The gas phase infrared spectrum of $(CD_3H_2Ge)_2O$

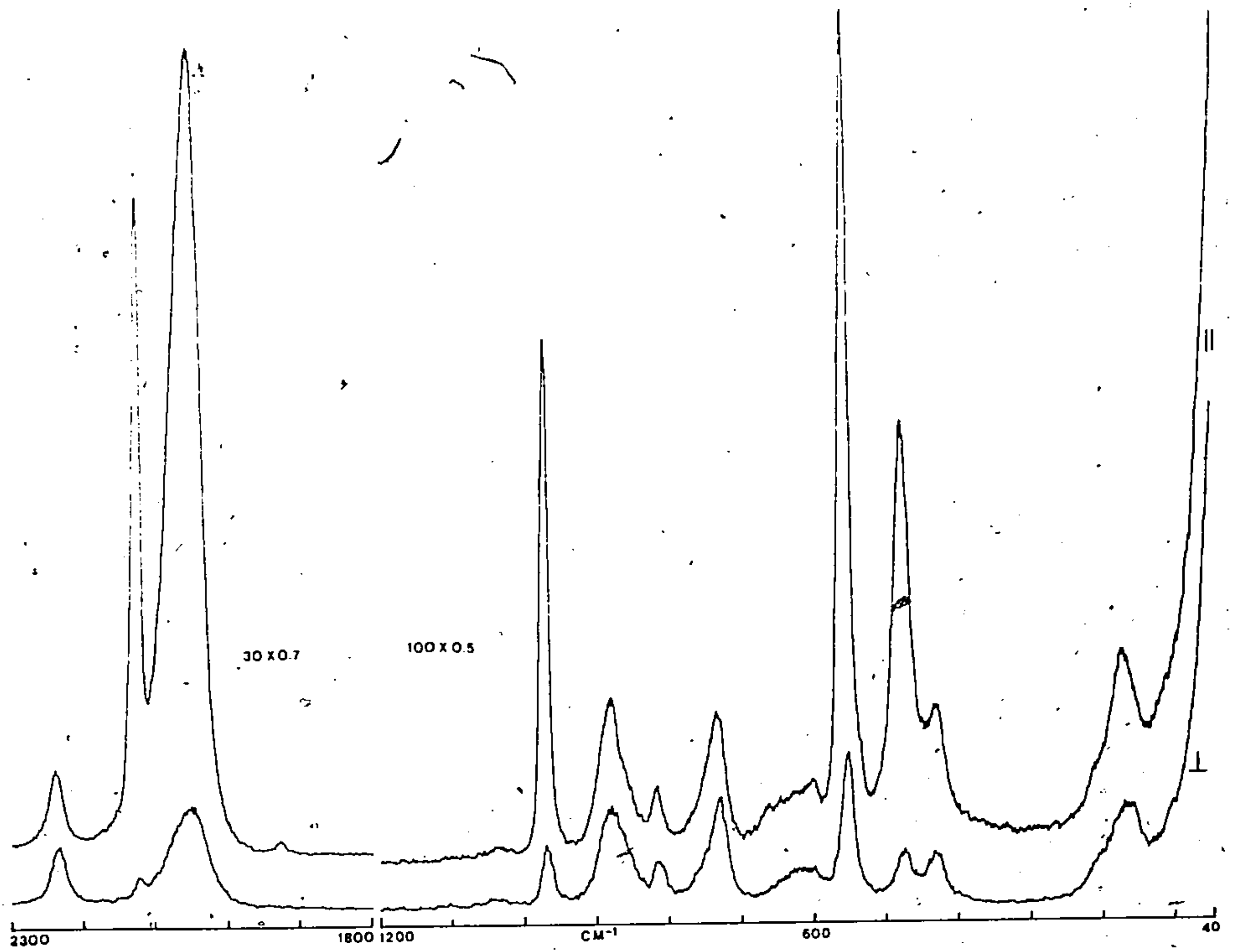
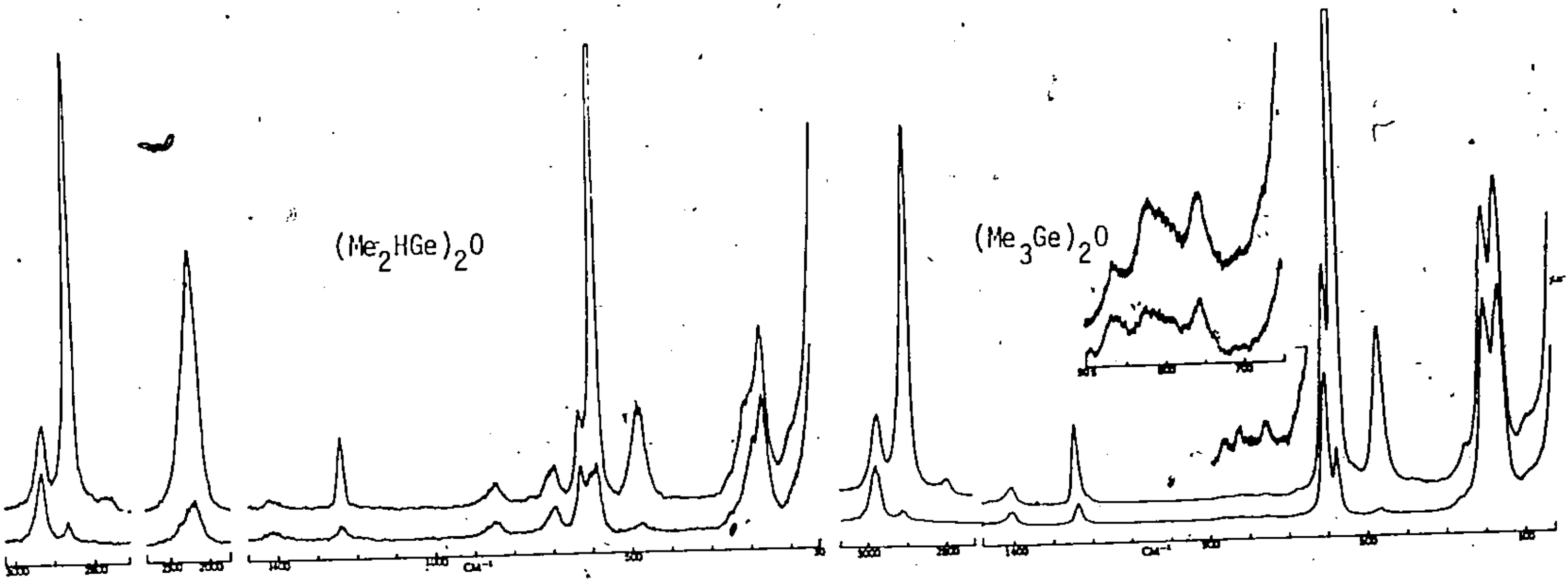
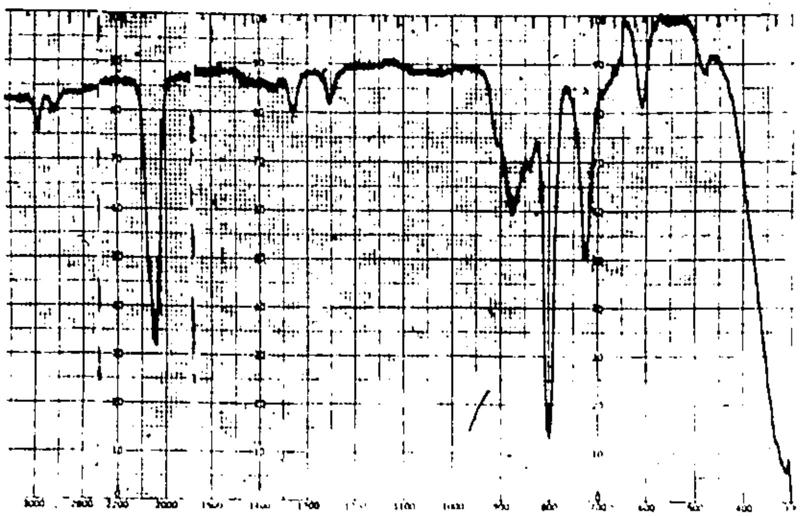


Figure V.10 The liquid phase Raman spectrum of $(CD_3H_2Ge)_2O$

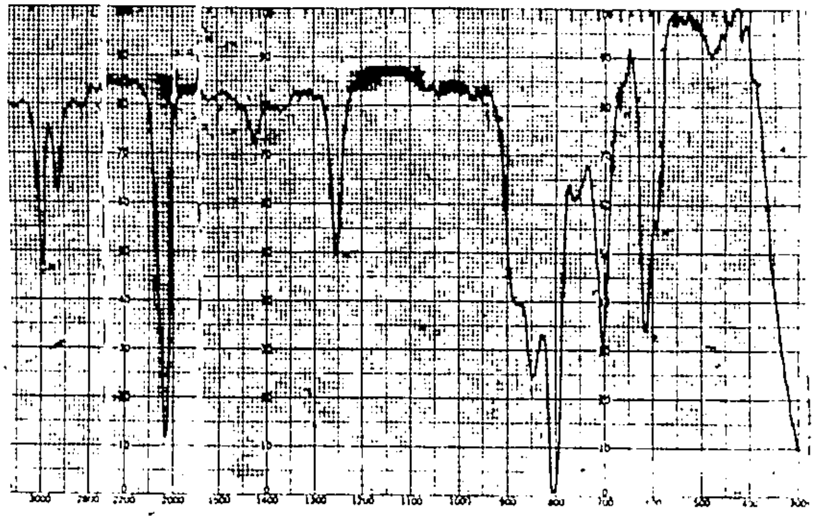
Figures V.11-V.12  The liquid phase Raman spectra of:



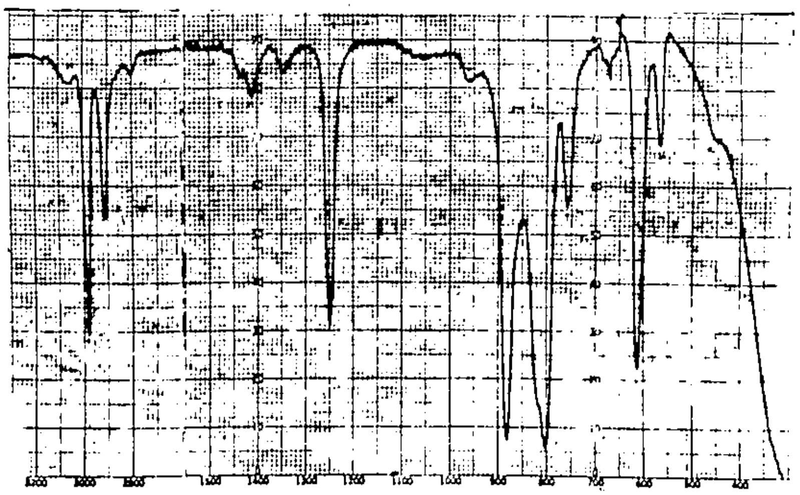
Figures V.13-V.15 The gas phase infrared spectra of:



$(MeH_2Ge)_2O$



$(Me_2HGe)_2O$



$(Me_3Ge)_2O$

Deuteriation at carbon produced the expected low frequency shift in all CH modes[27] (Figures V. 9 and V. 10) and comparison along the germoxane series (Tables V.5 - V.7, Figures V.9 - V.15) facilitated the assignment of the $\nu_a$(Ge-O) at ca.882 CM$^{-1}$.

The M-E-M deformation mode is clearly observed in the Raman spectra and the resulting trend of $O > S > Se > Te$ and $Si > Ge$ is a direct consequence of the weight of the E and M atoms. Thus for $(MeH_2M)_2E$ one can observe a shift in the M-E-M deformation as follows: Si 227 m,p, Ge 182 m,p [O]; Si 119 w,p, Ge 101 ms, p [S]; Si ca. 96 p, Ge 84 ms,p [Se]; Si ca. 85 vw,p and Ge 77 ms,p [Te] which is similar to that of the $(Me_2HM)_2E$ series, viz. - Si 193 s,p, Ge 169 m,p [O]; Si 103 mw,p, Ge 95 m,p [S]; Si 89 m,p, Ge 76 m,p [Se]; Si ca. 78 w and Ge 63 m,p [Te].

The $CH_3$ stretching and deformation modes are unambiguously assigned in the expected 3000-2890 cm$^{-1}$ and 1410-1235 cm$^{-1}$ regions as are the MH stretching modes at 2159-2125 cm$^{-1}$ (SiH) and 2080-2030 cm$^{-1}$ (GeH). The remainder of the assignments for the $Me_{\underline{n}}H_{3-\underline{n}}M$-moieties (i.e. $\rho CH_3$, $\delta MH_2$, $\rho MH_2$, $\delta MH$) are comparable to the related monohalogeno-silanes[46,147] and -germanes.[25,27,148]

## V.3. MASS SPECTRA

The mass spectra of the $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ species provided molecular weight confirmation and further support for the a priori assignment of the $^1H$ n.m.r. and vibrational spectra. Thus the molecular or "parent" ion $P^+$ or ions derived from the molecular ion by the loss of any number of hydrogen atoms $(P-nH)^+$ were consistently observed (except for the $(Me_3M)_2O$ where M=Si,Ge) in the expected m/e ranges as shown in Table V.8. For convenience and comparisons of the characteristic fragments resulting from molecular breakdown at the ionising potential of 70eV the intermediate ($\underline{n}$=1,2) and parent species ($\underline{n}$=0,3) are discussed separately. The polyisotopic nature of germanium, selenium and tellurium lead to complicated spectra but the observed distribution and intensities may be correlated with their known abundances, Table V.9. In addition, with the hydridic species, difficulty arises from overlapping polyisotopic fragments resulting from 'hydrogen stripping'. However, resolution of the ambiguities is largely made possible by summing the hydrogen loss and using computer programmed analysis[153] to produce a 'generalized' fragmentation assignment.

### V.3.(a) The mass spectra of $(MeH_2M)_2E$ and $(Me_2HM)_2E$ series

The ion clusters and their relative abundances for the intermediate chalcogen compounds of silicon and germanium are presented in Tables V.10 - V.13 and representative experimental spectra are displayed in Figures V. 16 - V. 18 . It can be seen from these data that the parent molecular ion (including $P-\underline{n}H^+$) is present in all cases but in larger abundances for the monomethylated species. For the silyl species the relative abundance of this ion varies in the order O > S > Se > Te. The germyl species, however, do not reflect this trend, and in the case of the sulfides,

Table V.8. Observed mass spectral parent peaks for the $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ species

| Parent fragment | Range, m/e | | | |
|---|---|---|---|---|
| | E = O | E = S | E = Se | E = Te |
| $(H_3Si)_2E^+$ | 72-80 | 88-96 | 130-146 | 178-194 |
| $(MeH_2Si)_2E^+$ | 102-108 | 118-125 | 160-174 | 208-222 |
| $(Me_2HSi)_2E^+$ | 132-136 | 148-153 | 190-202 | 238-250 |
| $(Me_3Si)_2E^+$ | 162-164* | 178-181 | 220-230 | 268-278 |
| $(H_3Ge)_2E^+$ | 146-174 | 172-190 | 216-238 | 264-285 |
| $(MeH_2Ge)_2E^+$ | 186-202 | 202-218 | 246-266 | 294-314 |
| $(Me_2HGe)_2E^+$ | 216-230 | 232-246 | 276-294 | 324-342 |
| $(Me_3Ge)_2E^+$ | 246-258* | 262-274 | 306-322 | 354-369 |

* not observed.

Table V.9. Mass and abundances of Ge,Si,S,Se and Te isotopes*

| Isotope | mass ($^{12}C$) | % abundance |
|---|---|---|
| $^{70}$Ge | 69.924277 | 20.56 |
| $^{72}$Ge | 71.921740 | 27.42 |
| $^{73}$Ge | 72.923360 | 7.79 |
| $^{74}$Ge | 73.921150 | 36.47 |
| $^{76}$Ge | 75.921360 | 7.76 |
| $^{28}$Si | 27.976929 | 92.21 |
| $^{29}$Si | 28.976497 | 4.70 |
| $^{30}$Si | 29.973772 | 3.09 |
| $^{32}$S | 31.972073 | 95.0 |
| $^{33}$S | 32.971459 | 0.76 |
| $^{34}$S | 33.967870 | 4.26 |
| $^{74}$Se | 73.922477 | 0.87 |
| $^{76}$Se | 75.919212 | 9.02 |
| $^{77}$Se | 76.919913 | 7.58 |
| $^{78}$Se | 77.917309 | 23.52 |
| $^{80}$Se | 79.916525 | 49.82 |
| $^{82}$Se | 81.916708 | 9.19 |
| $^{120}$Te | 119.904024 | 0.089 |
| $^{122}$Te | 121.903056 | 2.46 |
| $^{123}$Te | 122.904282 | 0.87 |
| $^{124}$Te | 123.902830 | 4.61 |
| $^{125}$Te | 124.904426 | 6.99 |
| $^{126}$Te | 125.903312 | 18.71 |
| $^{128}$Te | 127.904468 | 31.79 |
| $^{130}$Te | 129.906232 | 34.48 |

* Reference : 62, "Handbook of Chemistry and Physics", R.C.West, ed., The Chemical Rubber Co., Cleveland, Ohio (1975).

selenides and tellurides, the relative abundance varies in the opposite order, i.e., O $\gg$ Te $>$ Se $>$ S. Fragmentation along the CMEMC skeleton affords large abundances of ions resulting from loss of Me, $Me_{\underline{n}}H_{3-\underline{n}}M$ and $Me_{\underline{n}}H_{3-\underline{n}}ME$. The most abundant ion in the dimethylated germyl species is due to $(Me_3H_{\underline{n}}Ge)^+$ suggesting a migration of a methyl group from one germanium atom to the other. A similar rearrangement is not observed in the methylgermyl derivatives but could occur in the oxides and sulfides where the overlapping of fragments makes such an assignment purely speculative, as in bis(dimethylsilyl) - oxide and -telluride. The $(Me_2H_{\underline{n}}Ge_2)^+$, $(Me_4H_{\underline{n}}Ge_2)^+$ and $(Me_{\underline{n}}H_{\underline{n}}Si_2)^+$ fragments observed in the mass spectra of $(MeH_2Ge)_2Se$, $(Me_2HGe)_2Se$, $(Me_2HGe)_2Te$ and and $(Me_2HSi)_2Te$, respectively, result from the effective elimination of the central chalcogen atom. The elimination of the central atom in the M-E-M linkage is not uncommon and has been observed in the mass spectra of germyl phenyl ether,[154] germyl carbodiimides[125], trigermylphosphine, trisilyl-amine and -phosphine and N-methyl disilylamine.[155] However, since the oxides and sulfides do not undergo the condensation-type reactions observed for the selenides and tellurides where elimination of Se or Te affords $(Me_2HM)_2$ species, I assume that if these fragments do exist they will be in very small abundances.

### V.3.(b) The mass spectra of $(H_3M)_2E$ and $(Me_3M)_2E$ series

The mass spectra of the hydridic and fully methylated chalcogenides are summarized in Tables V.14. and V.15. The

Table V.10. Ion clusters in the mass spectra of the bis(methylsilyl)chalcogenides*

| Ion Fragment | Relative Abundance (%) | | | |
|---|---|---|---|---|
| | E = O | E = S | E = Se | E = Te |
| $(Me_2H_{\underline{n}}Si_2E)^+$ | 41.6 | 36.9 | 32.8 | 17.3 |
| $(MeH_{\underline{n}}Si_2E)^+$ | 17.4 | 17.5 | 12.0 | 5.5 |
| $(H_{\underline{n}}Si_2E)^+$ | 20.2 | 6.1 | 3.4 | 4.2 |
| $(H_{\underline{n}}Si_2)^+$ | + | 7.5 | 7.2 | 7.7 |
| $(MeH_{\underline{n}}SiE)^+$ | 9.3 | 13.9 | 29.5 | 41.9 |
| $(MeH_{\underline{n}}Si)^+$ | 4.7 | 10.0 | 9.6 | 14.5 |
| $(H_{\underline{n}}SiE)^+$ | 5.3 | 4.9 | 3.6 | 6.4 |
| $(H_{\underline{n}}Si)^+$ | 1.5 | 3.2 | 1.9 | 2.5 |

* The value of $\underline{n}$ is summed from 0→2 for Si and 0→4 for $Si_2$.

+ Contribution summarized with $(MeH_{\underline{n}}SiE)^+$.

Table V.11. Ion clusters in the mass spectra of the bis(dimethylsilyl)chalcogenides*

| Ion Fragment | Relative Abundance (%) | | | |
|---|---|---|---|---|
| | E = O | E = S | E = Se | E = Te |
| $(Me_4H_{\underline{n}}Si_2E)^+$ | 35.5 | 13.3 | 13.9 | 8.2 |
| $(Me_4H_{\underline{n}}Si_2)^+$ | - | - | - | 5.8 |
| $(Me_3H_{\underline{n}}Si_2E)^+$ | 40.9 | 28.8 | 15.6 | 1.2 |
| $(Me_3H_{\underline{n}}Si_2)^+$ | - | - | - | 1.7 |
| $(Me_2H_{\underline{n}}Si_2E)^+$ | 3.0 | 7.5 | 0.5 | - |
| $(Me_2H_{\underline{n}}Si_2)^+$ | - | - | - | 1.4 |
| $(MeH_{\underline{n}}Si_2E)^+$ | 1.8 | 1.1 | - | - |
| $(MeH_{\underline{n}}Si_2)^+$ | - | - | - | |
| $(Me_3H_{\underline{n}}Si)^+$ | 6.0 | 14.3 | 17.6 | 11.4 |
| $(Me_2H_{\underline{n}}SiE)$ | | 7.6 | 15.0 | 27.1 |
| $(H_{\underline{n}}Si_2E)^+$ | | | | |
| $(H_{\underline{n}}Si_2)^+$ | - | - | - | 1.1 |
| $(Me_2H_{\underline{n}}Si)^+$ | 6.1 | 7.9 | 16.1 | 15.2 |
| $(MeH_{\underline{n}}SiE)^+$ | | 8.2 | 8.0 | 17.9 |
| $(MeH_{\underline{n}}Si)^+$ | 3.7 | 5.3 | 7.5 | 5.3 |
| $(H_{\underline{n}}SiE)^+$ | | 3.0 | 2.6 | 1.8 |
| $(H_{\underline{n}}Si)^+$ | 3.0 | 3.0 | 3.2 | 1.9 |

* The value of n is summed from 0→1 for Si and 0→2 for $Si_2$.

