1984

Structure of triiodo (methyl) germane and reactions of tellurium (IV) chlorides with some organosilanes.

Mary Kiang Hwa. Neo

University of Windsor

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L’AVONS REÇUE
STRUCTURE OF TRIIODO(METHYL)GERMANE
AND
REACTIONS OF TELLURIUM (IV) CHLORIDES
WITH SOME
ORGANOSILANES

by

Mary Kiang Hwa Neo

A Thesis
submitted to the Faculty of Graduate Studies
through the Department of Chemistry
in Partial Fulfillment of the requirements
for the Degree of Master of Science at
The University of Windsor

Windsor, Ontario, Canada
1984
ABSTRACT

The structure of $\text{MesGeI}_3$ is orthorhombic with space group $Pnma$, $a = 6.374(3)$, $b = 10.412(4)$, $c = 12.683(4)$ Å and $Z = 4$. It has been solved by direct methods and refined by full matrix least-square techniques to a conventional $R$ factor of 0.0791 for 653 unique reflections. The crystal structure contains discrete molecules with mirror symmetry which are separated by normal van der Waals distances. The mean Ge-I distance is 2.500(2).

The reactions of several organosilanes with $\text{TeCl}_4$ in benzene afford chlorinated silyl products and tellurium metal. Similar reactions with trichloro(aryl)tellurium proceed in two different ways. On stirring at room temperature for 6-8 h, diarylditellurides and chlorinated silanes are obtained while on refluxing for 6-10 h, dichloro(diaryl)tellurium and tellurium powder are obtained along with the chlorinated silanes. Dichloro(diaryl)tellurium do not react with organosilanes. A reaction mechanism involving a four center intermediate is proposed.
Dedicated to my parents, 父母, 蔡瑞英

and brother, Philip
ACKNOWLEDGEMENTS

I would like to sincerely thank my advisor, Dr. John E. Drake and Dr. Raj K. Chadha for their guidance and support throughout the present work. Special thanks are also extended to all my friends and members of the staff, especially technical and secretarial, for all their assistance during my stay in the department.

I would like to acknowledge the National Research Council of Canada for financial support, the Faculty of Graduate Studies for University of Windsor Graduate Awards and the Department of Chemistry for teaching assistantships.

Finally, I would like to thank my husband, Terry Robinson, for his patience and encouragement.
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</tr>
<tr>
<td>bkgd</td>
<td>background</td>
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<tr>
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<td>dd</td>
<td>doublet of doublet</td>
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</tr>
<tr>
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</tr>
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RT
s
sh
SP
t
temp
TMS
v
VP
w

room temperature
strong
singlet
shoulder
silicon product
triplet
temperature
tetramethyldisilane
very
vapor pressure
weak
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CHAPTER ONE

STRUCTURE OF TRIIODO(METHYL)GERMANE
1.1 INTRODUCTION

The first indepth studies carried out on the halogeno-(methyl)germanes of the type $M_n GeX_{4-n}$ ($X = Cl, Br, n = 1 - 3$) were vibrational studies involving only infrared spectroscopy. The methyl-germanium bands or germanium-carbon stretching modes in the above mentioned compounds were studied in detail between 1953 and 1964 by Lippincott and Tobin (1), Stafford and Stone (2), Brown, Okawara and Rochow (3), Schmidbauer and Hussek (4), Aronson and Durig (5), Griffiths (6) and Batuer, Ponomarenko, Matvecua and Uzenhovo (7). Reports on the vibrational spectra of the iodo- and fluoro- species were limited to a mention in an article by Cross and Glocking (8). More thorough vibrational studies (9-14) of the halogeno-(methyl)germanes involving both infrared and Raman spectroscopy were done after 1964. These studies included the series of halogeno(ethyl)germanes (15), halogeno(phenyl)germanes (16-19) and halogeno(vinyl)germanes (20). A detailed vibrational study of triiodo(methyl)germane was first done by Durig et. al. (21) and later improved by Hemmings (22). The fact that both Durig and Hemmings assumed all the angles in the molecule to be tetrahedral in their normal coordinate analyses only serves to show the need for a direct structural investigation of the compound.