Table V.12. Ion clusters in the mass spectra of the bis(methylgermyl) chalcogenides*

| Ion Fragment | Relative Abundance (%) | | | |
|---|---|---|---|---|
| | E = 0 | E = S | E = Se | E = Te |
| $(Me_2H_{\underline{n}}Ge_2E)^+$ | 23.1 | 8.9 | 14.4 | 19.2 |
| $(MeH_{\underline{n}}Ge_2E)^+$ | 33.3 | 11.8 | 14.5 | 15.8 |
| $(Me_2H_{\underline{n}}Ge_2)^+$ | | 17.0 | 14.2 | 4.0 |
| $(H_{\underline{n}}Ge_2E)^+$ | 11.4 | | 10.9 | 11.2 |
| $(MeH_{\underline{n}}GeE)^+$ | 13.4 | 12.4 | 12.6 | 25.0 |
| $(Me_2H_{\underline{n}}Ge)^+$ | | 17.5 | – | – |
| $(H_{\underline{n}}GeE)^+$ | 15.6 | | 7.3 | 7.3 |
| $(MeH_{\underline{n}}Ge)^+$ | | 24.5 | 20.0 | 13.6 |
| $(MeH_{\underline{n}}Ge_2)^+$ | † | 1.1 | – | – |
| $(H_{\underline{n}}Ge_2)^+$ | 0.7 | 0.7 | 0.5 | 0.9 |
| $(H_{\underline{n}}Ge)^+$ | 2.5 | 6.1 | 5.6 | 3.0 |

* The value of $\underline{n}$ is summed from 0→2 for Ge and 0→4 for $Ge_2$.

† $(MeH_{\underline{n}}Ge_2)^+$ may give some contribution to the $(H_{\underline{n}}Ge_20)^+$ fragment but it is expected to be very small in abundance.

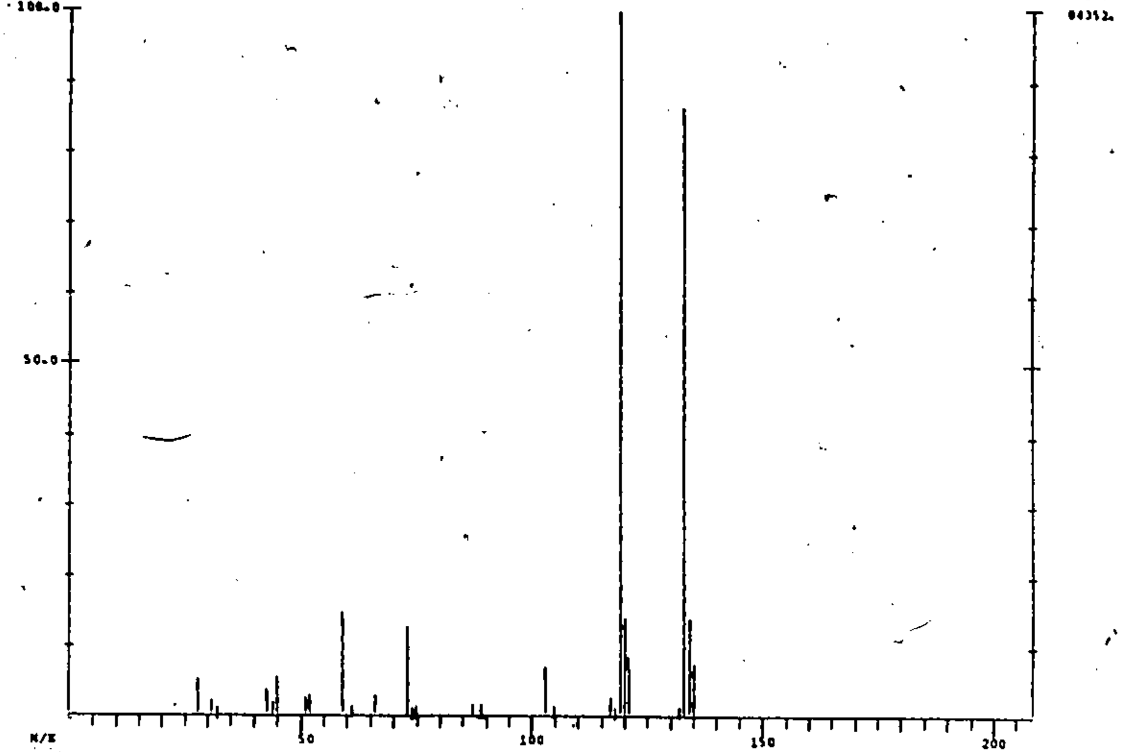
Table V.13. Ion clusters in the mass spectra of the bis(dimethylgermyl)chalcogenides*

| Ion Fragment | Relative Abundance (%) | | | |
|---|---|---|---|---|
| | E = 0 | E = S | E = Se | E = Te |
| $(Me_4H_{\underline{n}}Ge_2E)^+$ | 8.8 | 5.3 | 8.2 | 9.0 |
| $(Me_3H_{\underline{n}}Ge_2E)^+$ | 23.5 | 11.5 | 8.5 | 4.0 |
| $(Me_4H_{\underline{n}}Ge_2)^+$ | | 10.3 | 14.6 | † |
| $(Me_2H_{\underline{n}}Ge_2E)^+$ | 8.8 | | 1.8 | 3.7 |
| $(MeH_{\underline{n}}Ge_2E)^+$ | 4.0 | 3.9 | 0.7 | 6.2 |
| $(H_{\underline{n}}Ge_2E)^+$ | 4.7 | 2.8 | 4.9 | 5.3 |
| $(Me_2H_{\underline{n}}GeE)^+$ | 26.3 | 5.2 | 4.0 | 14.0 |
| $(Me_3H_{\underline{n}}Ge)^+$ | | 20.4 | 21.0 | 15.3 |
| $(MeH_{\underline{n}}GeE)^+$ | 11.4 | 3.6 | 3.0 | 12.8† |
| $(Me_2H_{\underline{n}}Ge)^+$ | | 19.8 | 17.1 | 15.6 |
| $(H_{\underline{n}}GeE)^+$ | 11.0 | | 1.5 | 1.9 |
| $(MeH_{\underline{n}}Ge)^+$ | | 13.7 | 12.4 | 9.6 |
| $(H_{\underline{n}}Ge)^+$ | 1.5 | 3.5 | 2.3 | 2.6 |

* The value of n is summed from 0→1 for Ge and 0→2 for $Ge_2$.

† Contribution summarized with $(MeH_{\underline{n}}GeE)^+$.

Figure V.16 The mass spectrum of $(Me_2HSi)_2O$



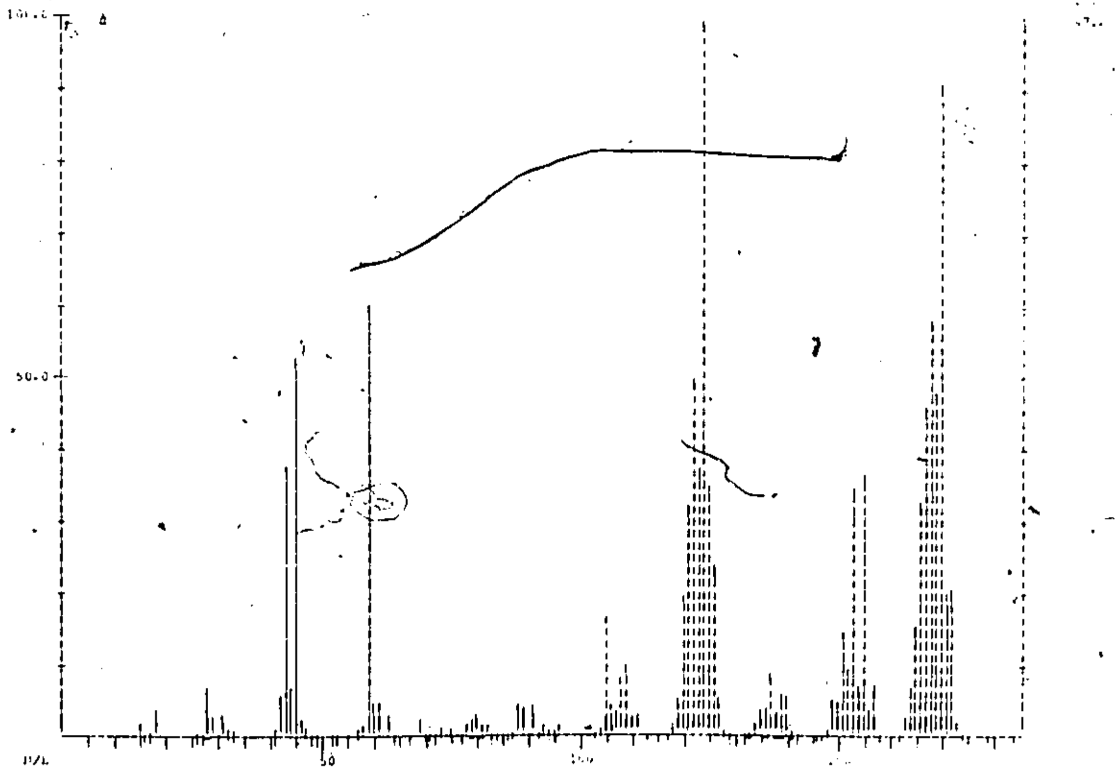


Figure V.17 The mass spectrum of $(MeH_2Si)_2Se$

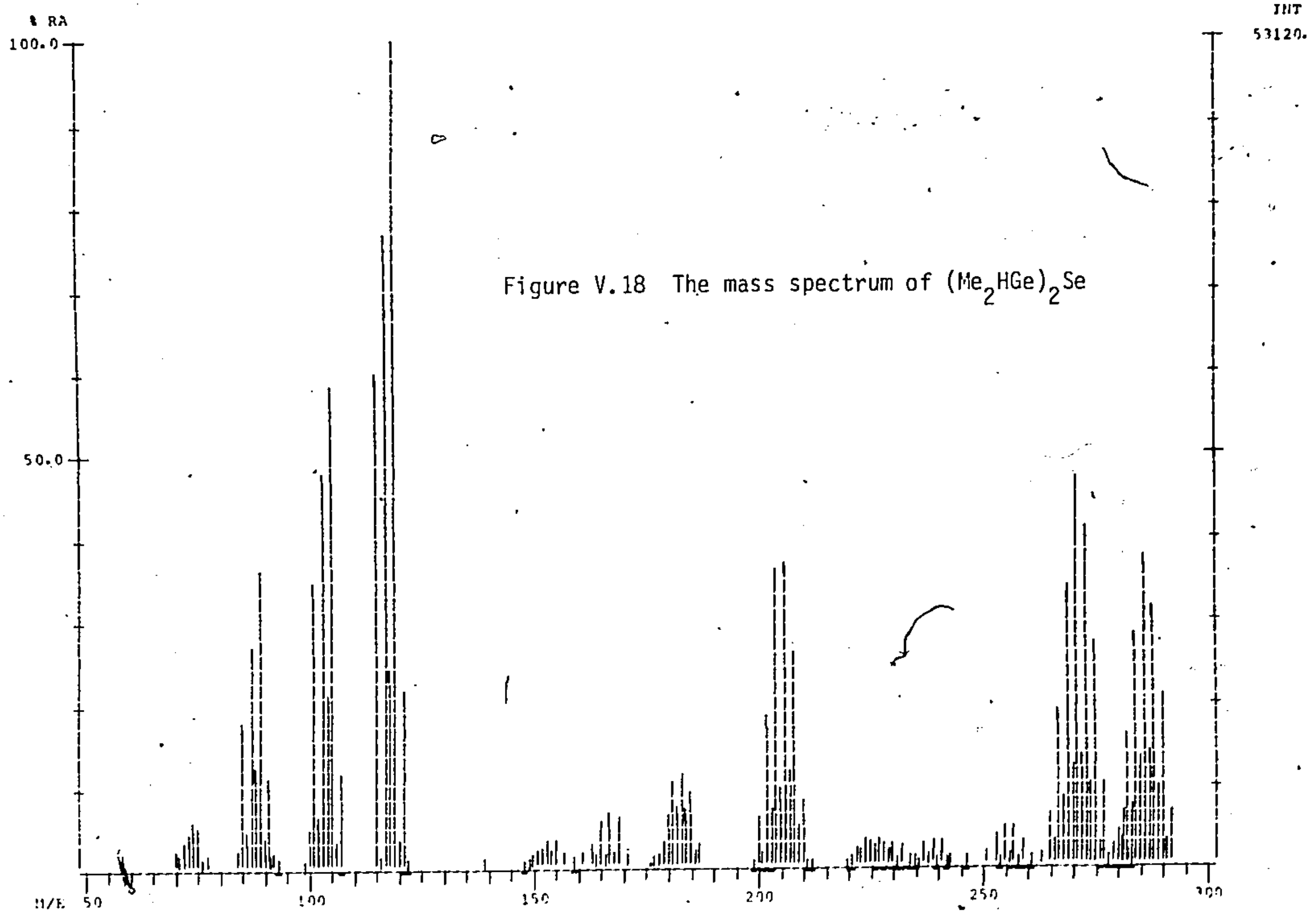


Figure V.18 The mass spectrum of $(Me_2HGe)_2Se$

molecular ion is the predominant ion in the former which is very similar to the corresponding carbodiimides,[125] $(H_3MN)_2C$. Although the fragment is complex, it appears that the P-1 ion is the principle contribution in the disilyl oxide and telluride, Figures V.19 and V.20, while the molecular ion is predominant in the disilyl sulfide and selenide. The principle fragmentation processes, aside from hydrogen stripping, involve the loss of the chalcogen atom [1], $H_nM$ [2], $H_nME$ [3], i.e.,

$$(H_nM)_2E^{+} \longrightarrow (H_nM)_2^{+} + E \qquad [1]$$

$$(H_nM)_2E^{+} \longrightarrow H_nME^{+} + H_nM \qquad [2]$$

$$(H_nM)_2E^{+} \longrightarrow H_nM^{+} + H_nME \qquad [3]$$

The appearance of $(H_nSi)_2^{2+}$ in the oxide and sulfide results from the loss of an electron from the $(H_nSi)_2^{+}$ ion, i.e.

$$(H_nSi)_2^{+} \longrightarrow (H_nSi)_2^{2+} + e \qquad [4]$$

In the methyl analogues, $(Me_3M)_2E$, the molecular ion is observed in all cases except for the oxides. However, these may be identified by the P-15 ion due to the loss of a methyl group, Figure V.21, i.e.

$$Me_3MOMMe_3^{+} \longrightarrow Me_3MOMMe_2^{+} + Me \qquad [5]$$

The loss of methyl group is a common process in the fully substituted chalcogenides as is the cleavage of the M-E-M bond to produce $(Me_3M)^{+}$, i.e.

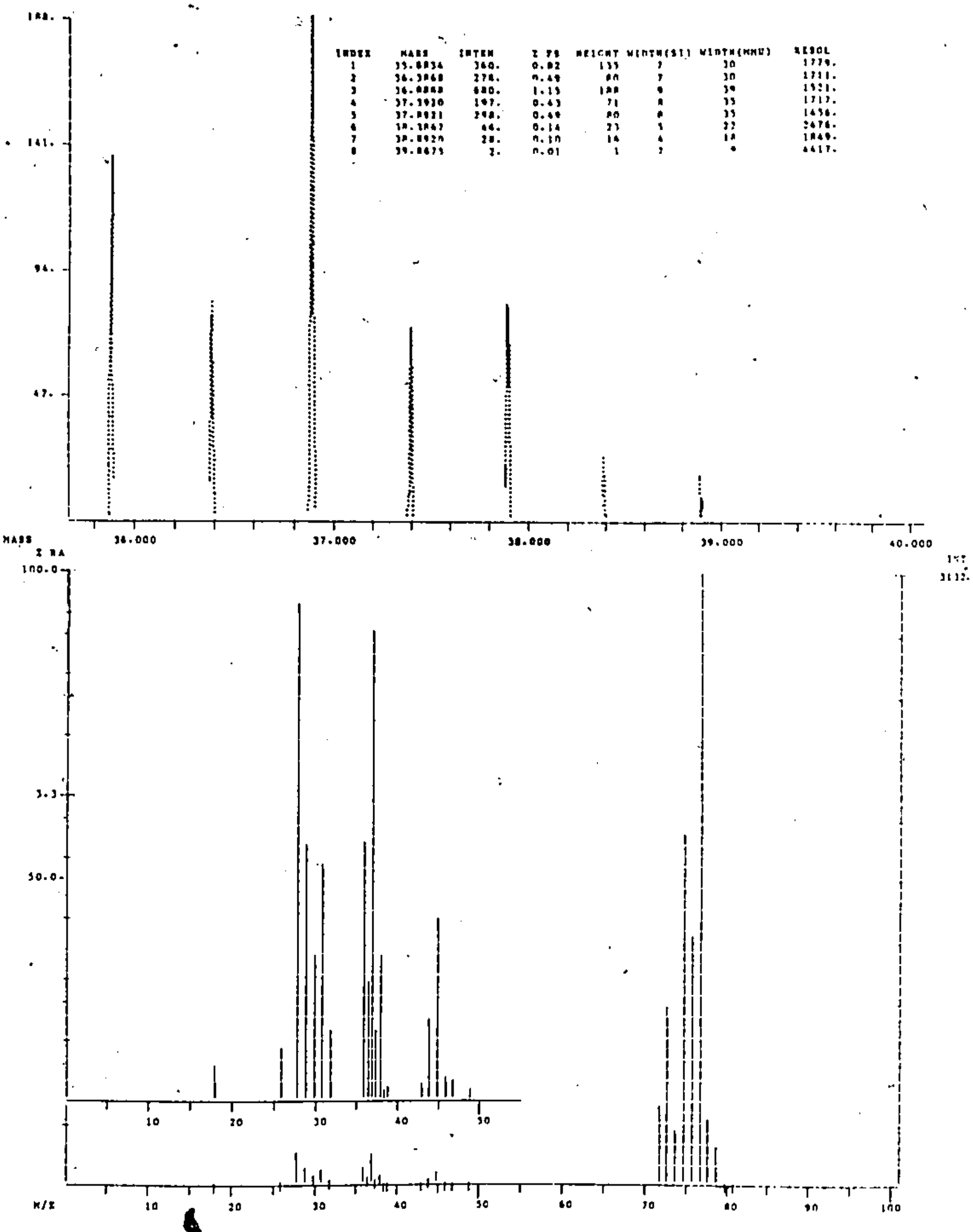
Table V.14. Ion clusters in the mass spectra of the bis(silyl)- and bis(germyl)- chalcogenides*

| Ion Fragment | Relative Abundance (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | E=0 | | E=S | | E=Se | | E=Te | |
| | Si | Ge | Si | Ge | Si | Ge | Si | Ge |
| $(H_{\underline{n}}M_2E)^+$ | 73.6 | 74.2 | 57.5 | 47.7 | 58.2 | 29.6 | 39.1 | 41.0 |
| $(H_{\underline{n}}M_2)^+$ | — | 3.5 | 1.4 | 10.7 | 0.8 | 42.5 | 0.9 | 26.8 |
| $(H_{\underline{n}}M_2)^{2+}$ | 12.0 | — | 2.5 | — | — | — | — | — |
| $(H_{\underline{n}}ME)^+$ | 4.6 | 15.1 | 28.7 | 26.4 | 35.7 | | 54.5 | 26.0 |
| $(H_{\underline{n}}M)^+$ | 9.8 | 7.2 | 9.9 | 15.2 | 5.3 | 27.9 | 5.5 | 6.2 |

* The value of n is summed from 0 ⟶ 3 for M and 0 ⟶ 6 for $M_2$. Peaks are summed together due to overlap.

Table V.15. Ion clusters in the mass spectra of the bis(trimethylsilyl)- and bis(trimethylgermyl)-chalcogenides

| Ion Fragment | Relative Abundance (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | O | | S | | Se | | Te | |
| | Si | Ge | Si | Ge | Si | Ge | Si | Ge |
| $(Me_6M_2E)^+$ | — | — | 9.2 | 1.2 | 19.2 | 8.1 | 5.7 | 13.0 |
| $(Me_5M_2E)^+$ | 78.6 | 72.78 | 43.5 | 7.7 | 30.0 | 27.6 | — | 7.8 |
| $(Me_4M_2E)^+$ | — | 2.43 | — | 41.2 | — | 1.9 | — | — |
| $(Me_3M_2E)^+$ | — | 0.78 | — | 4.6 | — | — | — | — |
| $(Me_2M_2E)^+$ | — | 0.50 | — | 1.0 | — | 1.5 | — | — |
| $(MeM_2E)^+$ | — | 1.76 | — | — | — | — | — | 1.1 |
| $(M_2E)^+$ | — | 1.42 | — | 1.2 | — | — | — | — |
| $(Me_3ME)^+$ | — | — | — | — | — | — | 2.7 | 1.3 |
| $(Me_2ME)^+$ | — | — | — | — | — | — | — | 7.1 |
| $(MeME)^+$ | — | — | — | — | 2.0 | 0.8 | — | 2.6 |
| $(ME)^+$ | 1.8 | — | — | — | — | — | — | 1.5 |
| $(Me_3M)^+$ | 12.7 | 14.98 | 43.4 | 29.7 | 42.7 | 47.2 | 64.9 | 54.2 |
| $(Me_2M)^+$ | 1.6 | 2.47 | — | 4.3 | 1.4 | 3.6 | 8.8 | 3.4 |
| $(MeM)^+$ | 1.1 | 2.78 | 2.7 | 7.1 | 1.7 | 8.4 | 12.4 | 7.0 |
| $(M)^+$ | 4.2 | 0.10 | 1.2 | 2.0 | 3.0 | 0.9 | 5.5 | 1.0 |



```
INDEX    MASS     INTEN    % FS  HEIGHT WIDTH(SI) WIDTH(MMU)  RESOL
  1    35.8834    360.    0.82    135      7        30        1779.
  2    36.3868    278.    0.49     80      7        30        1711.
  3    36.8868    680.    1.15    188      9        39        1521.
  4    37.3930    197.    0.43     71      8        35        1717.
  5    37.8921    298.    0.49     80      8        35        1456.
  6    38.3867     66.    0.14     23      5        22        2476.
  7    38.8926     28.    0.10     16      6        18        1849.
  8    39.8675      3.    0.01      1      2         6        4417.
```