Some time ago, the gas phase structures of the series of halogeno(methyl)germanes, $M_n GeX_{4-n}$, ($X = F$ (23), $Cl$ (24), $Br$ (25); $n = 1, 2$) were examined by electron diffraction. In
the structural determinations of $\text{Me}_2\text{GeF}_2$ and $\text{MeGeF}_3$, $\text{Me}_2\text{GeCl}_2$
and $\text{MeGeCl}_3$ and $\text{Me}_2\text{GeBr}_2$ and $\text{MeGeBr}_3$, it was found that the
bond lengths and valence angles varied with the number of halogen(X) atoms. When successive halogens were substituted
for methyl groups, both the Ge–C and Ge–X bonds became shorter and the angles deviated from that of the tetrahedron. The
observed trends in the Ge–C bond length suggested that the change had very little dependence on the species of halogen
atom. In the trihalides, $\text{MeGeX}_3$, $r(\text{Ge–C}) = 1.904(2)$ (F), 1.893(10) (Cl) and 1.889(32) (Br), while in the dihalides,$\text{Me}_2\text{GeX}_2$, $r(\text{Ge–C}) = 1.928(3)$ (F), 1.924(6) (Cl) and 1.911(10) (Br). The overall larger variation in bond length depended on
the number of halogen atoms, not on whether they were F, Cl or Br. The bond angles also remained constant for changing
halogen but altered considerably when the number of halogens was altered. Thus the angles in the dihalides were: $\text{XGeX} \sim$
$105^\circ$, $\text{CGeX} \sim 107^\circ$, while those in the trihalides were: $\text{XGeX} \sim 106^\circ$ and $\text{CGeX} \sim 112^\circ$ (More specific values are given
in Table 1.5).

Because of the lack of sufficient volatility for the iodides, an inclusion of them in the above mentioned studies
was not possible. To date, only two reports on crystal structure determination of compounds containing germanium-iodine
bonds, namely $\text{Ge}_4\text{S}_6\text{I}_4$ (26) and $\text{Ge}_4\text{Ph}_8\text{I}_2$ (27) have been made. An equally small number of studies on compounds containing
germanium-iodine bonds have been done through electron
diffraction. These studies include compounds such as GeI₂
(28), C₂H₂GeI₂ (29), GeI₄ (30, 31) and C₄H₄Ge₂I₄ (32). Therefore it seemed appropriate to try to obtain the structures
of at least one iodo(methyl)germane for the purpose of compara-
ing its geometry with the other halogeno(methyl)germanes
previously studied. We have successfully obtained the X-ray
diffraction data on the low melting, easily sublimable MeGeI₃
of sufficiently good quality to make a report on its structure
worthwhile.

1.2 PREPARATION OF TRIIODO(METHYL)GERMANE

1.2.1 The Vacuum Line

The vacuum line technique first used by Farkas and
Melville (33) and later by Sanderson (34) was developed by
Stock (35) in his classic work on silicon and boron hydrides.
It has been successfully extended by subsequent workers (36-
38) to deal with a wide variety of compounds. The technique
is particularly suited to the preparation of triiodo(methyl)-
germane because of its adaptability to the preparation of
chemical compounds which involve gaseous reactants (HI in
this particular case) and its ability to handle moisture and
oxygen sensitive compounds. Other advantages include the
study of compounds which are highly toxic and disagreeable
in odor.
Figure 1.1 The vacuum line
A conventional but highly adaptable Pyrex-glass vacuum line is shown in Figure 1.1. The line shown consisted of two manifolds (B1 and B2, volume ca. 150ml each) which were attached to a main manifold (B) and interconnected by four U-traps. The main manifold was connected to the pumping system and to a Pirani gauge (P). Pressure readings between 1-760 Torr were monitored by mercury manometers (M), while the Pirani gauge recorded pressures below 1 Torr. A pressure of 1.0 x 10⁻² Torr was maintained throughout this work, that being more than adequate for the compound under study. The pumping system consisted of a mechanical rotary pump (Edwards High Vacuum, Crawley, U.K.) and a glass mercury diffusion pump (D) with two liquid-nitrogen "backing" traps (T).

1.2.2 The Separation of Volatile Materials

Efficient separation of the volatile components of a mixture was done by trap-to-trap distillation using the various slush baths listed in Table 1.1. It should be emphasized that the efficiency of the separation was affected by factors such as the quantity and relative composition of the distillate, the rate of distillation, the condensation surface and the system's vacuum (36-38). Thus the trap temperatures quoted are therefore only one of the factors determining the course of a particular separation.
Table 1.1 Low temperature slush baths*

<table>
<thead>
<tr>
<th>Material</th>
<th>Slush temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice-water†</td>
<td>0</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>-23</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>-45</td>
</tr>
<tr>
<td>chloroform</td>
<td>-63</td>
</tr>
<tr>
<td>&quot;dry ice&quot;-acetone†</td>
<td>-78</td>
</tr>
<tr>
<td>toluene</td>
<td>-96</td>
</tr>
<tr>
<td>1-bromobutane</td>
<td>-112</td>
</tr>
<tr>
<td>methyl cyclohexane</td>
<td>-126</td>
</tr>
<tr>
<td>n-pentane</td>
<td>-132</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>-160</td>
</tr>
<tr>
<td>liquid nitrogen</td>
<td>-196</td>
</tr>
</tbody>
</table>

* The indicated slush temperatures (± 5°) were achieved by cooling the materials listed (except those marked †) with liquid nitrogen.

1.2.3 Storage and Reaction Vessels

The vessels used in this work are shown in Figure 1.2. These were constructed of Pyrex-glass, the design chosen being dictated by the volatility, thermal stability and quantity of the compound in question. In subsequent sections, the type of vessel used will be designated by letter identification.
A Storage vessel—(250-1000 ml capacity) used to store gases which are stable at room temperature (e.g. HI). The vessel is fitted with a MS 19 ball-joint for attachment to the vacuum line and a greased or greaseless stopcock (4-6 mm).

B Storage or reaction vessel (10-100 ml capacity) equipped with a MS 19 ball-joint and Teflon-in-glass stopcock. Used in reactions where the internal pressure did not exceed 1 atmosphere.

C Reaction vessel (50-300 ml capacity) equipped with a MS 19 ball-joint and used for reactions which are dependent on surface area.

C' The same as vessel "C", but with two or three necks to fit a dropping funnel (used in the preparation of HI).

D Drawn tube (ca. 2 mm o.d.) with a MS 19 ball-joint; used for collecting small samples for NMR. Samples were sealed 5-7 cm from the bottom.

E Tube breaker, equipped with a MS 19 ball-joint and a greased (6 mm tap). Used for the recovery of samples in semi-micro tubes or ampules.

F Gas-cell, fitted with a MS 19 ball-joint, Teflon-in-glass stopcock and CsI plates. Used for recording IR spectra of volatile compounds.
Figure 1.2 Storage and reaction vessels
1.2.4 Instrumentation and Physical Methods

(a) **Infrared Spectroscopy (IR):** For gases, a gas cell of 90 mm path length, fitted with CsI plates (4000-200 cm\(^{-1}\)) was used. This had a small finger which permitted liquids of low volatility to be directly distilled into the cell. Solids or involatile liquids were recorded as smears or mulls between CsI plates in an air-tight holder. The Beckman IR-12 and Perkin Elmer Spec 180 spectrometers were used. Their calibration was checked periodically against the 3027.1, 1601.4 and 1028.0 cm\(^{-1}\) bands of the polystyrene spectrum. Data were accurate to ± 1 cm\(^{-1}\).

(b) **Proton Nuclear Magnetic Resonance Spectroscopy (NMR):** The NMR spectra were recorded using a Varian EM-360 or a JEOL C-60HL NMR spectrometer operating at 60 MHz. Liquid samples were sealed in Pyrex-glass capillaries (ca. 2 mm o.d.) and placed in standard NMR tubes with CCl\(_4\) (to ensure good sample homogeneity) and tetramethylsilane (TMS) as an external standard. TMS was added directly to the solution when solid samples were dissolved in CCl\(_4\) in a standard NMR tube. On such occasions the sample was either prepared in a dry box or on a vacuum line where the tube was sealed before removal.

(c) **Melting points (mp)** were determined using Stock's plunger technique (35).

(d) **Vapor pressures (VP)** were measured using vapor pressure thermometers constructed as described by Stock (35) and a
capillary difference-manometer. The compound under investigation was distilled into a small finger and allowed to expand against the mercury column; the finger was immersed in various slush baths, the exact temperature being determined by the vapor pressure thermometer.