Figure V.19 The mass spectrum of $(H_3Si)_2O$

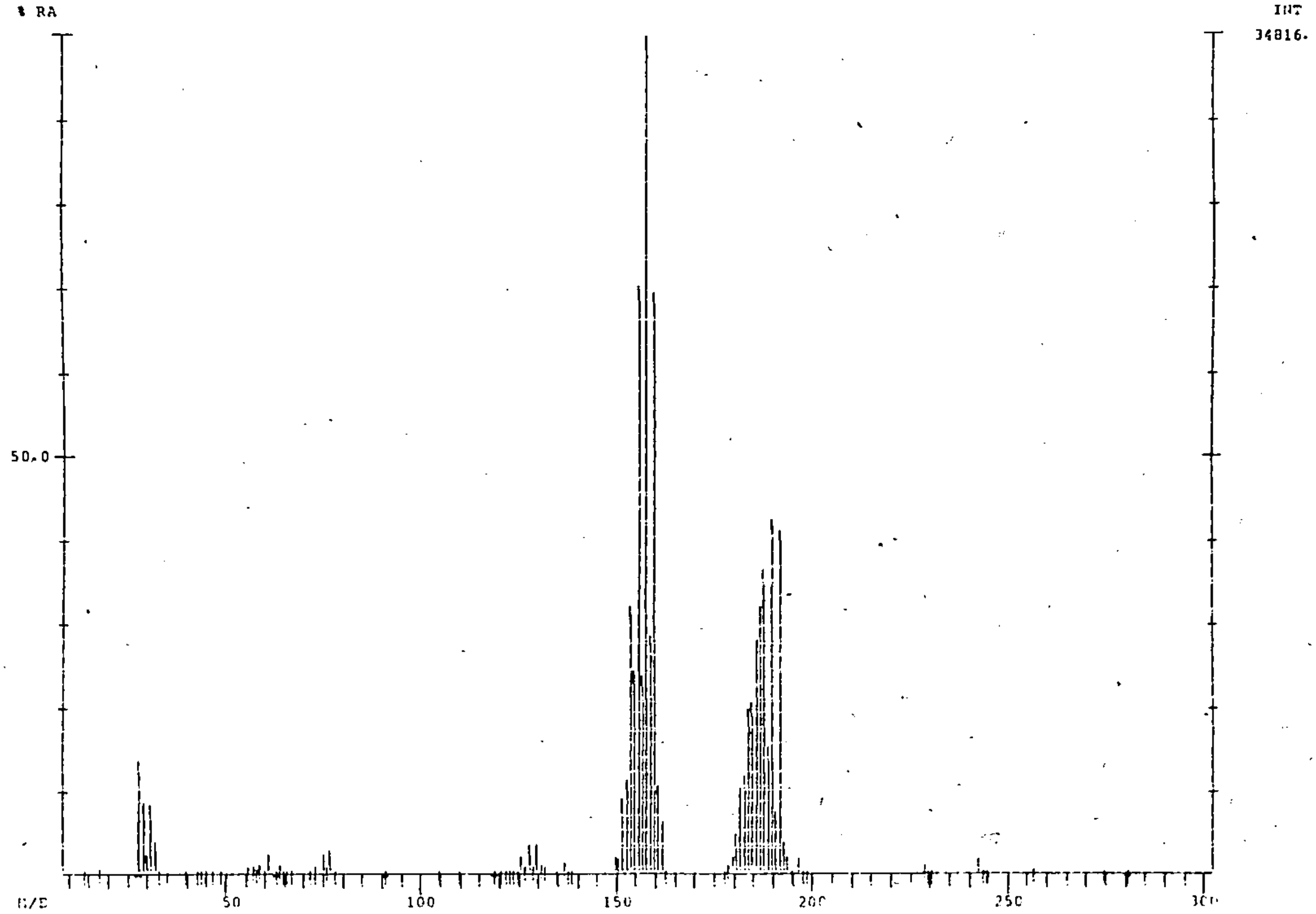


Figure V.20 The mass spectrum of $(H_3Si)_2Te$

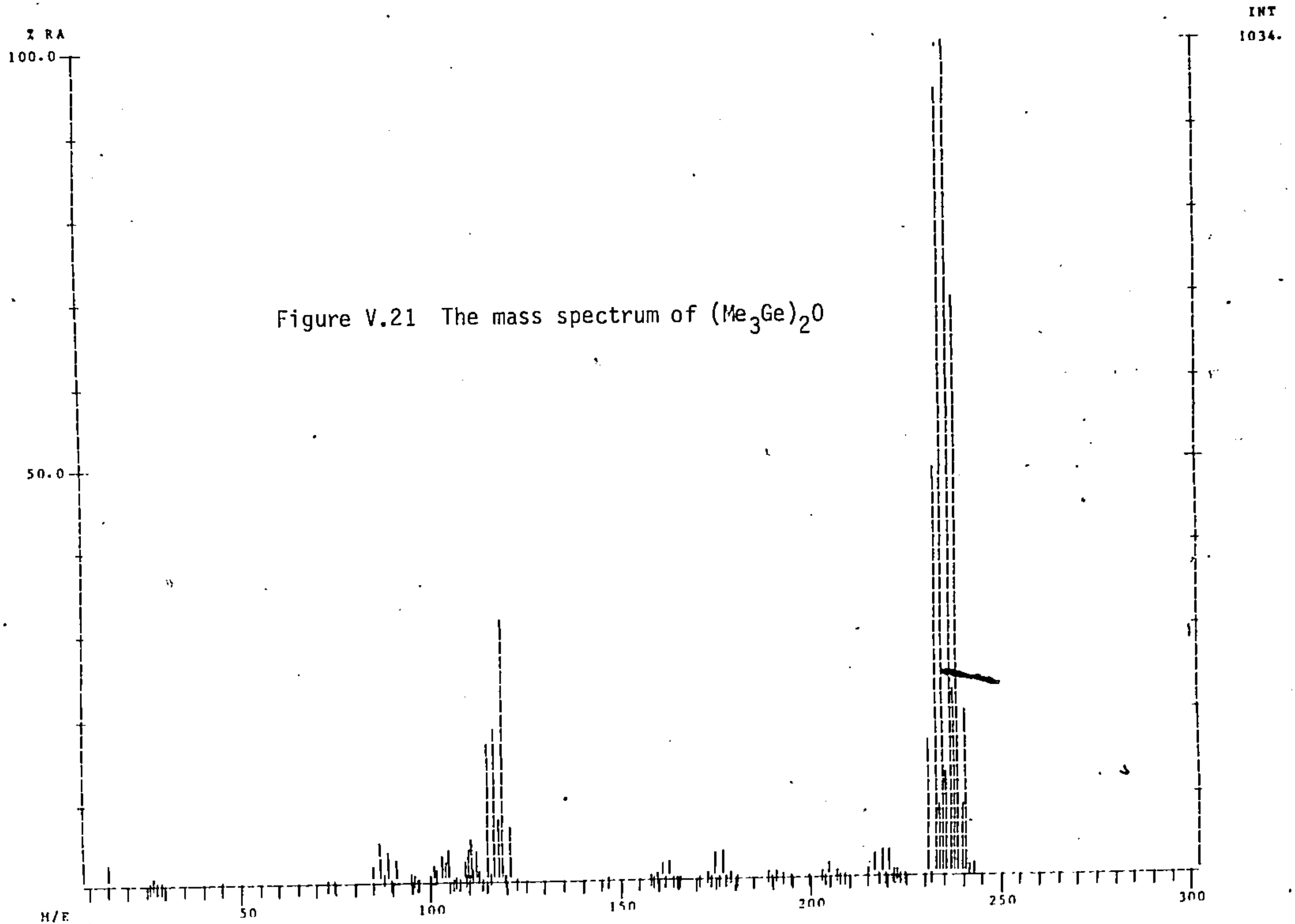


Figure V.21  The mass spectrum of $(Me_3Ge)_2O$

$$\mathrm{Me_3MEMMe_3^{+}} \longrightarrow \mathrm{Me_3M^{+}} + \mathrm{Me_3ME} \qquad [6]$$

The fragments attributable to $\mathrm{Me_{\underline{n}}ME^+}$ are observed in the selenides and tellurides and are of low abundance. In the silicon chalcogenides, only one methyl group is lost before fragmentation along the Si-E-Si bond results, although in the germanium analogues (particularly the oxide and sulfide) successive methyl stripping occurs until the Ge-E-Ge skeleton is formed. The $\mathrm{(Me_3M)^+}$ fragment is of considerable abundance and appears to increase along the series Te > Se > S > O. This is in contrast to the $\mathrm{(Me_5Si_2E)^+}$ ion which exhibits an opposite trend and parallels the bond strength of the Si-E bond.

## V.4. CLEAVAGE REACTIONS OF THE M-E BOND WITH HYDROGEN HALIDES

Further analysis of the $\mathrm{Me_{\underline{n}}H_{3-\underline{n}}M}$-moiety in the chalcogen series was accomplished by protolytic cleavage of the M-E bond with an excess of gaseous hydrogen bromide or iodide, e.g.

$$\mathrm{(Me_{\underline{n}}H_{3-\underline{n}}M)_2E + 2HBr} \longrightarrow \mathrm{2Me_{\underline{n}}H_{3-\underline{n}}MBr + H_2E} \qquad [7]$$

Stoichimetric quantities of the well-known bromo-silanes and -germanes were isolated and identified by their $^1$H n.m.r. and vibrational parameters.

Typically, $\mathrm{(MeH_2Ge)_2S}$ (1.25 mmol) and HBr (3.12 mmol) were condensed in vacuo into a small ampule (ca. 25 ml; type 'B', equipped with a Teflon-in-glass stopcock) held at -196°. The contents were subsequently allowed to warm to room temperature for ca. 20 minutes. Fractionation of the products at -78° and -196° gave $MeH_2GeBr$ (2.46 mmol; 98%; identified by $^1H$ n.m.r.[27,24] and vibrational spectroscopy[27,148]) condensing in the former and a mixture of $H_2S$ and unreacted HBr in the latter. Similar reactions with the other chalcogenides and HBr or HI provided indirect evidence for the monomeric nature of the $(Me_nH_{3-n}M)_2E$ where M=Si, E=S,Se,Te and M=Ge, E=O,S,Se,Te.

# CHAPTER VI

# X-RAY PHOTOELECTRON SPECTRA OF THE BIS(SILYL)- AND BIS(GERMYL)-CHALCOGENIDE SERIES AND RELATED SPECIES

The inclusion of X-ray Photoelectron Spectroscopy, which is commonly termed ESCA[156] (Electron Spectroscopy for Chemical Analysis), as a technique in this research is a logical extension to the attempt to develop an understanding of the reactivity-structure-bonding relationships within the analogous compounds of silicon and germanium.

## VI.1 INTRODUCTION

Few ESCA studies of related Group VI derivatives have appeared in the literature. Van Wazer et al.[157] reported silicon 2p level binding energies of several silicon-oxygen containing species and of the polymeric sulfide $(SiS_2)_\infty$ ; all recorded with solid or liquid samples. Their work was extended to similar derivatives of other Group IV elements.[158] Unfortunately, correlations between data collected from condensed phase samples are liable to be poor. Perry and Jolly have made extensive correlations between vapor-phase determined binding energies and calculated charge.[159] In discussing the importance of d-orbital participation they concluded that "the data offer little support for the participation of d-orbitals in the bonding of silicon and germanium compounds".[160] Although they mainly reported binding energies for simple hydrides and halides, two Group VI derivatives, $Me_2O$ and $(SiH_3)_2O$, were included.[159,160]

A communication by Pignataro et al.[161] reported sulfur 2p 3/2 binding energies for a series of compounds $H_5C_6$-S-$MMe_3$ where M=C, Si, Ge, Sn, Pb. These were compared with the $^{13}C$ NMR chemical shifts of the ring carbon attached to sulfur. The authors concluded that the concept of $(p \rightarrow d)\pi$ -bonding, from sulfur to the metal, M, is supported because the ionization energy of the sulfur 2p 3/2 level increases along the series $Si < Ge < Sn < Pb$. However, the value of the binding energy of sulfur for $H_5C_6$-S-$CMe_3$ falls between those of the germanium and tin derivatives.

The hydrides $(H_3M)_2E$ where M=C, Si, Ge and E=0, S, Se, Te have been the subject of a PES study[162] which assigned the observed bands to expected valence shell levels and concluded that the results were consistent with the existence of $(p \rightarrow d)\pi$ -bonding for all compounds where M=Si or Ge. Glidewell[163] reconsidered this data, taking into account that the ionization energies for the lone-pairs of the Group VI atoms increase in the order $(H_3C)_2E > (H_3Ge)_2E > (H_3Si)_2E$. This led him to conclude that the $SiH_3$ and $GeH_3$ groups are not electron acceptors by means of $(p \rightarrow d)\pi$ -interactions but are, in fact, net electron donors, relative to hydrogen. He suggested that a $\pi$-perturbation, caused by mixing of the $p\pi$ lone-pair orbital of M with another, more tightly bound, orbital of $\pi$-symmetry, is operative.

Bock et al have published the results of extensive molecular orbital calculations assigning the PES of the two series $(H_3C)_{\underline{n}}$-E-$(SiH_3)_{2-\underline{n}}$ where $\underline{n}$ = 0,1,2 and E = 0[164] and S.[165] For the ether series they concluded that conformational changes are surprizingly important and that the bond-angle widening on substitution of silyl groups "may as much be a mechanism to relieve coulombic repulsions ... as it is partially a result of oxygen - silicon $p\pi - d\pi$ interaction".[164] For the sulfide series, they conclude that $(p \rightarrow d)\pi$ interactions from sulfur to silicon play a significant role in increasing the binding-energy of the sulfur "lone-pair" in the 2b molecular orbital; also the concentration of localized charge in the sulfides is far less critical than in the ethers.[165]

With this limited background of ESCA and related studies, I decided to investigate a large number of silicon and germanium - Group VI species. Thus I have measured core-level binding energies of all atoms in closely related series of compounds. In this way I can study the changes in binding energy and thence in charge throughout each molecule, as stepwise substitutions of atoms or groups occur. The series reported in this chapter are the methyl substituted disilyl and digermyl chalcogenides, $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ where M = Si or Ge, E = O, S, Se, Te and $\underline{n} = 0 \rightarrow 3$. Binding energies are also reported for the dimethyl series $M_2E$ where E = O, S, Se, Te; for the hydrides $H_2E$ where E = O, S, Se and for the methyl hydrides MeEH where E = O, S.

## VI.2. EXPERIMENTAL

The core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer (located at the University of Western Ontario, London, Canada) using an energy source for photoexcitation of 1253.6 eV (200.8 aJ from Mg $K\alpha$ X-radiation). Samples were introduced into the spectrometer chamber at a pressure of *ca.* 5 X $10^{-2}$ torr (6.67 X $10^{-3}$ kPa).

Argon was bled into the system to form 20% of the sample and its $2p_{3/2}$ level at 248.63 eV (39.83 aJ)[5] was used as a reference for all atoms whose binding energies were greater than 120 eV (19.2 aJ). The germanium 3d and silicon 2p levels were referenced to the neon 2s level at 48.47 eV (7.76 aJ).[5] Each scan consisted of a five-fold accumulative scan over a 10 eV range, using a 111 point array. The dwell time was one second per point. A curve-fitting computer program (designated ESCAPLOT and developed by L. Coatsworth to run on the Windsor IBM S/360-50 series computer) was used for the observed spectral lines. Mixed Gauss-Lorentz band contours were fitted on a quadratic baseline while peak position calculations were performed without the introduction of constraints. Good spectra gave normal Gauss fractions ~~of~~ 0.3-0.9 while poorer quality spectra gave values either outside the range or would not give a computer fit. The reproducibility from separate runs was such that binding energies were quoted to ± 0.05 eV for C 1s, Si 2p, O is and S $2p_{3/2}$ and to ± 0.10 eV for Ge 3d, Se 3d and Te 4d.[5] A typical X-ray photoelectron spectrum for $(Me_3Si)_2O$ is displayed in Figure VI.1 and the computer-fitted peaks are displayed in Figures VI.2-VI.5.

## VI.3. RESULTS AND DISCUSSION

Table VI.1 gives a complete listing of the binding energies observed in this work. The previously reported values for $H_2O$, MeOH, $H_2S$[156] and for $Me_2O$ and $(H_3Si)_2O$[159,160] agrees well, allowing for minor calibration differences. In Table VI.2 two peak parameters are displayed, the full width at half maximum height, FWHM, and the Gauss Fraction, obtained from the collected computer fits of all the data. In general, the sharper the peak, i.e. the lower the FWHM value, the more precisely is its position determined. Thus oxygen, sulfur and carbon are the peaks showing best argument between duplicates. Silicon, germanium and tellurium are next best and selenium peaks exhibit the poorest statistics.

The quality of the peaks observed was also dependent upon the stability of the samples under the instrumental operating conditions. All the tellurides had a tendency to decompose in the instrument and frequent cleaning of the system was necessary. Peak quality suffered only slightly, mainly due to the count rates being reduced. It is possible however, that some of the minor anomalies in the data result from the effects of sample decomposition. Digermyl ether is known to be of low stability[104] and we were only able to obtain a weak spectrum, unsuitable for computer treatment, but of sufficient intensity to be able to fix the peak positions to ±0.2 eV.

The most striking feature of the binding energy data is the lack of any substantial shifts. Intuitively, large differences might be expected between binding energies of oxygen compounds and those of the other Group VI elements; or at least consistent trends along the series. Such is not generally the case.

Consider first the carbon 1s levels. Although it is true that in these levels the least change might be expected; along any series the value of the C 1s binding energy hardly varies, regardless of the nature of E. For example, in the series $(Me_3Ge)_2E$ the C 1s values are:- 289.79 (E=0); 289.81 (S); 289.82 (Se); 289.84 eV (Te). A few individual values do vary within some series. For example, the sulfur compound has a value ca. 0.15 eV higher ( $\Delta$ = +0.15 ev) than the mean in the $(MeH_2Si)_2E$ series; the oxygen compound has $\Delta$ = -0.13 for the $(Me_3Si)_2E$ series and $\Delta$ = +0.23 for the $(Me_2HGe)_2E$ series. The few exceptions are random and could result from aberrations in the experimental determinations. Thus, the postulate that the $R_3Ge$- and $R_3Si$- groups (R = Me or H) behave as invariant moieties regardless of whether they are attached to oxygen, sulfur, selenium or tellurium is generally upheld. Any changes in partial charges with a change in the central atom should therefore be most noticeable in the changing binding energies of the M and E atoms that are involved in mutual bonding. The slight general increase in the value of the C 1s level as H atoms replace methyl groups in the $R_3M$ moieties is possibly the result of changes in relaxation effects. In the studies on $Me_3MX$ (X = Cl,Br,I) compounds, Drake et al.[166] noted a small but consistently higher value for corresponding C 1s levels when M=Ge compared with M=Si. In these Group VI series, of the twelve possible corresponding pairs of compounds, the germanium compound has the higher C 1s value in all four $(Me_3M)_2E$ pairs of compounds, in three of the $(Me_2HM)_2E$ pairs, but only in one of the $(MeH_2M)_2E$ pairs. This could be related to the changes noted above on the introduction of H atoms into the $R_3M$ moiety.

In the $Me_2E$ series the C 1s binding energies are close for E=S, Se, Te but for E=0 a considerably higher value results $\Delta = +1.5$ eV. A large shift, $\Delta = +1.0$ eV, occurs between MeOH and MeSH also. This is discussed later.

Consider next the silicon 2p and germanium 3d binding energies. Again, along a series, there is no dramatic change or general trend. All sixteen silicon values are contained within a 1.2 eV spread and all the germanium values are within a 1.4 eV spread. Thus for the $(Me_3Si)_2E$ series the experimental value for Si 2p is constant for E=0, S and Se and rises for E=Te, whereas for the $(MeH_2Si)_2E$ series it is lowest for E=Te. The normal expectation, based on the relative Pauling electronegativities of 0, S, Se and Te would be for the silicon or germanium atoms to be relatively the most positive when attached to oxygen and therefore to have the highest binding energy for the $(R_3M)_2O$ species with a fairly regular decrease along the series $(R_3M)_2O \gg (R_3M)_2S > (R_3M)_2Se > (R_3M)_2Te$. Clearly the relative electron-withdrawing powers of the Group VI elements are being equalized by some mechanism. The results of the halogenomethylsilanes and -germanes also led to the conclusion that the halogens (Cl,Br and I) all "behave" as though they had similar electronegativities. Simple charge calculations suggest that this comes because the halogen s-orbitals are being utilized to varying degrees in the bonding between the halogen and the Group IV element. Indeed, if the s-orbital participation is only ca 5%

greater for Cl than for Br and a further 3-5% greater for Br than for I, then the similarity of binding energies of the $Me_{\underline{n}}MX_{3-\underline{n}}$ series can be explained.[166,167] It seems reasonable to assume, a similar argument applies to the Group VI elements. The increase in s-character would not be so large as to require a dramatic increase in the M-E-M angle, although it would require an angle greater than 90°. For example, the introduction of 10% s-character requires an increase in angle from 90 to 96°, which is approximately the angle at S or Se where known.[156]

The same mechanism cannot be used for the $(R_3M)_2O$ compounds. It is well established[156] that the M-O-M bond angles are appreciably larger than the corresponding M-E-M angles where E = S, Se, Te. This wide angle requires an even larger involvement of the s-orbital of oxygen and hence a much higher binding energy is expected for the silicon and germanium atoms. However, bond angles of 120° and more are those required to maximize $(p \rightarrow d)\pi$ -bonding.[60,69,164,165] Where this is extensive, a significant redistribution of charge back from oxygen to silicon and germanium is expected, thus reducing the electropositive nature of the atoms and hence the value of their binding energies; exactly the situation that we have here. The fact that the binding energies are so close is possibly fortuitous because relaxation effects have been ignored. Nonetheless, a model that suggests that there are varying degrees of small s-orbital participation by S, Se and Te to make the binding energies similar in $(R_3M)_2E$ compounds, without invoking d-orbital participation, is consistent with the observations. However, for $(R_3M)_2O$ species, where s-orbital participation must be large, the occurrence of $(p \rightarrow d)\pi$ -bonding appears to be the most logical rationalization. In the compounds MeOH and $Me_2O$, where $(p \rightarrow d)\pi$ -bonding cannot occur, there are indeed considerable binding energy shifts, the carbon atom being considerably more electropositive in the oxides than in the sulfides, selenides or tellurides.

Finally, I examine the binding energies of the central atoms themselves. With three exceptions, $[(H_3M)_2S$, $(Me_3M)_2S$ and $(Me_3M)_2Te]$ all of the silicon compounds have higher binding energies for the core-level of the Group VI elements than do the germanium analogues. In this respect the results parallel those found for the lone-pair orbitals in the two series $(H_3Si)_2E$ and $(H_3Ge)_2E$ where E = 0, S, Se.[159] Within the silicon and germanium compounds, as hydrogen atoms successively substitute for methyl groups, within the $R_3M$ moieties, there is a corresponding general increase in the binding energies of all levels measured. Such changes could be the result of relaxation effects, however the changes are as predicted if it is assumed that the hydrogen atom is "behaving" as a weakly electronegative halogen atom. This is not unreasonable as the Si-H and Ge-H bonds are polarized[168] with $H^{\delta-}$. Thus the successive introduction of the more electronegative hydrogen atom increases all the binding energies within the molecule. For example, the binding energy increases in the

$(R_3Si)_2O$ column as R = Me → H are: Δ O 1s = + 1.07; Δ Si 2p = +1.22; and Δ C 1s = +0.70 eV. With few exceptions, all columns show the same trend. This is exactly as in the $Me_{\underline{n}}GeX_{4-\underline{n}}$ series where X = Cl, Br, I.[166,167]

The collected data do not allow a definitive analysis of bonding mechanisms in the Group VI compounds. Assuming that the changes in binding energy reflect the overall changes in charge distribution that result from a variety of competing "mechanisms", such as $(p \rightarrow d)\pi$ – bonding varying s-orbital participation and inductive effects, then only the dominant mechanism, and not the relative importance of competing mechanisms, will be reflected in the data.