1.2.5 The Preparation and Purification of Starting Materials

The compounds listed below were used as starting materials in the preparation of triiodo(methyl)germane, or as spectroscopic standards. They were either obtained commercially or had well-established preparative routes. Their purity was checked by NMR and IR spectroscopy. Commercial suppliers are listed at the end of this section.

Carbon tetrachloride, CCl₄, and Carbon disulphide, CS₂: commercial, "spectral grade", distilled and stored in vessel "B" at RT. Purity checked by IR and VP (39).

Hydrogen iodide, HI: Although HI may be obtained by pumping on hydroiodic acid through a trap held at -78°C, it was quickly and efficiently prepared as follows (40). A reaction vessel "C" (250 ml; containing a stirring bar and fitted with a dropping funnel) was charged with red phosphorus (10g, 0.32mol) or with phosphorus pentoxide (40g, 0.28mol). The adapter to the vacuum line was plugged with glass wool to reduce contamination of the line with iodine vapor. The system was evacuated and a solution consisting of iodine (4g, 0.016mol) and hydroiodic acid
(ca. 50 ml) was added in a dropwise manner. The reaction was carried out at room temperature and HI was collected in a pure state at -196 °C, after first passing through traps held at -23 °C and -78 °C. The gas was then stored at RT in vessel "A"; IR (41, 42); VP (39).

**Hydroiodic acid, HI:** commercial\(^b\); 48% aqueous solution. Used as supplied.

**Iodine, I\(_2\):** commercial\(^c\); resublimed and degassed at -78 °C prior to use.

**Phosphorus pentoxide, P\(_2\)O\(_5\):** commercial\(^d\); stored and used as received.

**Tetramethylsilane, Me\(_4\)Si (TMS):** commercial\(^b\); NMR grade solvent; stored in vessel "B".

**Trichloro(methyl)germane, MeGeCl\(_3\):** commercial\(^e\); degassed at -78 °C before use; IR (5); NMR (43).

**Commercial Suppliers:**


c. The British Drug House Ltd., Poole, Dorset, Eng.


1.2.6 The Preparation of Triiodo(methyl)germane

When triiodo(methyl)germane was synthesized directly from elemental germanium and methyl iodide, it was found that the yield was affected by the size of the germanium used, the flow rate of the alkyl halide and the presence of a catalyst. When MeI was introduced at a flow rate of 4 ml/h onto a Ge sponge deposited on Penski rings at 360 °C, it was found that the yield was very poor indeed (44). The yield was improved when 50 µm particles of Ge and Cu, Ag or Pt were used as catalysts (45). An approximately 25% yield was obtained when the flow rate of MeI was increased to 100 drops/min and Cu was used as a catalyst (46).

The first detailed report of the synthesis of triiodo-(methyl)germane was done in 1950 (47). Nearly quantitative yields were obtained by allowing GeI$_2$ and MeI to react in a sealed tube at 110 °C for 24 h (47). Prolonged heating in a sealed ampule was not required when a mixture of 57% hydroiodic acid was added to the mixture of GeI$_2$/MeI (48) although the yield was reduced.

Triiodo(methyl)germane was also a minor product in the reaction of MeGeH$_3$ with BI$_3$, I$_2$ and HI (49), as it was in the reaction of HGeCl$_3$ with MeI (48). The ether complex of HGeI$_3$ gave triiodo(methyl)germane, in 47% yield, on reaction with CH$_3$I (50). Triiodo(methyl)germane was obtained in 52% yield when a mixture of GeI$_4$ and MeI in toluene was heated in the presence of Cu for 8 h (51). The NMR of the product mixture
resulting from the oxidative addition of MeI to Ge(OEt)_2. EtOH indicated the formation of MeGeI_3 along with mixed species such as MeGe(OEt)I_2 (52).