Table VI.1 Observed binding energies of Group VI derivatives.

| General Formula | Core Level | E | | | |
|---|---|---|---|---|---|
| | | O | S | Se | Te |
| $H_2E$ | E* | 539.93$^{+}$ | 170.51$^{+}$ | 62.62 | - |
| MeEH | C 1s | 292.42$^{+}$ | 291.41 | - | - |
| | E | 539.01 | 169.79 | - | - |
| $Me_2E$ | C 1s | 292.17$^{=}$ | 290.74 | 290.88 | 290.39 |
| | E | 538.50 | 169.28 | 61.52 | 47.02 |
| $(H_3Si)_2E$ | Si 2p | 107.79$^{=}$ | 107.45 | 107.72 | 107.50 |
| | E | 538.17 | 168.60 | 61.91 | 46.93 |
| $(MeH_2Si)_2E$ | Si 2p | 107.27 | 107.29 | 107.3 | 107.11 |
| | C 1s | 290.20 | 290.40 | 290.2 | 290.18 |
| | E | 537.80 | 168.29 | 61.6 | 46.60 |
| $(Me_2HSi)_2E$ | Si 2p | 106.83 | 106.85 | 106.99 | 106.70 |
| | C 1s | 289.93 | 289.93 | 289.97 | 289.90 |
| | E | 537.32 | 168.00 | 60.89 | 46.94 |
| $(Me_3Si)_2E$ | Si 2p | 106.57 | 106.57 | 106.58 | 106.67 |
| | C 1s | 289.64 | 289.79 | 289.79 | 289.85 |
| | E | 537.10 | 167.78 | 61.11 | 45.85 |
| $(H_3Ge)_2E$ | Ge 3d | 37.8 | 37.56 | 37.36 | 37.11 |
| | E | 537.2 | 168.66 | 61.05 | 46.86 |
| $(MeH_2Ge)_2E$ | Ge 3d | 36.82 | 36.92 | 36.93 | 36.78 |
| | C 1s | 290.25 | 290.10 | 290.14 | 290.10 |
| | E | 536.34 | 167.99 | 60.57 | 46.44 |
| $(Me_2HGe)_2E$ | Ge 3d | 36.91 | 36.62 | 36.51 | 36.78 |
| | C 1s | 290.23 | 289.94 | 289.99 | 289.84 |
| | E | 536.45 | 167.85 | 60.28 | 46.11 |
| $(Me_3Ge)_2E$ | Ge 3d | 36.53 | 36.50 | 36.40 | 36.39 |
| | C 1s | 289.79 | 289.81 | 289.82 | 289.84 |
| | E | 536.02 | 167.84 | 60.07 | 46.07 |

*The core levels observed and their average widths (eV) at half maximum height are: Si 2p (1.52), Ge 3d (1.53), C 1s (1.26), O 1s (1.21), S $2p^{3/2}$ (1.04), Se 3d (1.68), and Te 4d (1.35).

$^{+}$These values compare with the following reported in Siegbahn et al[156]: $H_2O$, O 1s 539.7; MeOH C 1s 292.3, O 1s 538.9; $H_2S$ S $2p^{3/2}$ 170.2.

$^{=}$These values compare with the following reported by Perry and Jolly[159,160] and referenced to Ar $2p^{3/2}$ at 248.46 eV: $Me_2O$, C 1s 292.14, O 1s 538.86; $(H_3Si)_2O$, Si $2p^{3/2}$ 107.68, O 1s 538.46.

Table VI.2 Average peak characteristics

| Core | FWHM | ±* | GFAC | ±* | No. of spectra |
|---|---|---|---|---|---|
| Si 2p | 1.52 | 0.13 | 0.73 | 0.16 | 22 |
| Ge 3d | 1.53 | 0.19 | 0.55 | 0.27 | 22 |
| C 1s | 1.26 | 0.14 | 0.53 | 0.26 | 40 |
| O 1s | 1.21 | 0.23 | 0.46 | 0.23 | 12 |
| S $2p^{3/2}$ | 1.04 | 0.29 | 0.67 | 0.34 | 15 |
| Se 3d | 1.68 | 0.13 | 0.88 | 0.21 | 16 |
| Te 4d | 1.35 | 0.35 | 0.57 | 0.26 | 9 |

*Standard deviation

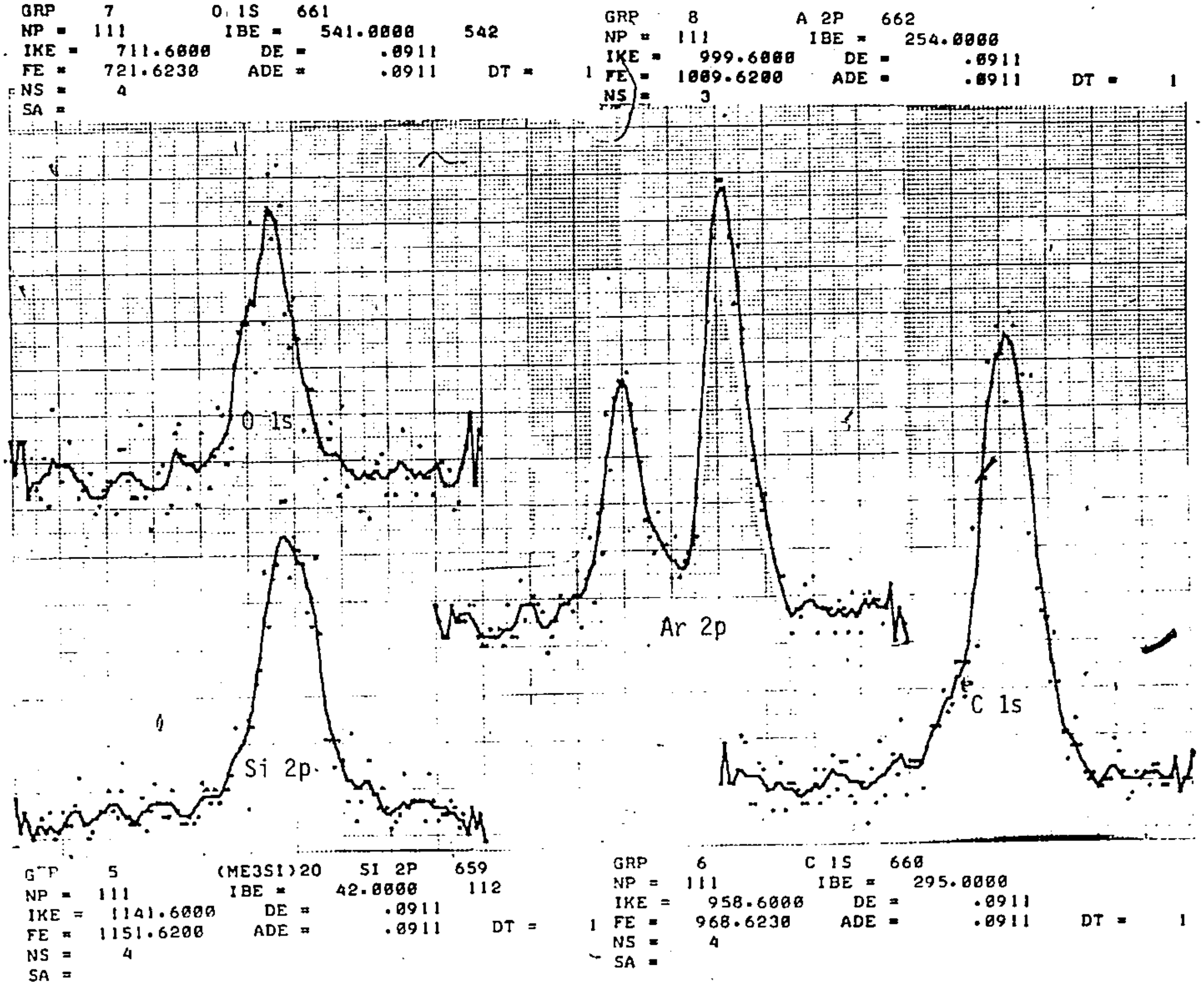


Figure VI.1 -The XPS spectrum of $(Me_3Si)_2O$

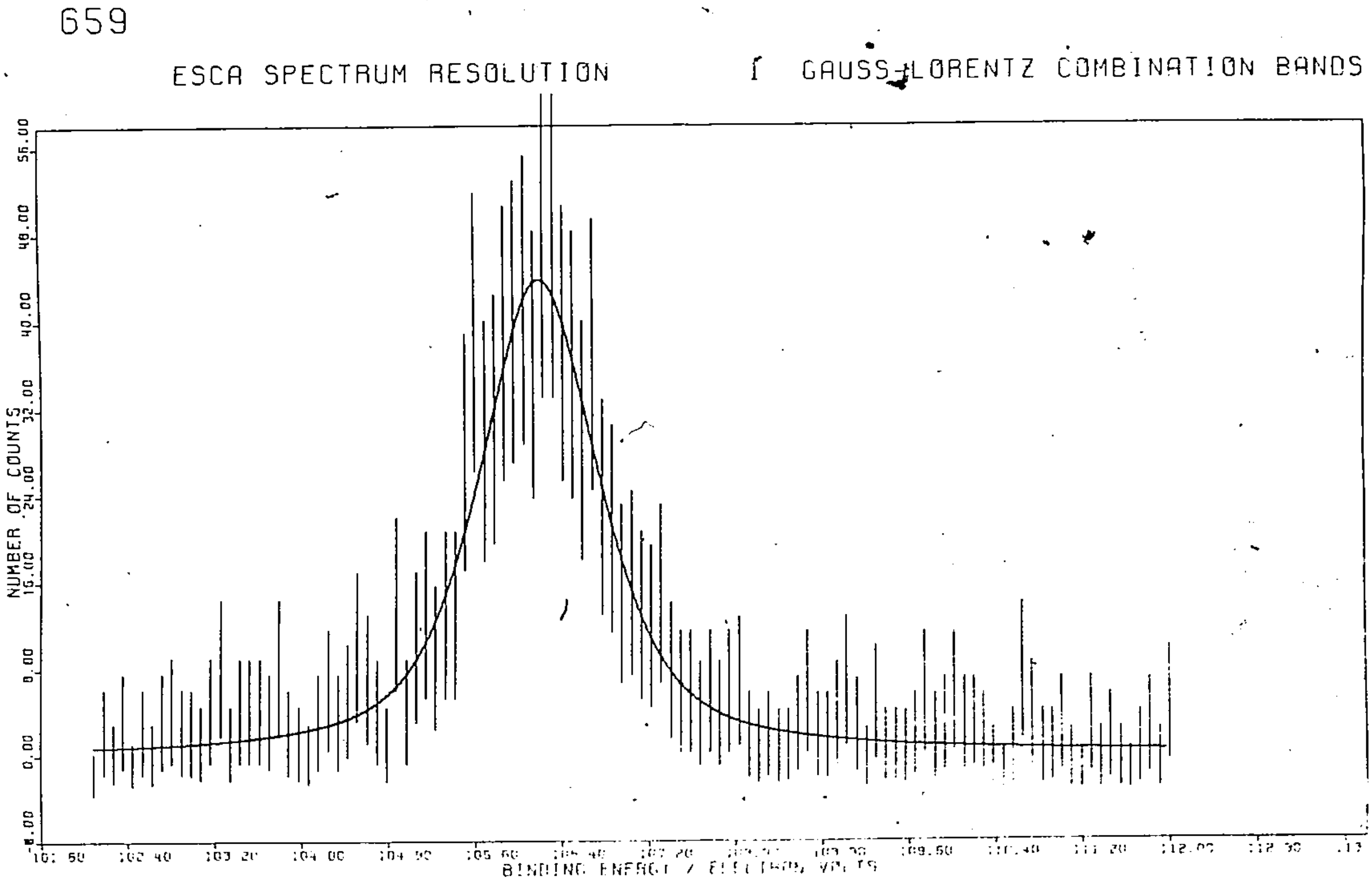


Figure VI.2 The computer-fitted Si 2p binding energy (eV) for $(Me_3Si)_2O$

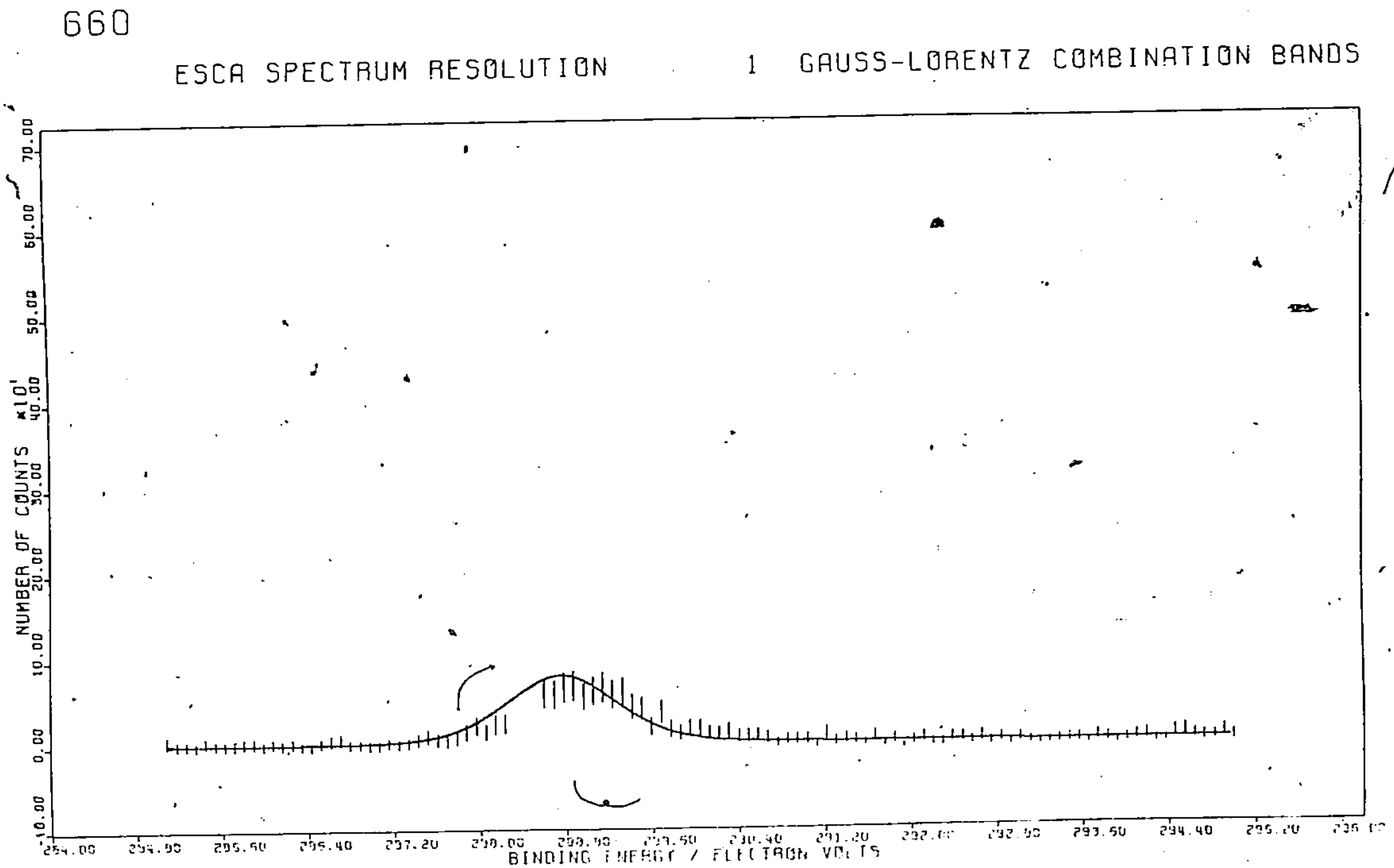


Figure VI.3 The computer-fitted C 1s binding energy (eV) for $(Me_3Si)_2O$

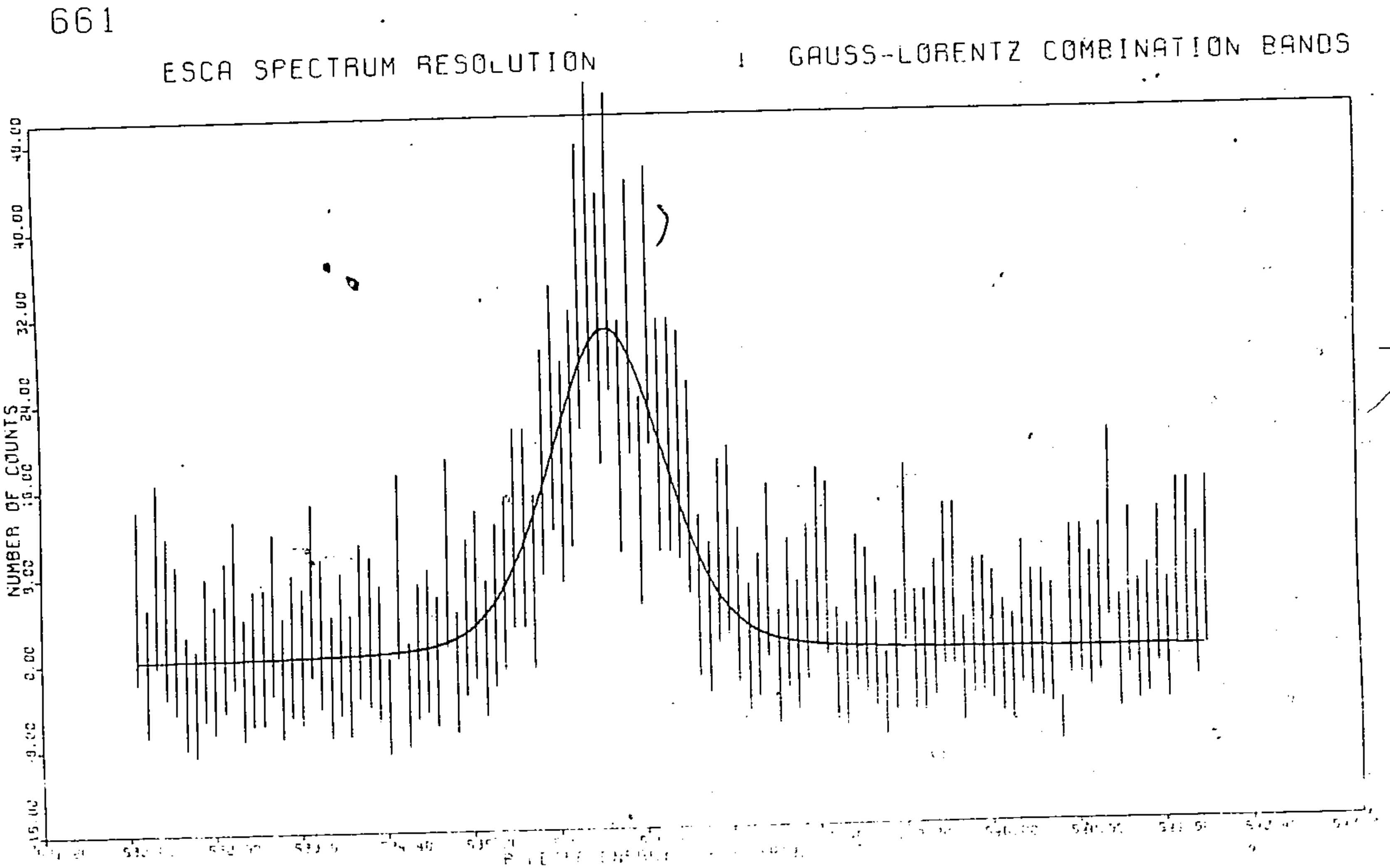


Figure VI.4 The computer-fitted O 1s binding energy (eV) for $(Me_3Si)_2O$

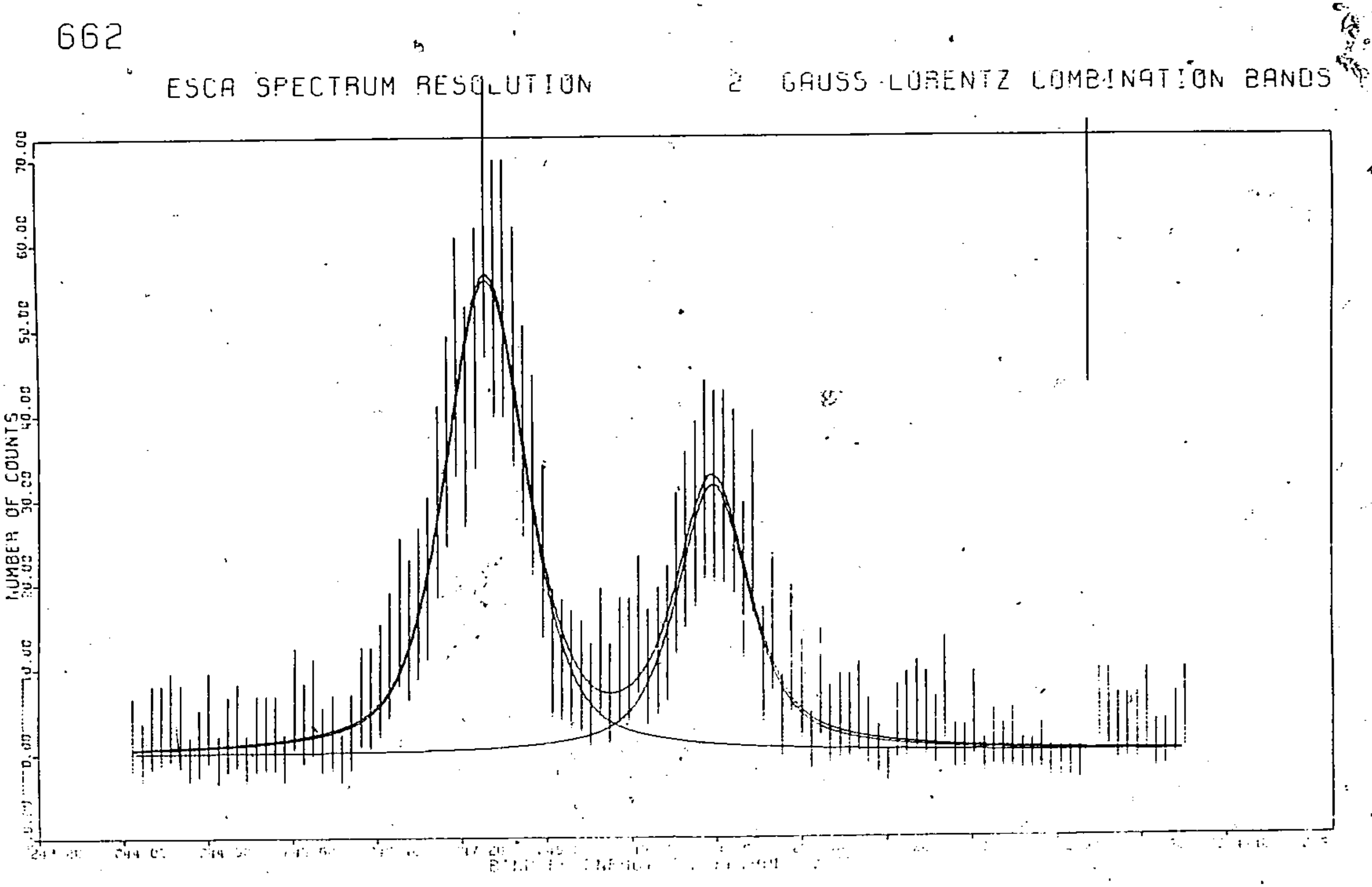


Figure VI.5 The computer-fitted Ar 2p reference binding energy (eV) for $(Me_3Si)_2O$

# CHAPTER VII

# THE FORMATION AND IDENTIFICATION OF SOME CONDENSED SPECIES

## VII.1. INTRODUCTION

The condensation phenomenon of many species containing silyl and germyl groups is a characteristic feature of their chemistry. The condensation mainly involves exchange, disproportionation, or elimination reactions with subsequent formation of condensed species. Stock[1] first noted the base-catalyzed condensation of $H_3SiCl$ with ammonia as indicated by the nonappearance of $H_3SiNH_2$ and $(H_3Si)_2NH$ to give $(H_3Si)_3N$. He also suggested that $(H_3Si)_2O$ readily loses $SiH_4$ to give polymeric prosiloxane, $(H_2SiO)_{\underline{n}}$. Campbell-Ferguson[170] re-examined this condensation in the presence of various bases as well as the reaction of dihalogenosilanes and water and found that both formed prosiloxane, $(H_2SiO)_4$ and higher oligomers. MacDiarmid reported that $(H_3Si)_2O$ gives $H_2Si(OSiH_3)_2$, $HSi(OSiH_3)_3$ and $SiH_4$ in the presence of Lewis bases,[171] while $(H_3Si)_2S$ gives $(H_2SiS{\cdot}base)_{\underline{n}}$ and $SiH_4$[172]. The condensed oxides are also identified in the interaction of $(H_3Si)_2O$ with $PBr_3$, but without formation of $SiH_4$[173]. Sujishi[113] suggested that $(H_3Ge)_2O$ slowly decomposes at 0° in unknown manner and may be catalyzed by the presence of water but $GeH_4$ was not formed. This implies that the condensation processes are governed by the nature of the catalyst and reaction conditions. More recently Drake[107] reported that $(H_3Ge)_2Se$ decomposes to $H_2Ge(SeGeH_3)_2$, $HGe(SeGeH_3)_3$ and $Ge(SeGeH_3)_4$ with evolution of $GeH_4$. He also reported the formation of $H_3MEH$ and $H_3SiEGeH_3$ via co-condensation of $(H_3Ge)_2E$ with $H_2E$ and in the silent electrical discharge reactions of the mixture $MH_4 - H_2E$ and $GeH_4 - SiH_4 - H_2E$ where M = Si, Ge and E = S, Se.[112] Van Dyke[174] prepared $H_3SiSGeH_3$ and $Me_3SiSGeH_3$ by incomplete exchange reactions of the corresponding disilthianes with fluorogermane, while the oxide, $Me_3SiOGeH_3$, is obtained from $Me_3SiOLi$ with $H_3GeCl$. Similarly, Ebsworth used $H_3SiELi$ (E=0,S,Se)[175] and $H_3SiE^-NH_4^+$ (E = S,Se)[176] as synthetic intermediates with $Me_3SiCl$ and $H_3GeBr$ to obtain $Me_3SiESiH_3$ and $H_3SiSGeH_3$. All these species were identified spectroscopically and their liquid-phase disproportionation leading to the parent species is a frequently noted occurrence. I used this background in my studies of the $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ compounds and I present a large number of reactions leading to various $Me_{\underline{n}}H_{3-\underline{n}}M$ - condensed species.