High yields of MeGeI_3 can be conveniently obtained (22, 53) by reacting excess hydrogen iodide with trichloro-(methyl)germane. Typically, MeGeCl_3 (ca. 1.1 mmol) and HI (ca. 4 mmol) were condensed into a reaction vessel "C" (50 ml) at -196 °C and allowed to warm to room temperature. The reaction was complete after an hour when infrared analysis showed the only volatile compounds to be hydrogen chloride (ca. 3.3 mmol) condensing in a trap held at -196 °C and hydrogen iodide (ca. 0.7 mmol) condensing in a trap held at -126 °C. The pale yellow crystals left in the reaction vessel were then purified by sublimation and subsequently shown from the melting point (45 °C, lit. (47) 45 °C) and the absence of proton containing impurities in the NMR spectrum (δ Me 2.80 ppm (g), lit. (54) δ Me 2.61 ppm (g)) to be pure MeGeI_3.

The IR spectrum in the region of 4000-200 cm⁻¹ was recorded with the sample (as a CsI smear) held between CsI plates in an air-tight liquid-cell. The IR (22) spectrum shown in Figure 1.3 gives the following bands in cm⁻¹: 3135 vw, 3000 m, 2920 m, 2845 vw, 2440 w, 2040 w, 1835 m, 1395 s, 1228 m, 1195 vw, 875 br, sh, 810 s, 630 w, sh, 600 s, 453 w, 260 s, 250 s and 204 s.
Figure 1.3 The infrared spectrum of Me3I2 (CS2 smear)
1.3 CRYSTAL STRUCTURE OF TRIODO(METHYL)GERMANE

1.3.1 Data Collection

An initial attempt to collect data (55, 56) using a crystal attached to a thin glass fibre failed because of crystal sublimation at room temperature (23 ± 2 °C) within a short period. A second crystal with approximate dimensions (0.27 x 0.46 x 0.58 mm) was then sealed in a thin-walled capillary at random orientation in a cold room (−20 ± 2 °C) and used for subsequent data collection which was done at 17 ± 2 °C. The data were collected on a Syntex P2 four-cycle automated diffractometer controlled by a Nova 1200 computer. The diffractometer, at a take-off angle of 6.1°, was equipped with a molybdenum X-ray tube and a highly oriented graphite monochromator (λ = 0.71069 Å, 2θm = 12.2°) and operated at 50 kV and 20 mA.

The determination of the unit cell parameters was accomplished by the following procedure:

(a) A random-orientation photograph was taken with 2θ = ω = Χ = 0° and the φ axis rotating at 234° min⁻¹. The x, y film coordinates for 8 reflections were entered for a centering reflection routine and then the program was set to search for a particular reflection by calculating 2θ and Χ, assuming ω = 0. The value of φ was determined by rotating around φ at low speed until a peak with intensity greater than 10³ counts s⁻¹ was found. The centering program found the refined values
of 2θ, θ and ω angles and those values were used in the subsequent autoindexing program, which produced a list of axial vectors and the angles between those vectors from which the unit cell dimensions were selected according to the standard symmetry rules. The three axial photographs which were taken about each of the three chosen axes of the cell displayed m symmetry and confirmed the orthorhombic system; all three axes selected were found, by inspection to be true solutions rather than submultiples of the true axial lengths.

(b) After the initial cell parameters were established, a unique set of data in the shell defined by 15° < 2θ < 30° was next collected at a fast scan rate (29.3° min⁻¹). From the data, 15 strong reflections widely separated in the reciprocal space were selected. Their refined angular values were used in the least squares refinement program, which gave the final cell constants and the orientation matrix for data collection.

(c) The intensity data (for th, tk and tl) were collected at a variable scan rate of 2-5° min⁻¹ via a θ(crytal)-2θ-(counter) scan using bisecting geometry with the scan from (2θ (MoKα₁ (0.70926 Å)) - 1.0°) to (2θ (MoKα₂ (0.71354 Å)) + 1.0°) in the 2θ range of 4-50°. Background (B₁ and B₂) were measured at the beginning and the end of the scan, each for 25% of the time of the scan. The stability of the system and the crystal was monitored by measuring three strong check
reflections (031, 122, 113) after every 50 data; the intensities of these reflections decreased by approximately 2.5% during the course of data collection (i.e. over 25 hours of beam time); and this was corrected for by applying an appropriate scaling factor during data reduction. An examination of the data showed systematic absences (0kl, k + 1 = 2n + 1; hko, h = 2n + 1) consistent with either of the space groups Pnma (No. 62) (57) or Pn2_1a (non-standard setting of Pna2_1 (No. 33)). The net intensity (I) and its standard deviation \(\sigma(I)\) were calculated from equations (1.1) and (1.2) respectively.