## VII.2. EXPERIMENTAL

A number of observations which were made in the early stages of this work had an influence on the choice of starting materials and conditions for subsequent reactions.

### (a) Formation of $Me_2Ge(SeGeHMe_2)_2$ and $(Me_2HGe)_2$

The lithium salt, containing excess of selenium, was prepared as described in Chapter IV.2.(f), and the volatile material was removed by back pumping and slight heating (ca. 70°, using a hair dryer) for 15-30 minutes. In another experiment, lithium selenide was prepared in a fume hood without the use of the vacuum line, but this procedure led to oxygen-containing products when tellurium was used. The iodide, $Me_2HGeI$ (0.84 g, 3.61 mmol) was allowed to react with an excess of lithium selenide in $Me_2O$ (ca. 10-15 ml) at -78° with occasional shaking. After ca. 100 hours the products were fractionated. The fraction at -196° was $Me_2O$ and that involatile at -78° was refractionated through traps held at ca. 0°, -23°, -78° and -196°. The first trap contained pure $Me_2Ge(SeGeHMe_2)_2$ (0.19 g, 0.41 mmol) while the -23° trap retained $(Me_2HGe)_2Se$ (0.08 g, 0.29 mmol) and that at -78° retained pure $(Me_2GeH)_2$ (0.18 g; 0.87 mmol). Metallic selenium was retained in the initial trap. The $^1H$ n.m.r. spectra showed resonances at: $Me'_2Ge(SeGeHMe_2)_2$ - $\delta$(Me) 0.31, $\delta$(GeH) 3.73, $\delta$(Me') 0.37 p.p.m., $J^{vic}_{HH}$ 3.98 Hz; - $(Me_2HGe)_2$ - $\delta$(Me) 0.29, $\delta$(GeH) 3.90 p.p.m., J(HGeCH) 4.5, J(HGeGeH) 3.8, J(CH) 130.5 Hz. The mass spectrum of $(Me_2HGe)_2$ showed the following cluster of peaks at m/e values: 200-214 $(Me_4H_{\underline{n}}Ge_2)^+$; 185-199 $(Me_3H_{\underline{n}}Ge_2)^+$; 170-184 $(Me_2H_{\underline{n}}Ge_2)^+$; 155-169 $(MeH_{\underline{n}}Ge_2)^+$; 140-154 $(H_{\underline{n}}Ge_2)^+$; 115-121 $(Me_3Ge)^+$; 100-107 $(Me_2H_{\underline{n}}Ge)^+$; 85-92 $(MeH_{\underline{n}}Ge)^+$ and 70-77 $(H_{\underline{n}}Ge)^+$. The i.r.[177] and Raman (parentheses) spectra of $(Me_2HGe)_2$ showed prominent features at ($cm^{-1}$): 2989 m (2982 m,dp) $\nu_a(CH_3)$; 2910 m (2913 s,p) $\nu_s(CH_3)$; 2020 vs (2017 s,p) $\nu$(GeH); 1416-1460 wbr (1466 wbr,p) $\delta_a(CH_3)$; 1252 mw (1271 m,p) $\delta_s(CH_3)$; 849 s, 815 vs (877 wbr, 840 vw, 803 vw) $\rho(CH_3)$; 753 mw, 652 mw (720 vwsh, 644 sh,dp) $\delta$(GeH); 598 s, 568 s (598 vs,P) $\nu$(CGe); (275 s,p) $\nu$(GeGe); (191 sh) $\delta(C_2Ge)$; (170 ms,p; 104 w) skeletal deformations. The Raman features of $Me_2Ge'(SeGeHMe_2)_2$ characteristic of the germyl group and heavy atom skeleton appeared at ($cm^{-1}$):

2982 m,dp $\nu_a(CH_3)$; 2913 s,p $\nu_s(CH_3)$; 2003 s,p $\nu(GeH)$; 1421 w,dp $\delta_a(CH_3)$; 1241 m,p $\delta_a(CH_3)$; 848 w,p $\rho(CH_3)$; 629 m,dp $\nu_a(CGe)$; 580 vs,p $\nu_s(CGe)$; 566 sh, dp $\nu(CGe)'$; 290 m,dp $\nu_a(GeSe_2)$; 251 s,p $\nu_s(GeSe_2)$; 157 s,p, 112 sh,p (skeletal modes); 58 sh $\delta(GeSe_2)$, $\delta(Ge_2Se)$.

(b) Reactions of $(Me_2GeH)_2$ with HCl, HBr and $H_2Se$

Typically, $(Me_2GeH)_2$ (0.60 mmol) and HCl (0.35 mmol) were sealed together in a semimicro n.m.r. tube and allowed to react at room temperature for ca. 15 minutes. Subsequent $^1H$ n.m.r. analysis showed that resonances [ $\delta$(Me) 0.40, $\delta$(Me') 0.73, $\delta$(GeH) 3.98 p.p.m.] indicative of $Me_2'ClGeGeHMe_2$ predominated. After four days ca. 10°, the $^1H$ n.m.r. spectrum was consistent with the quantitative formation of $Me_2ClGeGeHMe_2$ and traces of $(Me_2ClGe)_2$, Figure VII.1. Features in the Raman spectrum assignable to $\nu(GeCl)$ and $\nu(GeGe)$ were at ($cm^{-1}$): 363 ms,p and 268 vs,p.

In an exactly analogous reaction, $(Me_2GeH)_2$ (0.04 mmol) and HBr (0.07 mmol) were sealed in a semimicro n.m.r. tube with a trace of TMS and allowed to warm to room temperature. After ca. 10 minutes the $^1H$ n.m.r. spectrum indicated a rapid formation of $Me_2'BrGeGeHMe_2$ [ $\delta$(Me) 0.42, $\delta$(Me') 0.90, $\delta$(GeH) 4.12 p.p.m.] which was accompanied with a trace of $(Me_2BrGe)_2$ $\delta$(Me) ca. 1.00 p.p.m. In another experiment, $(Me_2HGe)_2$ (0.05 mmol) and $H_2Se$ (1.00 mmol) were combined together as above. Sequential recording of the $^1H$ n.m.r. spectra revealed no reaction had occurred after ca. 2 hours.

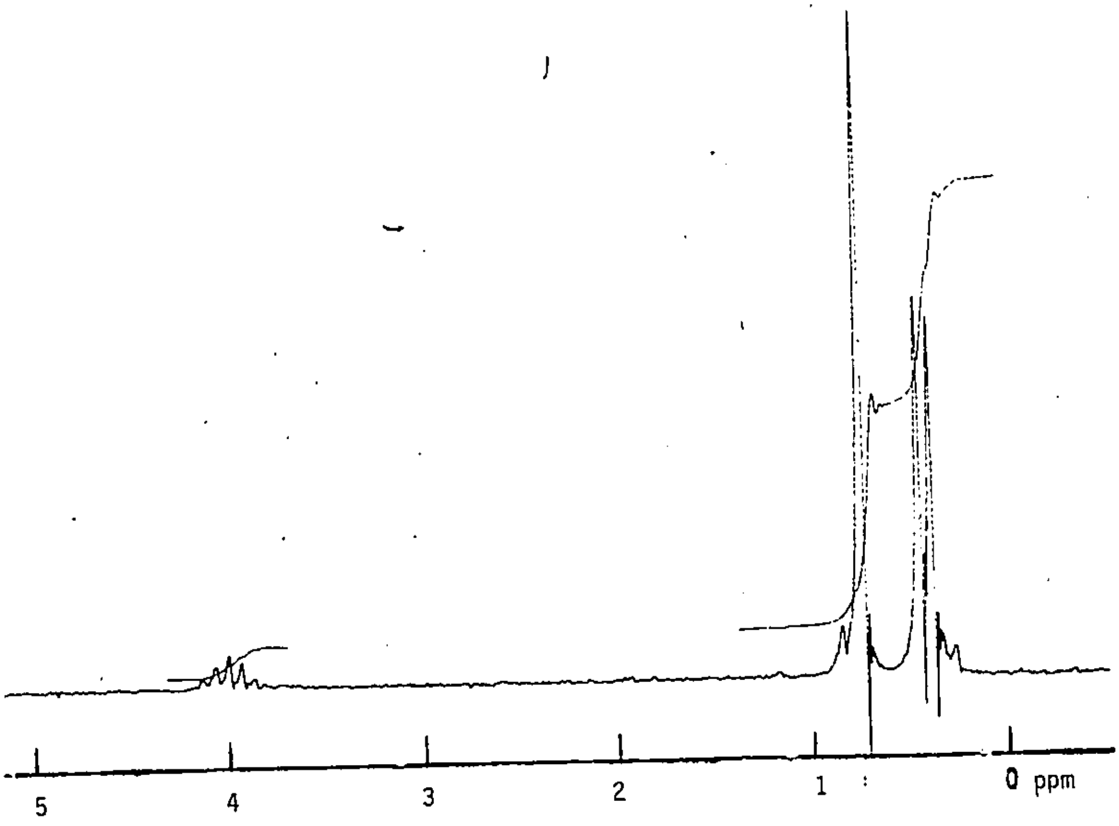


Figure VII.1 The $^1H$ n.m.r. spectrum of $Me_2ClGeGeHMe_2$

### (c) Elimination of tellurium

Typically, $(Me_3Si)_2Te$ (0.50 mmol) and $Me_3GeCl$ (1.30 mmol) were sealed in a semimicro n.m.r. tube and allowed to react at room temperature for ca. 30 minutes. The $^1H$ n.m.r. analysis of the mixture indicated the formation of mixed telluride, $Me_3SiTeGeMe_3$. The tube was then placed in an oven which was set at 100° for ca. 15 hours. Tellurium was deposited and subsequent Raman analysis showed the absence of Si-Te and traces of Ge-Te stretching mode. Fractional condensation through traps held at -15°, -23° and -78° gave $Me_3SiCl$ and unreacted $Me_3GeCl$ in the latter trap, while pure $(Me_3Ge)_2$ (0.28 mmol) was retained in the former traps as identified by its $^1H$ n.m.r. parameters[178] $\delta$(Me) 0.20 p.p.m., J(CH) 125.3 Hz.

In another experiment $(Me_2HSi)_2Te$ (1.20 mmol) was accidently exposed to air. Immediately tellurium was deposited in the reaction vessel. Fractionation through traps held at -23°, -78° and -196° gave $H_2Te$ in the latter trap which readily decomposed on warming to $H_2$ and Te. Traces of $(Me_2HSi)_2Te$ were retained at -23° while a mixture of predominantly $(Me_2HSi)_2$ and some $(Me_2HSi)_2O$ was retained in the -78° trap. The attempts to separate $(Me_2HSi)_2$ from $(Me_2HSi)_2O$ by trap to trap distillation were unsuccessful. The $^1H$ n.m.r. spectrum[179] of the mixture showed resonances at $\delta$(SiH) 4.71, 3.75 and $\delta$(Me) 0.15 p.p.m., relative to TMS. The Raman features characteristic for $(Me_2HSi)_2O$ were at: (SiH) 2128 sh,p; $\nu_s$(SiO) 547 m,p; and for $(Me_2HSi)_2$[179] - $\nu$(SiH) 2106 vs,p, $\nu$(SiSi) 408 vs,p $cm^{-1}$.

In one case a sample of $(MeH_2Ge)_2Te$ was moderately heated (ca. 60°) over an extended period of time. Subsequent $^1H$ n.m.r. analysis showed resonances assignable to $MeHGe'(TeGeH_2Me)$: - $\delta$(Me) ca. 0.93, $\delta$(GeH) ca. 4.12, $\delta$(Me') 1.53, $\delta$(GeH') 5.75 p.p.m.; and $MeGe'(TeGeH_2Me)_3$ - $\delta$(Me) ca. 0.93, $\delta$(GeH) ca. 4.12, $\delta$(Me') 2.13 p.p.m. Darkening of the tube walls was indicative of the elimination of tellurium.

## (d) Disproportionation of $(H_3Ge)_2O$

The $(H_3Ge)_2O$ (ca. 0.71 mmol) was sealed in a semimicro n.m.r. tube and its decomposition was monitored by $^1H$ n.m.r. spectroscopy at room temperature. The first spectrum recorded within ca. 7 minutes indicated its purity (ca. 99%) by the absence of other proton-containing impurities. After ca. 15 minutes resonances, indicative of the formation of $H_2O$, $GeH_4$ and higher germanes, appeared and continued to grow for ca. 1 hour, Figure VII.2. After this time, the sample became milky and contained immiscible droplets and the peaks in the $^1H$ n.m.r. spectrum became broad. Raman analysis showed features at 139 vs,p; 214 w, 279 s,p; 462 m,p ($cm^{-1}$), which have been also observed by Cradock.[114] In the following hour the sample turned yellow and further observations were disregarded.

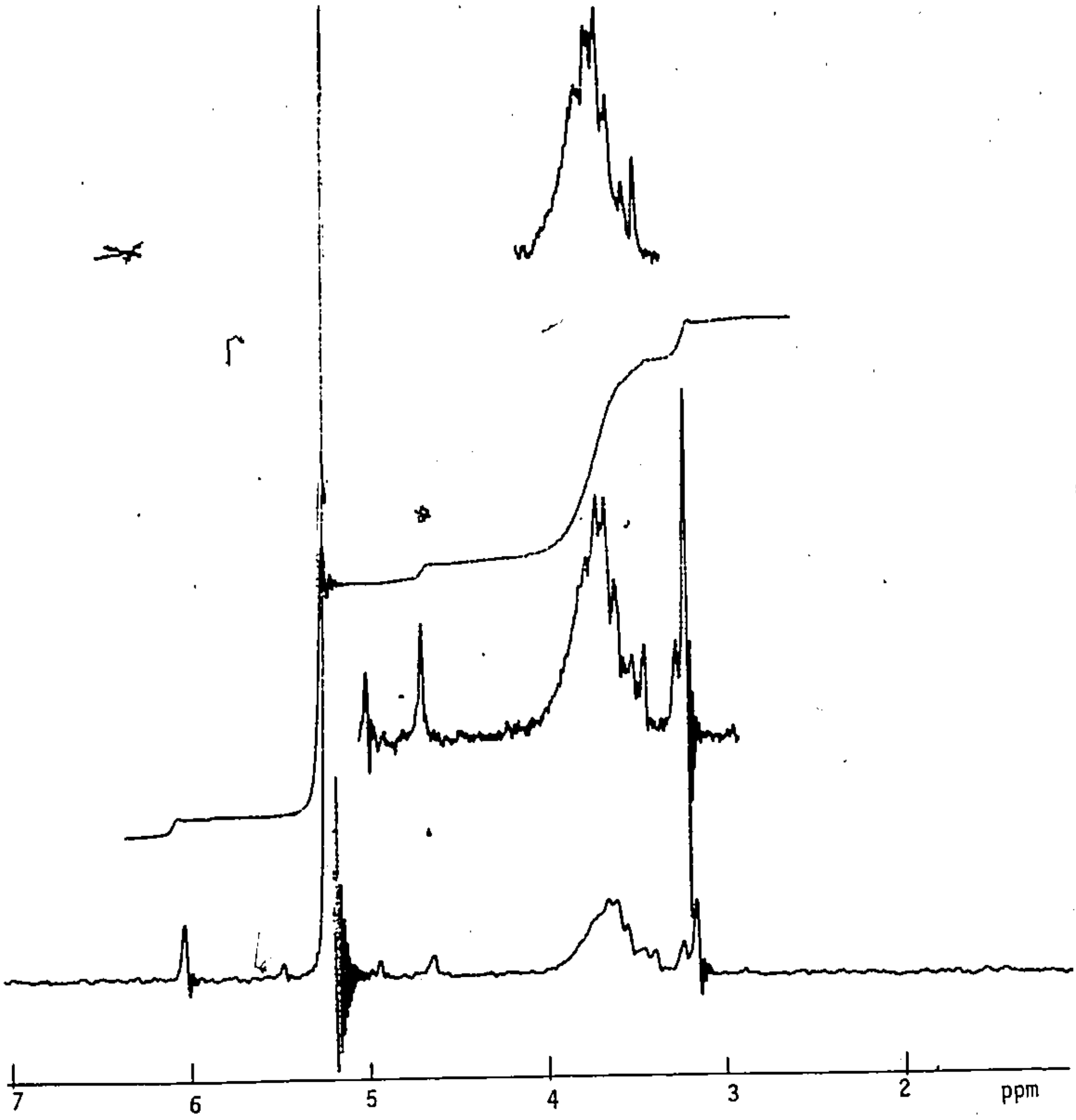


Figure VII. 2 The $^1H$ n.m.r. spectrum of the disproportionation of $(H_3Ge)_2O$

### (e) Co-condensation of $(R_3M)_2E$ with $H_2E$ where M = Si,Ge; E = S,Se and R = H,Me

Typically, $(H_3Ge)_2S$ (0.23 mmol) and $H_2S$ (1.6 mmol) were condensed into a semimicro n.m.r. tube which was then sealed and allowed to warm to room temperature. The $^1H$ n.m.r. spectrum showed the resonances to be expected for $(H_3Ge)_2S$ and $H_2S$ and the doublet-quartet pattern readily assignable to $H_3GeSH$. The latter resonances grew in intensity to reach equilibrium in ca. 50 minutes by which time ca. 80% conversion into $H_3GeSH$ had occurred. The thiol was sufficiently stable at low temperature to permit the recording of its mass spectrum. Thus, with the vessel held at -78°, $H_2S$ was pumped away and the thiol was passed into the mass spectrometer, P m/e 102-112 $(H_nGeS)^+$. The analogous reactions with $H_2Se$ readily gave the corresponding germaneselenol, P m/e 146-162 $(H_nGeSe)^+$, in contrast to the slow formation of $H_3SiEH$ and $Me_3MEH$ where M = Si,Ge and E = S,Se. Although the reactions of the $(Me_3M)_2E$ species with $H_2E$ occurred relatively slowly, the formation of $Me_3MEH$ was quantitative. Alternatively, the germanethiols were formed from the oxides; the germaneselenols from the oxides or sulfides [P m/e 147-155 $(Me_3GeSH)^+$, P m/e 191-204 $(Me_3GeSeH)^+$]; and the silane-thiols and -selenols from the tellurides with $H_2E$. All these species were identified by their $^1H$ n.m.r. parameters which are collected in Table VII.1. After extended periods of time, the reactions gave no indication of further condensed species, but the $^1H$ n.m.r. analysis of the reaction of $(H_3Ge)_2Se$ with $H_2Se$ in the presence of TMS after ca. 40 days showed resonances assignable to $H_2Ge(SeGeH_3)_2$[107] - $\delta(GeH_2)$ 5.40, $\delta(GeH_3)$ 4.33 p.p.m. and $GeH_4$ - $\delta(GeH)$ 3.20 p.p.m.

### (f) Redistribution reactions and the identification of mixed species

Approximately equimolar quantities of the symmetrical species were sealed in semimicro n.m.r. tubes. The course of the reactions was monitored, by $^1H$ n.m.r. spectroscopy, by comparing the peak hights and positions of the new resonances relative to those of the parent species or TMS. Typically, $(H_3Ge)_2Se$ (0.04 mmol) and $(Me_3Ge)_2Se$ (0.04 mmol) were allowed to react at room temperature. After ca. 10 minutes resonances attributable only to the symmetrical selenides were observed at $\delta(GeH)$ 4.23 and $\delta(Me)$ 0.56 p.p.m. After ca. 2 hours additional resonances had appeared at 4.06 and 0.62 p.p.m. in the ratio 1:3 assignable to the mixed species $H_3GeSeGeMe_3$ which accounted for ca. 80% of the redistribution mixture, Figure VII.3. After ca. 33 days, further condensation was observed as evident from the appearance of additional resonances at 5.10, 4.96, 4.23, 3.15, 0.64, 0.62 and 0.20 p.p.m. presumably assignable to $H_2Ge(SeGeH_3)(SeGeMe_3)$, $H_2Ge(SeGeMe_3)_2$ and $Me_3GeH$ relative to the peak at 3.15 p.p.m. assignable to $GeH_4$. The mass spectrum was then recorded and indicated only the presence of $H_3GeSeGeMe_3$ [P m/e 261-280 $(Me_3H_{\underline{n}}Ge_2Se)^+$], but yellowish involatile material in the tube

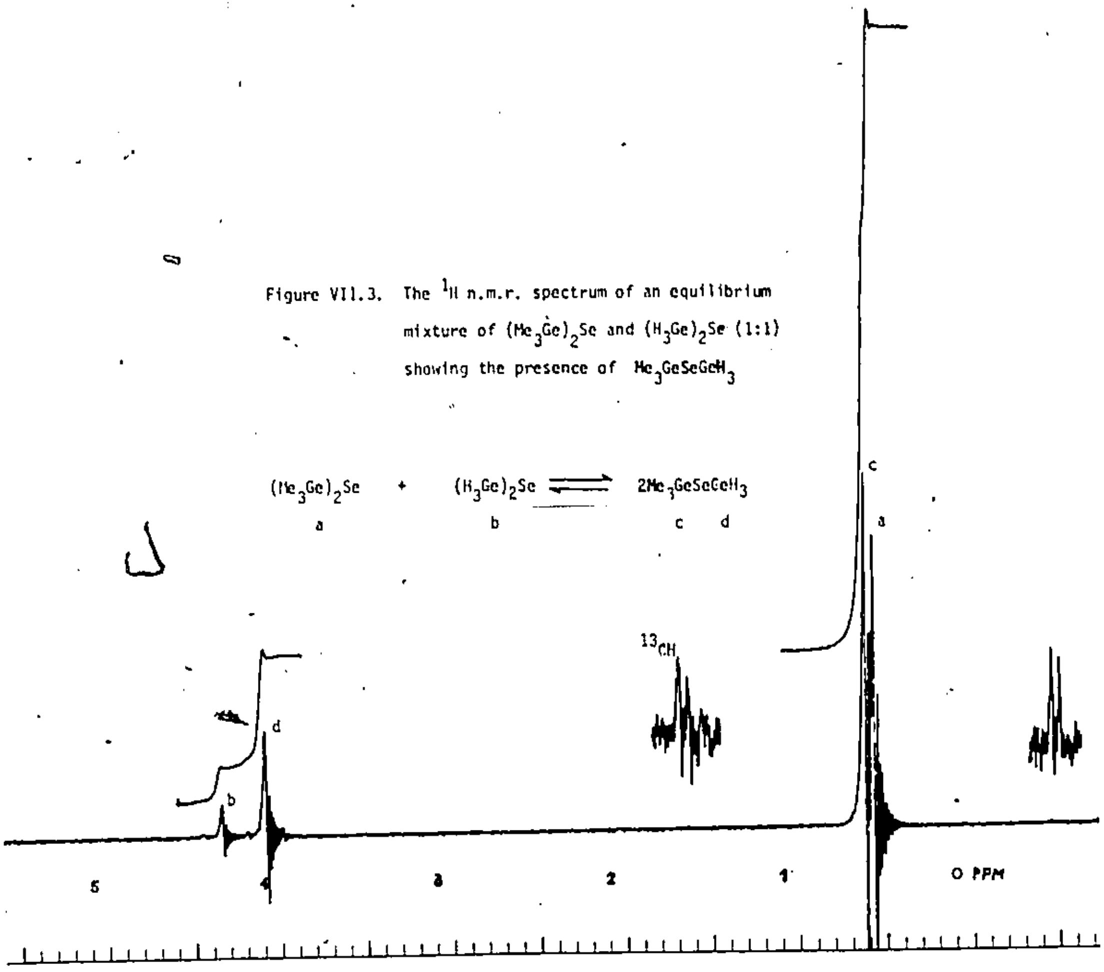


Figure VII.3. The $^{1}H$ n.m.r. spectrum of an equilibrium mixture of $(Me_3Ge)_2Se$ and $(H_3Ge)_2Se$ (1:1) showing the presence of $Me_3GeSeGeH_3$

$$\underset{a}{(Me_3Ge)_2Se} + \underset{b}{(H_3Ge)_2Se} \rightleftharpoons 2\underset{c}{Me_3Ge}Se\underset{d}{GeH_3}$$

breaker remained unidentified. Germyltrimethygermyl selenide was also obtained from an incomplete exchange reaction between $(Me_3Ge)_2Se$ and $H_3GeF$.

A similar redistribution reaction of $(Me_3Si)_2Se$ (0.12 mmol) with $(H_3Ge)_2Se$ (0.13 mmol) did not occur to the same extent. The additional resonances at 0.47 and 3.98 p.p.m. in the ratio ca. 1:3 were assigned to $H_3GeSeSiMe_3$ [P m/e 219-234 (228) $(H_nGeSeSiMe_3)^+$] which accounted for about 15-20% of the redistribution mixture. Further $^1H$ n.m.r. observations, after ca. 15 days, showed additional resonances attributable to: $H_2Ge(SeGeH_3)_2$[107] - $\delta(GeH_2)$ ca. 5.31 and $\delta(GeH_3)$ 4.33 p.p.m.; and presumably assignable to: $H_2Ge(SeGeH_3)(SeSiMe_3)$ - $\delta(GeH_2)$ 5.28, $\delta(GeH_3)$ 5.11 and $\delta(Me)$ 0.50 p.p.m., Figure VII.4.

In the same manner, $H_3GeSGeMe_3$ [P m/e 217-232 $(Me_3H_nGe_2S)^+$] $H_3GeTeGeMe_3$ [P m/e 309-327 $(Me_3H_nGe_2Te)^+$] and $H_3SiESiMe_3$ where E = S,Se,Te were formed and identified by their $^1H$ n.m.r. parameters, Table VII.1.

### (g) Fast exchange reactions between digermoxanes and iodo- and bromo- germanes

Typically, $(Me_2HGe)_2O$ [ $\delta(Me)$ 0.40, $\delta(GeH)$ 5.40 p.p.m.] and $Me_2HGeI$ [ $\delta(Me)$ 1.08, $\delta(GeH)$ 4.71 p.p.m.] in a ratio of ca. 1:1 and a trace of TMS were sealed in a semimicro n.m.r. tube. The $^1H$ n.m.r. spectrum showed resonances centered at $\delta(Me)$ 0.78 and $\delta(GeH)$ 5.17 p.p.m. Similarly, $(MeH_2Ge)_2O$ and $(Me_3Ge)_2O$ with

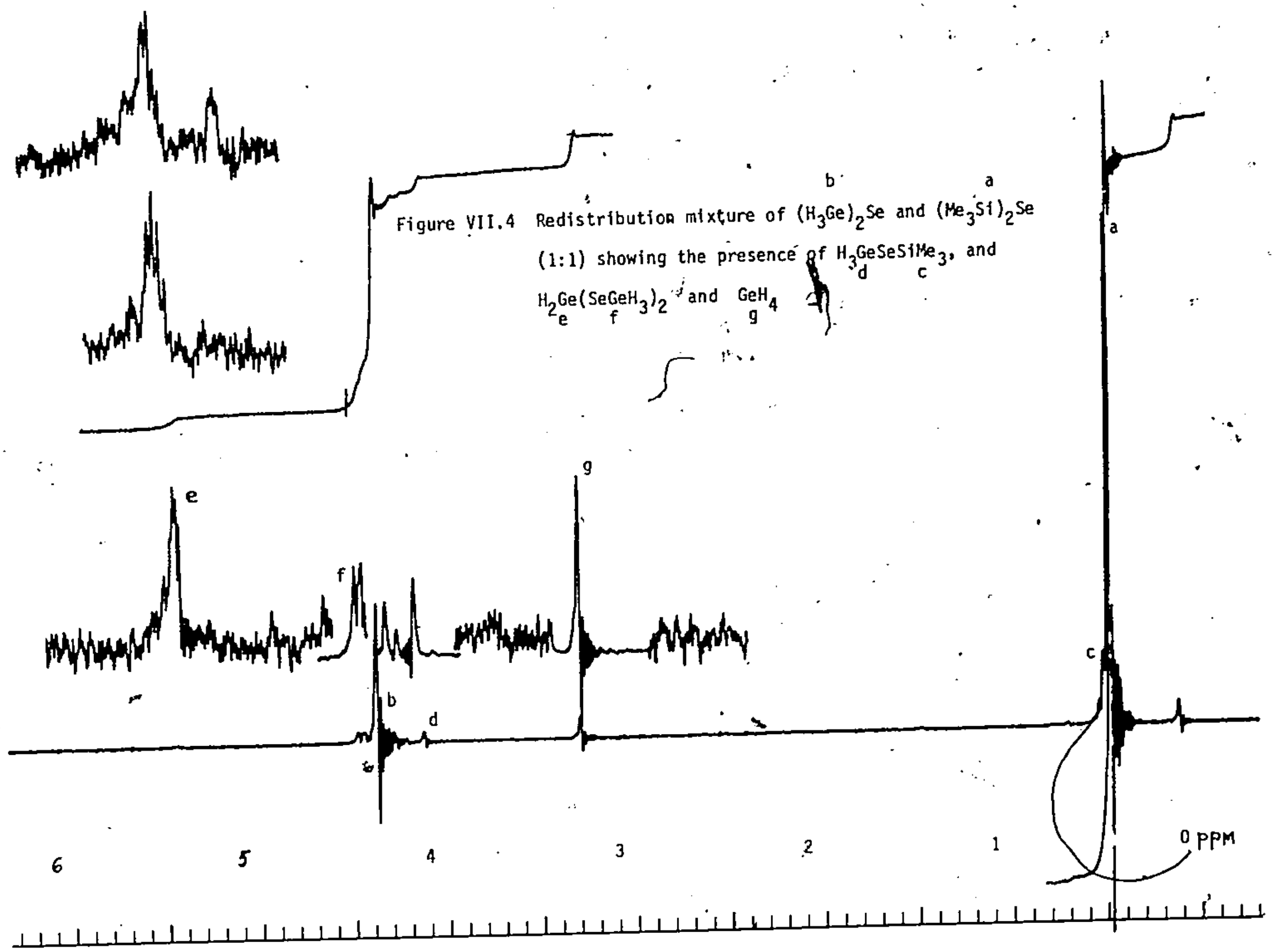


Figure VII.4 Redistribution mixture of $\overset{b}{(H_3Ge)_2Se}$ and $\overset{a}{(Me_3Si)_2Se}$ (1:1) showing the presence of $\underset{d}{H_3}Ge Se Si\underset{c}{Me_3}$, and $\underset{e}{H_2}Ge(Se Ge\underset{f}{H_3})_2$ and $\underset{g}{GeH_4}$

the corresponding iodo-, and bromo-methylgermanes gave a single, well resolved resonance intermediate to the resonance positions of the pure compounds.

## VII.3. DISCUSSION

The difficulties encountered in my initial attempts at the synthesis of $(Me_2HGe)_2Se$ from the metathesis reaction of iodo-dimethylgermane with lithium selenide are clarified when condensation reactions are considered. Thus, the reduction of the yield of $(Me_2HGe)_2Se$ with formation of the condensed selenide, $Me_2Ge(SeGeHMe_2)_2$; 1,1',2,2' - tetramethyldigermane, $(Me_2HGe)_2$, and the deposition of metallic selenium is consistent with the base-catalyzed condensation-type reaction, ie.

$$2(Me_2HGe)_2Se \xrightarrow{NH_3,LiNH_2} Me_2Ge(SeGeHMe_2)_2 + Me_2GeH_2 \quad [1]$$

$$Me_2Ge(SeGeHMe_2)_2 \xrightarrow{NH_3,LiNH_2} (Me_2HGe)_2 + (Me_2GeSe)_{\underline{n}} + Se \quad [2]$$

An unusual feature of this condensation is the formation of tetramethyldigermane, $(Me_2HGe)_2$. In view of this, very few, low yield, preparative routes have been reported for the formation of digermanes,[177,179,180] so these side reactions could represent viable synthetic methods for $(Me_2HGe)_2$. In passing, I should comment that a vile feature of this dihydride is its property to cause severe itching. By contrast to monogermanes, the digermane reacts readily and selectively with hydrogen chloride or bromide without a catalyst, i.e.

$$(Me_2HGe)_2 + HX \longrightarrow Me_2HGeGeXMe_2 + H_2 \qquad [3]$$

$$Me_2HGeGeXMe_2 + HX \longrightarrow (Me_2XGe)_2 + H_2 \quad (X = Cl,Br) \qquad [4]$$

Cleavage of phenyl groups from $(PhMe_2Ge)_2$ with HCl; redistribution of methyl groups on $(Me_3Ge)_2$ with $SnCl_4$[181]; demethylation of $(Me_3Ge)_2$ with $H_2SO_4$ and $NH_4Cl$;[182] and halogenation of $(Me_2HGe)_2$ with $Br_2$ and $I_2$ have previously been used to prepare 1,2 - dihalotetramethyldigermanes, but these procedures are not as convenient as the direct halogenation of $(Me_2HGe)_2$ with HX to give $Me_2HGeGeXMe_2$ and $(Me_2XGe)_2$, selectively and quantitatively.

Pure samples of the chalcogenides, in general showed little evidence for condensation or elimination. However, increased condensation was observed in the telluro species, as was evident from the slow condensation of $(MeH_2Ge)_2Te$ at room temperature over an extended period of time, i.e.

$$2(MH_2Ge)_2Te \longrightarrow MeHGe(TeGeH_2Me)_2 + MeGeH_3 \qquad [5]$$

$$2MeHGe(TeGeH_2Me)_2 \longrightarrow MeGe(TeGeH_2Me)_3 + MeGeH_3 \qquad [6]$$

Moderate heating of the condensed species in this instance led to the elimination of tellurium and formation of $(MeH_2Ge)_2$[177]. By contrast the fully methylated species, $(Me_3M)_2Te$ where

M = Si,Ge, did not release tellurium even when heated to ca. 200°, but they turned to a redish colour. However, the reaction between $(Me_3Si)_2Te$ and $Me_3GeCl$ readily proceeded at ca. 100° with elimination of tellurium and formation of $(Me_3Ge)_2$. Similarly, condensation and elimination of tellurium were observed when telluro- germanes and -silanes were sealed over extended periods (ca. 30 days) in cyclohexane solution.

Previous reports[106,107] have shown that hydrogen sulfide and selenide react with either germyl- phosphine or -arsine to give $(H_3Ge)_2E$ via $H_3GeEH$ intermediates. In an analogous manner, $(Me_nH_{3-n}M)_2E$ species react with $H_2E$ in sealed tube conditions with the formation of $Me_nH_{3-n}MEH$ where M = Si,Ge; E = S,Se and n = 0,3; e.g.

$$(H_3Ge)_2S \;+\; (\text{excess})\, H_2S \;\overset{\text{fast}}{\rightleftarrows}\; 2H_3GeSH \qquad [7]$$

$$(Me_3Ge)_2S \;+\; (\text{excess})\, H_2S \;\xrightarrow{\text{slow}}\; 2\,Me_3GeSH \qquad [8]$$

The silyl species react similarly but more slowly under comparable conditions. Attempts to isolate the hydridic chalcogenols failed, since only the symmetric chalcogenides could be obtained by fractionation. By contrast, the trimethylated chalcogenols are more stable and showed slow condensation to the symmetric chalcogenides. This observation suggests that the hydridic chalcogenols are more acidic than the trimethylated analogs. However, both types of chalcogenols were sufficiently stable at low temperature to permit the recording of their mass spectra which confirmed the presence of the parent ions. Species of this kind, $H_3MEH$, were further studied by Ebsworth.[183]

The formation of mixed silyl and germyl chalcogenides, $Me_3MEMH_3$, resulted from the equimolar exchange interaction of the symmetric species, i.e.

$$(Me_3M)_2E \quad + \quad (H_3M)_2E \quad \rightleftharpoons \quad 2Me_3MEMH_3 \qquad [9]$$

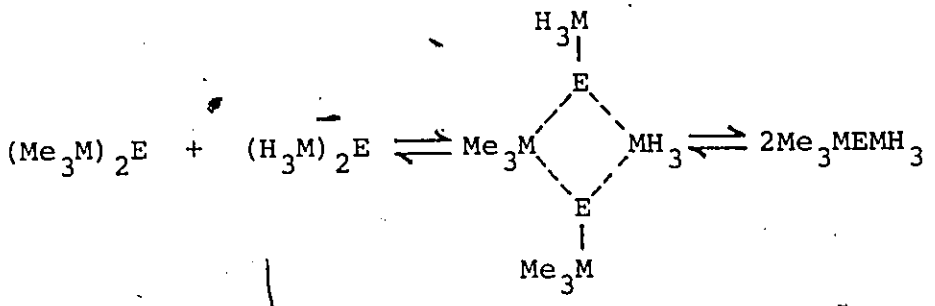
Whereas the silyl mixtures took longer time to come to equilibrium the germyl mixtures in general reached equilibrium relatively quickly implying that the Ge-E bonds are more labile to redistribution than the Si-E bonds. An excess of one of the components [e.g. $(H_3Ge)_2Se$] forces the equilibrium to the right to give essentially quantitative formation of $Me_3GeSeGeH_3$.

The values obtained for the equilibrium constant, $K_{25°}$, were: Si- ca. 0.12; 0.16; 0.19; Ge- 0.05; 0.09; 0.18 (S ⟶ Se ⟶ Te) where $K_{25°}$ traditionally is defined by

$$K_{25°} = [(Me_3M)_2E][(H_3M)_2E] / [Me_3MEMH_3]^2 \qquad [10]$$

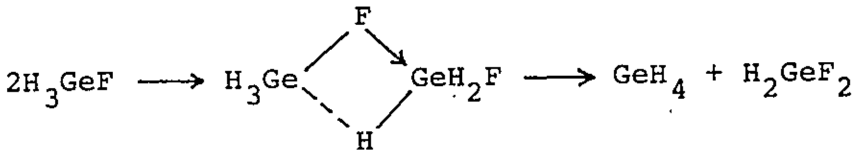
These values are approximate because of difficulties in integrating the methyl resonances. Nevertheless, the values are clearly less than the statistical random value of 0.25 and exhibit the consistent trends $K(Si) > K(Ge)$ and $K(Te) > K(Se) > K(S)$. The latter trend has been also observed for the $H_3MEH$ species.[118]

The mechanism for these redistribution reactions may proceed through a four center intermediate involving expanded coordination spheres for silicon and germanium, i.e.



[11]

A similar four center reaction mechanism has been proposed for the disproportionation of hologenosilanes[184] and fluorogermane[185] to dihalogenosilanes and silane, and difluorogermane and germane respectively, but this disproportionation is non-reversible, e.g.



[12]

The formation of $GeH_4$ and $Me_3GeH$ from the disproportionation of the selenogermanes is apparently indicative of the same mechanism. [In view of this, I confirmed the decomposition of $(H_3Ge)_2Se$ to $H_2Ge(SeGeH_3)_2$ and $GeH_4$[107]]. The formation of $Me_3GeH$ is indicative of the formation of further condensed species:

$$(Me_3Ge)_2Se + (H_3Ge)_2Se \rightleftharpoons 2Me_3GeSeGeH_3 \qquad [13]$$

$$2(H_3Ge)_2Se \longrightarrow H_2Ge(SeGeH_3)_2 + GeH_4 \qquad [14]$$

$$(H_3Ge)_2Se + Me_3GeSeGeH_3 \longrightarrow H_2Ge(SeGeH_3)_2 + Me_3GeH \qquad [15]$$

$$2Me_3GeSeGeH_3 \longrightarrow H_2Ge(SeGeH_3)(SeGeMe_3) + Me_3GeH \qquad [16]$$

$$2Me_3GeSeGeH_3 \longrightarrow H_2Ge(SeGeMe_3)_2 + GeH_4 \qquad [17]$$

$$(Me_3Ge)_2Se + Me_3GeSeGeH_3 \longrightarrow H_2Ge(SeGeMe_3)_2 + Me_3GeH \qquad [18]$$

Similarly, the disproportionation of $(H_3Ge)_2O$ observed in this work is suggestive of an analogous initial mechanism, i.e.

$$3(H_3Ge)_2O \longrightarrow H_2O + 2(GeH_2) + GeH_4 + H_2Ge(OGeH_3)_2 \qquad [19]$$

$$(GeH_2) + GeH_4 \longrightarrow H_3GeGeH_3 \quad (Ge_nH_{2n+2}) \qquad [20]$$

As previously mentioned, the attempts by others to clarify the decomposition of $(H_3Ge)_2O$ by vibrational spectroscopy[113,114] failed, so monitoring by $^1H$ n.m.r. is a much more reliable approach to the elucidation of the disproportionation pathway. The peak centered at ca. 6.02 p.p.m. is assignable to the $H_2Ge$-proton resonance of $H_2Ge(OGeH_3)_2$, whereas that of $OGeH_3$ is presumably overlapping with the parent resonance of $(H_3Ge)_2O$. The other resonances in the region ca. 3.15 - 3.62 p.p.m. are attributable to $Ge_{\underline{n}}H_{2\underline{n}+2}$ species and that at ca. 4.52 p.p.m. to $H_2O$, Figure VII.2.

Apparently there is no long range coupling, in contrast to the coupling in $H_2Ge(SeGeH_3)_2$, J(HH) 0.85 Hz. The hydridic chalcogenols, $H_3MEH$, also gave long range, first order, coupling between the three hydrogen atoms attached to M and the lone hydrogen attached to the chalcogen atom. The resultant doublet-quartet pattern (intensity 3:1) has been observed previously[107,118]. The coupling, H-H, is not observed in the case of $Me_3MEH$ species nor is the longer range H-H coupling observed in $Me_3MEMH_3$ where the spectra showed two singlet peaks (intensity 3:1) attributable to $\delta$(Me) and $\delta$(MH), Figure VII.4. However, the dihydrides, $(Me_2HM)_2$, showed multiplet resonances only for the HM protons and doublet for the methyl protons, while $(MeH_2Si)_2$ showed complex resonances for both the methyl and silicon protons. The lowering of the M-H stretching frequencies for $(Me_2HGe)_2$ 2017 $cm^{-1}$ and $(Me_2HSi)_2$ 2106 $cm^{-1}$ as well as $Me_2Ge(SeGeHMe)_2$ 2003 $cm^{-1}$ is a distinctive feature as compared with the chalcogen species, $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2E$ 2082-2036 $cm^{-1}$, and $(Me_{\underline{n}}H_{3-\underline{n}}Si)_2E$ 2159-2125 $cm^{-1}$; $E = O \longrightarrow Te$, Tables V.3 - V.6.

An examination of the proton chemical shifts in Table VII.1 shows that they follow the trends observed for the parent species described in Chapter V.4. The sequential shifts in both the $H_3C$- and HM- proton resonances with changing chalcogen electronegativity permit the a priori assignment of the signals for the mixed species. Based on the observed $H_3Ge$ shifts; the order of the inductive withdrawal of the SR entity is: $SSiH_3 < SSiMe_3$ $SH < SGeMe_3 < SGeH_3$. Thus for the series $H_3GeSSiH_3 \longrightarrow$

Table VII.1 The $^{1}$H n.m.r. parameters* of the condensed species

| Compound | δ(Me) | δ(MH) | δ(EH) | J(HH) | J(CH) | J(SeH) |
|---|---|---|---|---|---|---|
| $H_3SiSH$[a] | - | 4.31 | -0.01 | 4.70 | - | - |
| $Me_3SiSH$ | 0.34 | - | -0.05 | - | 121.5 | - |
| $H_3SiSeH$[a] | - | 4.24 | -2.14 | 4.90 | - | 51.0 |
| $Me_3SiSeH$ | 0.44 | - | -2.26 | - | - | - |
| $H_3SiTeH$[a] | - | 3.77 | -7.46 | 4.80 | - | 57.6 |
| $H_3GeSH$[a] | - | 4.52 | -0.23 | 4.10 | - | - |
| $Me_3GeSH$ | 0.56 | - | -0.32 | - | 129.0 | - |
| $H_3GeSeH$[a,b] | - | 4.26 | -2.23 | 4.30 | - | 41.1 |
| $Me_3GeSeH$ | 0.66 | - | -2.38 | - | 128.7 | 42.6 |
| $H_3GeTeH$[a] | - | 3.62 | -7.44 | 4.40 | - | 51.9 |
| $Me_3SiOSiH_3$[c,c'] | 0.08 | 4.61 | - | - | - | - |
| $Me_3SiOGeH_3$[d] | 0.05 | 5.18 | - | - | - | - |
| $Me_3SiSSiH_3$[c,e] | 0.36 | 4.28 | - | - | - | - |
| $Me_3SiSGeH_3$[d] | 0.31 | 4.43 | - | - | - | - |
| $H_3SiSGeH_3$[d,e] | - | 4.59(GeH) | 4.41(SiH) | - | - | - |
| $Me_3SiSeSiH_3$[e] | 0.47 | 3.98 | - | - | - | - |
| $Me_3SiSeGeH_3$ | 0.44 | 4.05 | - | - | - | - |
| $Me_3SiTeSiH_3$ | 0.58 | 3.43 | - | - | - | - |
| $Me_3GeSGeH_3$ | 0.56 | 4.54 | - | - | - | - |
| $Me_3GeSeGeH_3$ | 0.62 | 4.06 | - | - | - | - |
| $Me_3GeTeGeH_3$ | 0.73 | 3.38 | - | - | - | - |
| $H_2Ge(SeGeH_3)_2$[b] | - | 5.31($H_2Ge$) | 4.33($GeH_3$) | - | - | - |
| $Me'_2Ge(SeGeHMe_2)_2$ | 0.31 0.37' | 3.73 | - | 3.98 | - | - |
| $Me_2HGeGeClMe'_2$ | 0.40 0.73' | 3.98 | - | - | - | - |
| $Me_2HGeGeBrMe'_2$ | 0.42 0.90' | 4.12 | - | - | - | - |
| $(Me_2ClGe)_2$ | 0.83 | - | - | - | - | - |
| $(Me_2BrGe)_2$ | 1.00 | - | - | - | - | - |
| $(Me'_2HGe)_2$[f] | 0.29 | 3.90 | - | 4.50(HH')<br>3.80(HH) | 130.5 | - |

*The spectra were recorded at room temperature. Chemical shifts of $Me_{\underline{n}}H_{3-\underline{n}}SiEH$ were recorded in cyclohexane (5% v/v).

[a] Ref. 118. [b] Ref. 107. [c] Ref. 175. [c'] Ref. C.H. Van Dyke and A.G. MacDiarmid, Inorg. Chem., 3, 747 (1964). [d] Ref. 174. [e] Ref. 176. [f] Ref. 177.

$H_3GeSSiMe_3 \rightarrow H_3GeSH \rightarrow H_3GeSGeMe_3 \rightarrow (H_3Ge)_2S$ the $H_3Ge$ -proton resonances shift to lower field, i.e. 4.41 → 4.43 → 4.52 → 4.54 → 4.64 p.p.m., while the $H_3Si$ - proton shifts suggest the order $Me_3SiS < SH < H_3SiS < H_3GeS$ in the series $Me_3SiSSiH_3$ $\delta(SiH)$ 4.28 → $H_3SiSH$ $\delta(SiH)$ 4.31 → $(H_3Si)_2S$ $\delta(SiH)$ 4.35 → $H_3GeSSiH_3$ $\delta(SiH)$ 4.59 p.p.m. The same is true for the $H_3C$ - proton resonances in both silyl and germyl species. Thus for the series $Me_3SiSGeH_3 \rightarrow (Me_3Si)_2S \rightarrow Me_3SiSH \rightarrow Me_3SiSSiH_3$ the $H_3C$ - resonance moves to the low field, i.e.: 0.31 → 0.33 → 0.34 → 0.36 p.p.m. The observation of separate signals for the components of the equilibria confirms that the exchange process is slow on the n.m.r. time scale. However, the $^1H$ n.m.r. spectra of the iodo-, and bromo- germanes with the corresponding digermoxanes are explainable as being the average resulting from fast exchange.

# CHAPTER VIII

## THE REACTIVITY AND CHARACTERIZATION OF M-E SPECIES

## VIII.1. INTRODUCTION

In this chapter emphasis is placed on the reactivity of metal-chalcogen bonds from which synthetic routes are devised for large scale preparations of samples of the highest purity, in a relatively short time. Although the analogous silyl and germyl species show similar properties, considerable differences exist between the Si-E and Ge-E (E=O,S,Se) bond. Interconversions of metal-chalcogen bonds have been noted for both silicon and tin.[195] Similar reactions for germanium have gone virtually unrecognized. This lesser interest in germanium species is probably due to the scarcity of synthetic procedures or to the obnoxious nature of the compounds.

## VIII.2. EXPERIMENTAL

The many types of reactions that result in the formation of M-E-R species are classified under the following headings:

### (a) Reactions of $(Me_nH_{3-n}Si)_2S$ with ROH

(1) - With $CF_3CH_2OH$ and $CCl_3CH_2OH$

Glidewell[129] has reported the preparation of $H_3SiOCH_2CF_3$ from the reaction of $H_3SiPH_2$ with $CF_3CH_2OH$. However, disilathianes are readily accessible and react with $CX_3CH_2OH$ according to [1].

$$(H_3Si)_2S + 2CF_3CH_2OH \longrightarrow 2H_3SiOCH_2CF_3 + H_2S \quad [1]$$

In a typical reaction $(H_3Si)_2S$ (1.57 mmol) and $CF_3CH_2OH$ (3.14 mmol) were condensed at -196°, in vacuo, in a reaction vessel (ca. 10 ml) attached to the vacuum line via a Teflon-in-glass stopcock. The reactants were isolated and allowed to react at room temperature. After ca. 15 minutes the volatile products were fractionated through traps held at -96° and -196°. The former trap contained $H_3SiOCH_2CF_3$ [3.12 mmol, 99%; P-69 $(H_3SiOCH_2)^+$ 61 (100%)] while the latter retained $H_2S$ (1.57 mmol).

By the same procedure the remainder of the siloxy species $MeH_2SiOCH_2CF_3$ [P-15 $(H_2SiOCH_2CF_3)^+$ 129 (7%)], $Me_2HSiOCH_2CF_3$ [P m/e $(Me_2HSiOCH_2CF_3)^+$ 158 (3%)], $Me_3SiOCH_2CF_3$ [P-15 $(Me_2SiOCH_2CF_3)^+$ 157 (42%)], $H_3SiOCH_2CCl_3$ [P-117 $(H_3SiOCH_2)^+$ 61 (100%)], $MeH_2SiOCH_2CCl_3$ [P-1 $(MeHSiOCH_2CCl_3)^+$ 191 (6%)], $Me_2HSiOCH_2CCl_3$ [P m/e $(Me_2HSiOCH_2CCl_3)^+$ 207 (2%)] and $Me_3SiOCH_2CCl_3$ [P-15 $(Me_2SiOCH_2CCl_3)^+$ 207 (9%)] were produced in high yields, ca. 95%. The $^1H$ n.m.r. parameters and the core-level binding energies for each atom in every compound are summarized in Tables VIII.2 and VIII.3.

### (2) - With MeOH and EtOH

Most of the general methods useful for the preparation of organosilicon alkoxides are unsuccessful for silicon hydrides because of the reactivity of the Si-H bond. The interaction of disilathianes with MeOH has been described.[186-188] Alkoxysilanes prepared by this route, as in (1), include $H_3SiOMe$ [P-1 $(H_2SiOMe)^+$ 61 (100%)]; $MeH_2SiOMe$; $Me_2HSiOMe$ [P-1 $(Me_2SiOMe)^+$ 89 (74%)]; $Me_3SiOMe$ [P m/e $(Me_3SiOMe)^+$ 104 (3%)], $H_3SiOEt$ [P m/e $(H_3SiOEt)^+$ 76 (23%)], and $Me_3SiOEt$. The $^1H$ n.m.r. parameters and the core-level binding energies for each atom in every compound are listed in Tables VIII.2 and VIII.3.

### (b) Reactions of $(Me_2HSi)_2O$ with n-$Bu_3SnOMe$

Typically, $(Me_2HSi)_2O$ (2.00 mmol) was distilled into a reaction vessel (ca. 15 ml, type 'B') containing 6.10 mmol of degassed n-$Bu_3SnOMe$. The reactants were isolated and allowed to react at room temperature for ca. 22 hours with occasional shaking. Fractionation of the volatile material through traps held at −23° and −196° gave pure $[Me_2(MeO)Si]_2O$ (1.87 mmol) [P-15 179 $(Me_5Si_2O_3)^+$; $\delta$(Me) 0.08, $\delta$(MeO) 3.41 p.p.m.], in the former trap, while an involatile material was retained in the reaction vessel.

### (c) Reactions of $Me_nH_{3-n}MX$ and $Me_nMX_{4-n}$ with n-$Bu_3SnOMe$

Preliminary experiments showed that the H-M and M-X (X=Cl,Br,I) bonds react competitively with n-$Bu_3SnOMe$, so the attempts to prepare $Me_nH_{3-n}MOMe$ (M=Si,Ge; n=0,1,2) species were unsuccessful. When $MeH_2GeF$ was allowed to react with a slight excess of n-$Bu_3SnOMe$, as in (b), at room temperature for ca. 5 minutes, n-$Bu_3SnF$ was rapidly formed as a white solid. Upon fractionation a pure sample of $MeH_2GeOMe$ was retained at -78° trap in a 80% yield. Similarly $Me_2HGeOMe$ was isolated in a 83% yield. These compounds and $H_3GeOMe$ were also obtained, in an analogous manner, from the reaction of $(Me_{\underline{n}}H_{3-\underline{n}}GeN)_2C$ with MeOH.

By an identical procedure, $Me_{\underline{n}}MX_{4-\underline{n}}$ reacted exothermically with $n\text{-}Bu_3SnOMe$ to give $Me_{\underline{n}}M(OMe)_{4-\underline{n}}$ where M=Si,Ge and $n=0 \rightarrow 3$ in about 96% yeilds. The purity of these species was ascertained by $^1H$ n.m.r., X-ray photoelectron and mass spectral analyses.

(d) Reactions of germoxanes with REH species

(1) - Preparation of MeSeH and EtSeH

Methane-, and ethane- selenol were not commercially available. Three methods for methaneselenol have been reported,[134,189,190] i.e.,

$$NaSeH + MeI \longrightarrow MeSeH + NaI \qquad [2]$$

$$Me_2Se_2 + 2Li \xrightarrow{NH_3} 2MeSeLi \xrightarrow{H_2SO_4} 2MeSeH + Li_2SO_4 \qquad [3]$$

$$MeLi + Se \xrightarrow{THF} MeSeLi \xrightarrow{HBr} MeSeH + LiBr \qquad [4]$$

The methods exemplified by [3] and [4] were very tedious and time consuming, running into days. For this reason my attention was centered on developing more convenient, high yield, syntheses of both MeSeH and EtSeH.

In a typical experiment, $Li_2Se_2$ (10.00 mmol) was prepared from the elements in liquid ammonia as described in Chapter IV.2(f). MeI (15 mmol) was then condensed into the reaction vessel (ca. 125 ml, type 'A') and allowed to react by shaking and cautious warming while monitoring the $NH_3$ pressure. Heavy reddish droplets of $Me_2Se_2$ were readily formed and after ca. 1 hour the volatile material was fractionated through traps held at -78° and -196°. After ca. 1 1/2 hours, fractionation gave pure $Me_2Se_2$ in a 89% yield [ $\delta$(Me) 2.48 p.p.m.][191] retained at -78° while $NH_3$ was collected in the -196° trap. The diselenide was stored in a storage vessel (ca. 20 ml) of type 'I'. The same procedure was used to prepare $Et_2Se_2$.

In one experiment, $Me_2Se_2$ (0.30 mmol) and $H_2Se$ (1.20 mmol) were sealed in a semimicro n.m.r. tube and allowed to react at room temperature. Selenium was deposited in the tube and the $^1H$ n.m.r. spectrum revealed the high yield formation of MeSeH [ $\delta$(Me) 1.86 and $\delta$(SeH) - 0.80 p.p.m.].[191] In another experiment, $Me_2Se_2$ (1.53 mmol) and $H_2Se$ (6.02 mmol) were condensed in a reaction vessel (ca. 20 ml) attached to the vacuum line via a Teflon-in-glass stopcock. The reactants were isolated and allowed to react at room temperature with shaking. Large quantities of Se were deposited and after ca. 10 minutes the stopcock was carefully opened (to prevent sudden expansion of the very volatile material and contamination of the vacuum line with Se) allowing the volatile material to pass through traps held at -78°, -96° and -196°. The fractions: ($H_2Se$) at -196° and $Me_2Se_2$ at -78° trap were returned to the reaction vessel and allowed to react as above. Further deposition of Se was observed and after 5 minutes the material was fractionated. Small amounts of $Me_2Se_2$ were again retained at -78° which in a similar manner reacted with $H_2Se$ to give MeSeH. The overall yield of MeSeH retained in the -96° trap was 90%. By the same procedure $Et_2Se_2$ reacted with $H_2Se$ to give EtSeH in a yield of 86%.

(2) $(Me_{\underline{n}}H_{3-\underline{n}}Ge)_2O$ with $H_2E$, MeEH and EtEH where E=S,Se

The work described herein is synthetically important and represents the quickest method to prepare a required thio-, or seleno-germane.

Typically, the germoxane and hydrogen chalcogenide were condensed, in vacuo, into a reaction vessel (ca. 5 ml) attached to the vacuum line via a Teflon-in-glass stopcock. The reactants were allowed to react at room temperature for ca. 15 minutes with some shaking. The volatile products were subsequently passed through glass wool supporting a small amount (ca. 0.5 g) of $P_2O_5$ to remove the water and collected in a U-trap held at -78°. The presence of the chalcogermane in question was confirmed by $^1$H n.m.r. spectroscopy, Table VIII.2. Any excess water in the product mixture was removed by repeating the preceeding drying procedure. To ensure complete conversion of the germoxanes, a slight excess of the hydrogen chalcogenide was used. With a large excess, $Me_3GeEH$ was formed in large quantities. Preparative details are given in Table VIII.1.

Table VIII.1 Protolysis of digermoxanes with $H_2S$ and $H_2Se$

$$(Me_2HGe)_2O + H_2Se \longrightarrow (Me_2HGe)_2Se + H_2O$$

| Reactant germoxane | (mmol) |  | Product chalcogenide | (mmol) |  | Yield % |  |
|---|---|---|---|---|---|---|---|
|  | E=S | E=Se |  | E=S | E=Se | E=S | E=Se |
| $(H_3Ge)_2O$ | 1.23 | 1.01 | $(H_3Ge)_2E$ | 1.17 | 0.94 | 95 | 93 |
| $(MeH_2Ge)_2O$ | 1.12 | 1.31 | $(MeH_2Ge)_2E$ | 1.07 | 1.24 | 96 | 95 |
| $(Me_2HGe)_2O$ | 2.35 | 2.12 | $(Me_2HGe)_2E$ | 2.32 | 2.06 | 98 | 97 |
| $(Me_3Ge)_2O$ | 1.67 | 1.03 | $(Me_3Ge)_2E$ | 1.54 | 0.96 | 92 | 93 |

The analogous reactions of germoxanes with excess of methane-, and ethane- thiol and selenol also gave excellent yields of the corresponding thio- and seleno-germanes, viz. - $H_3GeSMe$ (94%), $MeH_2GeSMe$ (92%), $Me_2HGeSMe$ (96%), $Me_3GeSMe$ (91%); $H_3GeSEt$ (95%), $MeH_2GeSEt$ (97%), $Me_2HGeSEt$ (93%), $Me_3GeSEt$ (89%); ($H_3GeSeMe$ (92%), $MeH_2GeSeMe$ (97%), $Me_2HGeSeMe$ (94%), $Me_3GeSeMe$ (90%); $H_3GeSeEt$ (98%), $Me_3GeSeEt$ (93%).

Principle features in the i.r. spectra of the ethylselenogermanes occurred at: $H_3GeSeEt$ - 2979 ms, 2940 ms, 2880 m, 2140 sh, 2100 vs, 2070 vs, 1455 mw, 1385 w, 1241 s, 1080 w, 960 w, 870 s, 815 vs, 750 w, 540 ms ($cm^{-1}$); $Me_3GeSeEt$ - 2993 m, 2920 mw, 2879 w, 1430 wbr, 1240 m, 1150 vw, 1075 wbr, 965 vw, 830 s, 755 w, 660 w, 609 m, 568 mw ($cm^{-1}$).

### (3) - $Me_2Ge(OMe)_2$ and $MeGe(OMe)_3$ with MeSH, $H_2S$ and $H_2Se$

The protolytic cleavage of the Ge-O bond was extended further in an anologous manner, as in (2), to provide the synthesis of $Me_2Ge(SMe)_2$ and $MeGe(SMe)_3$. In this case the other product is MeOH which can be easily separated from the less volatile methylthiogermane.

In view of the reactions involving $Me_2Ge(OMe)_2$ and $H_2E$ (E=S,Se) it is important to make a comment. Most chemists approach the synthesis of chalcogen species with the feeling that if one can make a sulfur compound, its selenium analog can be made by the same method. This approach is viable on occasions, but it is certainly fallible. This is the case with the reactions described herein.

In a typical reaction $Me_2Ge(OMe)_2$ (0.13 mmol) and excess $H_2S$ (1.00 mmol) were condensed in a semimicro n.m.r. tube attached to the vacuum line via a Teflon-in-glass stopcock. The reactants were isolated and allowed to react at room temperature for <u>ca</u>. 20 minutes with some shaking. After this time the tube was reattached to the vacuum line and the stopcock was opened slowly (to prevent contamination of the vacuum line with the product) and the volatile material was allowed to pass through traps held at -78° and -196°. The trap at

-78° contained MeOH and that at -196° unreacted $H_2S$. A white solid, which was subsequently identified as $(Me_2GeS)_3$[192] (0.045 mmol, 100%), [$^1H$ n.m.r. ($CCl_4$, TMS) $\delta$(Me) 0.93 p.p.m.; J(CH) 129.9 Hz] was retained in the tube. The mass spectrum gave the molecular ion $(Me_6Ge_3S_3)^{+\cdot}$ at 396-412, 404 (41%).

The analogous reaction of $Me_2Ge(OMe)_2$ with $H_2Se$ gave an oily immiscible liquid in the reaction mixture. After the removal of the volatile material, $CCl_4$ and a trace of TMS were condensed into the n.m.r. tube. When the tube was warmed two layers were formed. The $^1H$ n.m.r. spectrum showed a singlet centered at 0.95 p.p.m. presumably assignable to $(Me_2GeSe)_{\underline{n}}$ species.[192,193] Further efforts to prepare $(Me_2GeSe)_3$ from the reaction of $(Me_2GeS)_3$ with $H_2Se$ were also unsuccessful.

An identical procedure involving $MeGe(OMe)_3$ and $H_2E$ gave readily heterocyclic species of the type $(MeGe)_4E_6$ in a 100% yield. The mass spectrum gave a molecular ion at: $(MeGe)_4S_6$ [P m/e 532-556 $(Me_4Ge_4S_6)^+$ 544 (100%)][194] and $(MeGe)_4Se_6$ [P m/e 814-837 $(Me_4Ge_4Se_6)^{+\cdot}$ 827 (100%)].

### (e) Reactions of $(Me_3Ge)_2O$ with $SbF_3$

The interaction of $(Me_3Ge)_2O$ and related germoxanes with $AsF_3$ has been demonstrated as a convenient route to fluoromethylgermanes.[28] I found that $SbF_3$ is a useful fluorinating agent for $(Me_3Ge)_2O$.

Typically, $(Me_3Ge)_2O$ (5.02 mmol) was set aside with $SbF_3$ (*ca*. 15 g) at room temperature (*ca*. 3 hours) in a reaction vessel (*ca*. 75 ml) fitted with a Teflon-in-glass stopcock. Fractional condensation of the volatile material gave $Me_3GeF$[24] (9.51 mmol, 95%) [ $\delta$(Me) 0.51 p.p.m.].

## (f) Preparation of some new methylthiosilanes: $MeH_2SiSMe$, $Me_2HSiSMe$ and $MeHSi(SMe)_2$

An exactly analogous procedure as described in Chapter IV.2(d) was further extended to include the preparation of $Me_{\underline{n}}H_{3-\underline{n}}SiSMe$ ($n=0\rightarrow3$), $MeHSi(SMe)_2$ and $Me_2Si(SMe)_2$ in *ca*. 96% yields, i.e.

$$Li[AlH_4] + 4MeSH \xrightarrow{Me_2O} Li[Al(SMe)_4] + 4H_2 \qquad [5]$$

$$Li[Al(SMe)_4] + 4Me_2HSiI \rightarrow 4Me_2HSiSMe + LiI + AlI_3 \qquad [6]$$

The nature of the compounds was unequivocally confirmed by their spectroscopic parameters, which can be found in Tables VIII.2 and VIII.3. The observation of parent peaks in the expected m/e ranges provided confirmatory evidence for the proposed species: $H_3SiSMe$ - [P m/e 75-80 $(H_3SiSMe)^+$ 78 (100%)]; $MeH_2SiSMe$ - [P m/e 90-94 $(MeH_2SiSMe)^+$ 92 (50%)]; $Me_2HSiSMe$ - [P m/e 105-108 $(Me_2HSiSMe)^+$ 106 (20%)]; $MeHSi(SMe)_2$ - [P m/e 137-141 $(Me_3HSiS_2)^+$ 138 (100%)]; $Me_3SiSMe$ - [P m/e 120-122 $(Me_3SiSMe)^+$ 120 (38%)] and $Me_2Si(SMe)_2$ - [P m/e 152-155 $(Me_4SiS_2)^+$ 152 (71%)].

Major features in the vibrational spectra were observed at:

Raman (liq.): $\underline{\mathrm{H_3SiSMe}}$ - 2995 w,dp; 2927 s,p; 2899 w,p; 2179 sh; 2151 vs,p; 1441 wbr,dp; 1319 w,p; 968 sh; 914 w,dp; 690 m,p; 624 w,dp; 507 vs,p; 466 w,p; 202 m,p (cm$^{-1}$).

$\underline{\mathrm{MeH_2SiSMe}}$ - 2990 sh,dp; 2967 mw,dp; 2926 vs,p; 2907 vs,p; 2844 w,p; 2142 vs,p; 1430 w,dp; 1410 vwbr; 1319 w,p; 1250 w,p; 958 wsh; 929 w,dp; 876 w, 734 m,p; 701 vs,p; 669 sh; 50$\overset{6}{0}$ vs,p; 483 vs,p; 241 ms,p; 177 m,p (cm$^{-1}$).

$\underline{\mathrm{Me_2HSiSMe}}$ - 2991 sh; 2967 m,dp; 2928 vs,p; 2904 vs,p; 2848 w,dp; 2126 s,p; 1428 wbr; 1318 w; 1251 w; 970 vw; 896 w; 870 w; 840 vw; 763 w,dp; 699 s,p; 661 s,p; 630 sh; 481 vs,p; 472 sh; 261 m,p; 229 sh; 208 m,dp; 150 w,p (cm$^{-1}$).

$\underline{\mathrm{Me_3SiSMe}}$ - 2990 sh; 2963 m,dp; 2930 s,p; 2900 vs,p; 2850 w,p; 1442 w; 1411 w; 1252 w,p; 863 sh; 839 w; 747 w; 702 ms,p; 463 vs,p; 272 m,p; 231 ms,p; 207 ms,p; 190 m,p; 146 w,p (cm$^{-1}$).

$\underline{\mathrm{MeHSi(SMe)}}_2$ - 2995 w,dp; 2970 w,dp; 2927 vs,p; 2905 s,p; 2843 w,dp; 2147 m,p; 1435 w,dp; 1403 wbr; 1318 w,p; 1255 w,p; 972 w,p; 862 w; 814 w,p; 730 m,p; 698 s,p; 666 sh,dp; 530 w,dp; 472 sh; 451 vs,p; 294 w,p; 252 m,p; 199 w,dp; 133 w,p (cm$^{-1}$).

Infrared(gas): $\underline{MeH_2SiSMe}$ - 2990 sh, 2974 m, 2939 m, 2921 m, 2850 w, 2179 sh, 2154 sh, 2146 s, 1441 w, 1326 w, 1270 m, 972 sh, 960 sh, 929 sh, 899 vs, 892 vs, 885 sh, 740 m, 710 sh, 498 m ($cm^{-1}$).

$\underline{Me_2HSiSMe}$ - 2970 s, 2931 ms, 2850 w, 2189 sh, 2175 sh, 2157 sh, 2139 sh, 2130 vs, 1435 mw, 1329 mw, 1265 s, 960 sh, 880 vs, 840 s, 769 s, 710 s, 665 m, 635 w, 487 s ($cm^{-1}$).

$\underline{Me_3SiSMe}$ - 3025 sh, 2970 vs, 2929 sh, 2908 sh, 2856 sh, 1445 m, 1410 m, 1326 m, 1260 vs, 1075 vs, 845 vs, 755 ms, 700 m, 638 m, 466 m ($cm^{-1}$).

$\underline{MeHSi(SMe)_2}$ - 2998 w, 2970 w, 2930 m, 2846 w, 2160 s, 2151 vs, 1440 w, 1410 vw, 1325 w, 1261 m, 969 w, 865 s, 820 vs, 735 m, 702 w, 540 s, 479 w, 456 w ($cm^{-1}$).

## VIII.3 Discussion

The differences in the reactivity of silyl- and germyl-Group VI species are readily illustrated by the favoured formation of silicon-oxygen over silicon-sulfur bonds in contrast to germanium-sulfur over germanium-oxygen bonds. This contrast is intriguing and probably reflects metalloid-chalcogen orbital overlap differences in the two types of compounds. Interestingly, the reactions of the germyl species closely parallel those of the corresponding organotin derivatives.[195] This property has been described in terms of the increasing degree of soft acid characteristics of the $Me_3M$- group as the atomic weight of M increases.[143] Consequently, it is not surprising that iodo-, and bromo- silanes and -germanes underwent exothermic reactions with $n-Bu_3SnOMe$ to produce methoxy- silanes and -germanes in excellent yields.[196]

$$Me_3GeBr + n\text{-}Bu_3SnOMe \longrightarrow Me_3GeOMe + n\text{-}Bu_3SnBr \qquad [7]$$

However, $(Me_2HSi)_2O$ reacted sluggishly with $n-Bu_3SuOMe$ to give $[Me_2(MeO)Si]_2O$. Whilst the exchange between silicon and tin is predictable on the basis of thermodynamic arguments, the relative softness of $Me_3Ge$- group compared with silicon and tin should be rationalized carefully. A steady increase in ΔH for the reaction [8] is quoted, supporting the proposal that it is reasonable to prepare alkylthio derivatives of tin from aqueous solutions but not for silicon or germanium.[143]

$$Me_3MOEt \ + \ n\text{-}BuSH \longrightarrow Me_3MSBu\text{-}n \ + \ EtOH \qquad [8]$$

However, the position of germanium in this situation is less clear. On the one hand, $(Me_2GeS)_3$ slowly undergoes hydrolysis in moist air[197] while $H_2S$ reacts readily with e.g. $(Me_3Ge)_2O$ to give $(Me_3Ge)_2S$ and $H_2O$. In addition, the equilibrium for the exchange reaction between thiosilanes and alkoxygermanes strongly favours the thiogermane and alkoxysilane.[198]

$Me_2Si(SMe)_2 + Me_2Ge(OMe)_2 \longrightarrow Me_2Si(OMe)_2 + Me_2Ge(SMe)_2$ [10]

Nevertheless, the reactions involving disilthianes and hydroxyl reagents, ROH, occur cleanly and readily as do those of the germoxy species with RSH and RSeH.

Alkylthio—silanes and -germanes have been prepared by the reaction of the appropriate halogeno—silane and -germane with MeSMgI,[93] MeSH in the presence of base[93,199] and NaSR[195]. The use of complex aluminates as synthetic reagents has been studied considerably.[128,134] These were extended to $Li[Al(ER)_4]$ to include a convenient preparation of alkylthiosilanes and an alternative preparation of alkylthiogermanes in high yields in a relatively short time.

The purity of the compounds was initially confirmed by $^1H$ n.m.r. spectroscopy. The first-order spectra (summarized in Table VIII.2) are consistent with the free rotation about the skeletal bonds. The $MeH_2M$- and $Me_2HM$- species gave the expected quartet-triplet and septet-doublet $^1H$ n.m.r. patterns. The alkyl group of the thio-entity in $Me_{\underline{n}}H_{3-\underline{n}}MSR$ ($\underline{n}$=1,2) did not couple, however, with the substituents attached to M as do those at M atom, when E=Se. Although structural information is not available, the long-range coupling appears to be dependent on the presence of fluorine atoms in the species $Me_{\underline{n}}H_{3-\underline{n}}SiOCH_2CF_3$ where $\underline{n}$=0,1,2, since the analogous coupling in $Me_{\underline{n}}H_{3-\underline{n}}SiOCH_2CH_3'$ is not observed. The chemical shifts of the germyl or silyl and methyl protons of $Me_{\underline{n}}H_{3-\underline{n}}M$

Table VIII.2 The $^{1}H$ n.m.r. parameters* of Group VI derivatives

| Compound | $\delta(Me)$ | $\delta(MH)$ | $\delta(CH_{\alpha})$ | J(CH) | J(SiH) | J(HH) | J(HF) | $\delta(CH_{\beta})$ |
|---|---|---|---|---|---|---|---|---|
| $H_3SiOMe^{a}$ | - | 4.50 | 3.41 | - | 216.2 | | | |
| $MeH_2SiOMe^{a}$ | 0.23 | 4.56 | 3.42 | - | 207.6 | | | |
| $Me_2HSiOMe^{a}$ | 0.12 | 4.60 | 3.39 | - | 200.5 | | | |
| $Me_3SiOMe^{a,b,d}$ | 0.04 | | 3.27 | 118.0 | - | | | |
| $Me_2Si(OMe)_2{}^{b,d}$ | 0.01 | - | 3.34 | 118.5 | - | | | |
| $MeSi(OMe)_3{}^{b,d}$ | 0.02 | - | 3.39 | 119.4 | - | | | |
| $Si(OMe)_4{}^{b,d}$ | 0.00 | - | 3.43 | - | - | | | |
| $H_3SiOEt^{c}$ | - | 4.48 | 3.60 | - | 218.1 | | | 1.13 |
| $Me_3SiOEt^{d}$ | 0.23 | - | 3.57 | 117.0 | - | | | 1.10 |
| $Me_2Si(OEt)_2{}^{d}$ | 0.20 | - | 3.66 | 118.0 | - | | | 1.12 |
| $H_3SiOCH_2CF_3{}^{c}$ | - | 4.62 | 3.89 | - | 221.9 | | 0.98 | |
| $MeH_2SiOCH_2CF_3$ | 0.35 | 4.70 | 3.91 | 123.6 | 217.1 | 3.42 | 0.92 | |
| $Me_2HSiOCH_2CF_3$ | 0.25 | 4.72 | 3.92 | 121.1 | 206.1 | 3.02 | 0.84 | |
| $Me_3SiOCH_2CF_3$ | 0.16 | - | 3.93 | 120.2 | - | | | |
| $H_3SiOCH_2CCl_3$ | - | 4.80 | 4.20 | - | 222.4 | | | |
| $MeH_2SiOCH_2CCl_3$ | 0.43 | 4.83 | 4.23 | 123.0 | 217.8 | 3.36 | | |
| $Me_2HSiOCH_2CCl_3$ | 0.31 | 4.79 | 4.17 | 121.3 | 207.0 | 2.97 | | |
| $Me_3SiOCH_2CCl_3$ | 0.22 | - | 4.19 | 120.6 | - | | | |
| $H_3GeOMe^{e}$ | - | 5.12 | 3.49 | - | - | | | |
| $MeH_2GeOMe'$ | 0.56 | 5.20 | 3.47 | | - | | | |
| $Me_2HGeOMe'$ | 0.45 | 5.28 | 3.45 | | - | | | |
| $Me_3GeOMe^{f}$ | 0.33 | - | 3.43 | 128.3 | - | | | |
| $H_3SiSMe^{g}$ | - | 4.29 | 2.02 | - | 218.9 | | | |
| $MeH_2SiSMe^{+}$ | 0.42 | 4.45 | 2.03 | 123.0 | 211.3 | 4.09 | | |
| $Me_2HSiSMe^{+}$ | 0.34 | 4.58 | 1.98 | 122.3 | 205.1 | 3.60 | | |
| $Me_3SiSMe^{+\,b,f}$ | 0.26 | - | 1.92 | 121.5 | - | | | |
| $MeHSi(SMe)_2{}^{+}$ | 0.49 | 5.01 | 1.99 | 124.2 | | 3.21 | | |
| $Me_2Si(SMe)_2{}^{b}$ | 0.35 | - | 1.84 | 122.3 | - | | | |

Con'd

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[+] Cyclohexane used as solvent and internal standard. [a] Ref.:187,188. [b] Ref.:140, 141. [c] Ref. 129. [d] Ref.BB.K. Hunter and L.W. Reeves, Can. J. Chem., 46, 1399 (1968). [e] Ref. G.A. Gibbon, Y. Rousseau, C.H. Van Dyke, and J. Mains, Inorg. Chem., 5, 114 (1966). [f] Ref. 139.

Table VIII.2. Con'd

| Compound | (Me) | (GeH) | J(HH) | J(CH) | (Me) | ($CH_2$) |
|---|---|---|---|---|---|---|
| $H_3GeSMe$ [g] | - | 4.48 | - | - | 2.05 | |
| $MeH_2GeSMe$ [h] | 0.65 | 4.77 | 3.52 | 130.7 | 2.11 | |
| $Me_2HGeSMe$ [h] | 0.56 | 4.86 | 3.24 | 129.5 | 2.04 | |
| $Me_3GeSMe$ [f,i] | 0.51 | - | - | 125.7 | 1.97 | |
| $Me_2Ge(SMe)_2$ [i] | 0.85 | - | - | 130.0 | 2.16 | |
| $MeGe(SMe)_3$ [i] | 1.26 | - | - | 132.0 | 2.38 | |
| $H_3GeSeMe$ [j] | - | 4.19 | - | - | 1.95 | |
| $MeH_2GeSeMe$ [j] | 0.74 | 4.46 | 3.50 | - | 1.88 | |
| $Me_2HGeSeMe$ [j] | 0.67 | 4.68 | 3.20 | 129.6 | 1.85 | |
| $Me_3GeSeMe$ [j,k] | 0.55 | - | - | 128.0 | 1.78 | |
| $H_3GeSEt$ | - | 4.50 | - | - | 1.31 | 2.59 |
| $MeH_2GeSEt$ | 0.63 | 4.67 | 3.42 | 130.5 | 1.29 | 2.56 |
| $Me_2HGeSEt$ | 0.54 | 4.88 | 3.06 | 129.0 | 1.28 | 2.54 |
| $Me_3GeSEt$ | 0.46 | - | - | 128.0 | 1.25 | 2.49 |
| $H_3GeSeEt$ | - | 4.15 | - | - | 1.44 | 2.58 |
| $Me_3GeSeEt$ | 0.53 | - | - | - | 1.37 | 2.46 |

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[g] Ref. J.T. Wang and C.H. Van Dyke, Inorg. Chem., 7, 1319 (1968).

[h] Ref. 105. [i] Ref. E.V.Van den Berghe, D.F. Van de Vondel and G.P. Van der Kelen, Inorg. Chim. Acta, 1, 97 (1967). [j] Ref.134. [k] Ref.134, 190.

*The spectra were recorded at room temperature in $CCl_4$ (ca. 5% v/v). Chemical shifts ($\delta \pm 0.02$ p.p.m.) are given in p.p.m. to the low field of internal tetramethylsilane (TMS).

show similar changes with substituent electronegativity as the halide series $Me_{\underline{n}}H_{3-\underline{n}}MX$ (X=F $\longrightarrow$ I, n=0 $\longrightarrow$ 3)[11,25,47,135]. Thus for any series, as E=O $\rightarrow$ S $\rightarrow$ Se, the value of $\delta$(MH) moves to higher field values consistent with a decrease in the inductive deshielding. The accompanying downfield shift in $\delta$(Me) may be related to anisotropic effects.[8,136] Additional confirmation of the molecular species came from vibrational, mass and X-ray photoelectron analysis, while the cleavage reactions of the M-E bonds with REH reagents confirmed their monomeric nature. The chalcogen species are all clear, colorless liquids, but aside from the oxides vile smelling.

The experimentally-determined computer-fitted binding energies for the silyl and germyl chalcogenide series are listed in Table VIII.3. The data are used as an aid for identification of the compounds. A more detailed study in relation to their structure and bonding mechanism is another research project. Nevertheless, it is important to make a few comments. The most striking feature of the binding energy data is the lack of any substantial shifts which parellels the results observed in the $(Me_{\underline{n}}H_{3-\underline{n}}M)_2E$ series. Inductive effects of the alkyl groups attached to the chalcogen atom on germanium and silicon may be anticipated via observation of the S $2p_{3/2}$ Ge 3d and Si 2p binding energies but the shifts are either small or within the experimental limits.

Table VIII.3. Observed binding energies of Group VI derivatives

| Compound | Core level |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Si 2p | C 1s | O 1s | $X^+$ | Ge 3d | C 1s | O 1s |
| $H_3MOMe$ | 1o7.63 | 292.18 | 537.97 |  | 37.74 | 292.09 | 537.90 |
| $MeH_2MOMe$ | 107.11 | 291.95<br>289.83 | 537.69 |  | 37.22 | 291.79<br>290.01 | 537.20 |
| $Me_2HMOMe$ | 106.81 | 291.83<br>289.65 | 537.52 |  | 37.09 | 291.49<br>289.78 | 536.99 |
| $Me_3MOMe$ | 106.57 | 291.38<br>289.44 | 537.30 |  | 36.82 | 291.47<br>289.66 | 536.84 |
| $MeHM(OMe)_2$ | 106.94 | 291.64<br>289.70 | 537.60 |  |  |  |  |
| $Me_2M(OMe)_2$ | 107.01 | 291.83<br>289.51 | 537.47 |  | 36.91 | 291.89<br>289.79 | 537.04 |
| $(Me_2MeOM)_2O$ | 107.10 | 291.82<br>289.51 | 537.34 |  |  |  |  |
| $MeM(OMe)_3$ | 107.55 | 291.89<br>289.54 | 537.63 |  | 37.33 | 291.71<br>289.77 | 537.14 |
| $M(OMe)_4$ | 107.87 | 291.97 | 538.10 |  | 38.07 | 292.09 | 537.70 |
| $H_3MOEt$ | 107.12 | 291.80<br>289.94 | 538.21 |  |  |  |  |
| $Me_3MOEt$ | 106.25 | 291.07<br>289.18 | 536.86 |  |  |  |  |
| $Me_2M(OEt)_2$ | 106.69 | 291.60<br>289.91 | 537.81 |  |  |  |  |
| $H_3SiOR$ | 107.70 | 293.60<br>290.31 | 538.94 | 694.20 |  |  |  |
| $MeH_2SiOR$ | 107.39 | 293.43<br>290.00 | 538.64 | 694.09 |  |  |  |
| $Me_2HSiOR$ | 107.07 | 292.91<br>289.85 | 538.43 | 693.99 |  |  |  |
| $Me_3SiOR$ | 106.80 | 292.60<br>289.60 | 538.12 | 693.80 |  |  |  |
| $MeHSi(OR)_2$ | 107.81 | 293.00<br>290.00 | 538.75 | 694.14 |  |  |  |
| $Me_2Si(OR)_2$ | 107.57 | 292.96<br>289.90 | 539.04 | 694.05 |  |  |  |
| $H_3SiOR'$ | 107.65 | 294.45<br>292.61 | 538.55 | 207.74<br>206.09 |  |  |  |
| $MeH_2SiOR'$ | 107.24 | 294.39<br>292.59<br>289.82 | 538.20 | 207.63<br>206.01 |  |  |  |
| $Me_2HSiOR'$ | 106.75 | 294.78<br>292.49<br>289.61 | 537.97 | 207.91<br>205.98 |  |  |  |
| $Me_3SiOR'$ | 106.58 | 294.12<br>292.38<br>289.35 | 537.84 | 207.62<br>205.81 |  |  |  |
| $CH_3CH_2OH$ |  | 291.63<br>290.22 | 538.49 |  |  |  |  |
| $CF_3CH_2OH$ |  | 292.99<br>289.82 | 539.79 | 694.20 |  |  |  |
| $CCl_3CH_2OH$ |  | 294.38<br>300.64 | 539.29 | 207.99<br>206.80 |  |  |  |
| $CH_2(SH)CH_2OH$ |  | 290.26 | 538.62<br>169.84 (S 2p)<br>168.65 |  |  |  |  |

Con'd.

$R=CH_2CF_3$ ; $R'=CH_2CCl_3$ ; $^+X$=F 1s or Cl $2p_{3/2}$

Table VIII.3. Con'd

| Compound | Core level | | | | | |
|---|---|---|---|---|---|---|
| | Si 2p | C 1s | S 2p$^{3/2}$ | Ge 3d | C 1s | E$^{+}$ |
| $H_3MSMe$ | 107.38 | 291.12 | 168.98 | 37.11 | 290.59 | 169.96<br>168.74 |
| $MeH_2MSMe$ | 107.05 | 290.71 | 168.96 | 36.95 | 291.93<br>290.55 | 169.73<br>168.62 |
| $Me_2HMSMe$ | 106.81 | 289.98 | 168.92 | 36.82 | 289.90 | 169.43<br>168.31 |
| $Me_3MSMe$ | 106.72 | 289.80 | 168.55 | 36.40 | 290.97<br>289.75 | 169.02<br>167.92 |
| $MeHM(SMe)_2$ | 106.81 | 290.24 | 169.32<br>168.35 | | | |
| $Me_2M(SMe)_2$ | 106.83 | 290.20 | 169.42<br>168.40 | 36.49 | 290.73 | 169.74<br>168.46 |
| $MeM(SMe)_3$ | | | | 36.52 | 290.81 | 168.21 |
| $H_3MSEt$ | 107.35 | 291.21 | 168.90 | 37.09 | 290.48 | 170.14<br>168.81 |
| $MeH_2MSEt$ | 106.92 | 291.10<br>290.00 | 168.95<br>168.62 | 36.91 | 290.46 | 169.26<br>168.43 |
| $Me_2HMSEt$ | 106.78 | 290.90<br>289.89 | 169.72<br>168.56 | 36.52 | 290.22 | 169.15<br>168.09 |
| $Me_3MSEt$ | 106.45 | 290.79<br>289.85 | 169.30<br>168.10 | 36.48 | 289.83 | 169.00<br>168.00 |
| $MeHM(SEt)_2$ | 106.95 | 290.62 | 169.01<br>168.23 | | | |
| $H_3MSeMe$ | | | | 37.12 | 290.85 | 61.15 |
| $MeH_2MSeMe$ | | | | 36.80 | 291.20<br>290.46 | 60.98 |
| $Me_2HMSeMe$ | | | | 36.53 | 289.92 | 60.70 |
| $Me_3MSeMe$ | | | | 36.27 | 290.83<br>289.84 | 60.35 |
| $CH_3CH_2SH$ | | 290.26 | 169.84<br>168.65 | | | |
| $(CH_3)_3CSH$ | | 289.86 | 169.36<br>168.18 | | | |
| $CH_3(CH_2)_2SH$ | | 289.96 | 169.31<br>168.41 | | | |
| $CH_3(CH_2)_3SH$ | | 290.86 | 169.71<br>168.51 | | | |
| $CH_3(CH_2)_4SH$ | | 289.71 | 169.66<br>168.37 | | | |
| $CH_3(CH_2)_5SH$ | | 289.66 | 169.46<br>168.76 | | | |
| $C_6H_5CH_2CH_2SH$ | | 289.36 | 169.16<br>168.56 | | | |

$^{+}$E=S 2p$^{3/2}$ or Se 3d

Resolution of the C 1s signal into separate peaks is best achieved for the oxygen series than for the fully methylated sulfur species. For the hydrido-sulfur series the separation is either small or not observed. In the case of $[Me_2(MeO)Si]_2O$ two peaks are observed for the C 1s level but only one for the O 1s level. There are marked changes in the binding energies of the carbon atom directly attached to F, Cl or H. With the $CX_3$ groups of the silicon series, the highest binding energy in general and hence relatively highest positive charge, resides on carbon attached to X. The increase of the binding energy for O 1s and Si 2p could indicate the greater stiffness of the molecule with fluorine relative to hydrogen.

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