\[
I = SC - \tau (B_1 + B_2) \tag{1.1}
\]

\[
\sigma(I) = (SC + (B_1 + B_2) + \rho^2 \tau^2)^{1/2} \tag{1.2}
\]

where \(SC\) = count during the scan

\(\tau\) = ratio of scan time to background time

(\(\approx 2.0\text{ for triiodo(methyl)germane}\))

\(\rho\) = ignorance factor (\(\approx 0.05\) in the present work).

From the intensity of the reflections the structure factors \(|F_0|\) were calculated according to equation (1.3) and its standard deviation \(\sigma|F_0|\) was given by equation (1.4).

\[
|F_0| = (I/L_p)^{1/2} \tag{1.3}
\]

\[
\sigma|F_0| = \sigma(I)/2|F_0|L_p \tag{1.4}
\]

The \(L_p\) factor for a monochromator in the equatorial mode was given by equation (1.5); the equation assumes that...
the graphite

\[
L_p = \frac{0.5}{\sin \theta} \left( \frac{1 + (\cos^2 \theta_m) (\cos^2 2\theta)}{1 + \cos^2 2\theta_m} \right) + \\
\left( \frac{1 + \left| \frac{\cos 2\theta_m}{\cos 2\theta} \right| \cos^2 2\theta}{1 + \left| \cos 2\theta_m \right|} \right)
\]  (1.5)

monochromator is 50% mosaic and 50% perfect. The monochromator angle \(2\theta_m\) is 12.2° for \(MoK\alpha\) radiation. Absorption corrections (\(\mu = 137.62\) cm\(^{-1}\) for \(MoK\alpha\) radiation) were made based on the dimensions and crystal face assignments (100, \(\overline{1}00\), 01\(\overline{1}\), 011, 0\(\overline{1}1\), 10\(\overline{1}\), 101, 1\(\overline{1}\)0, 110). The resulting absorption correction factors ranged from 17.175 to 64.585.

Since \(MeGeI_3\) is extremely soluble in almost all organic solvents; its density could not be determined. Other pertinent details of the crystal and data collection are provided in Table 1.2.

1.3.2 Structure Determination and Refinement

Programs used during the structural analysis include local versions of CHECK(check reflections), PROC(data reduction), ABSORB(analytical absorption correction), SHELX 77(full matrix least square refinement and Fourier Synthesis), Xanadu (bond length and angle calculations) and ORTEP (thermal ellipse-ellipsoid plotting program). Scattering factors including anomalous dispersion corrections for I and Ge were
Table 1.2 Crystallographic Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>6.374(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.412(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.683(4)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>841.8(5)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Mol. wt.</td>
<td>468.3</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρc (g cm⁻³)</td>
<td>3.695</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα, λ = 0.71069 Å</td>
</tr>
<tr>
<td>Monochromator</td>
<td>highly oriented graphite</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>Abs coeff, μ (cm⁻¹)</td>
<td>137.62</td>
</tr>
<tr>
<td>Min abs corr</td>
<td>17.175</td>
</tr>
<tr>
<td>Max abs corr</td>
<td>64.585</td>
</tr>
<tr>
<td>2θ angle (°)</td>
<td>4-50</td>
</tr>
<tr>
<td>Scan type</td>
<td>coupled θ (crystal)/2θ(counter)</td>
</tr>
<tr>
<td>Scan width</td>
<td>Kα₁-1° to Kα₂ + 1°</td>
</tr>
<tr>
<td>Scan speed (°min⁻¹)</td>
<td>variable, 2.02-4.88</td>
</tr>
<tr>
<td>Bkgd time/scan time</td>
<td>0.5</td>
</tr>
<tr>
<td>Total reflns measd</td>
<td>915(+h, +k, +l)</td>
</tr>
<tr>
<td>Unique data used</td>
<td>653 with (I &gt; 3σ(I))</td>
</tr>
<tr>
<td>No. of parameters (NP)</td>
<td>29</td>
</tr>
<tr>
<td>R</td>
<td>0.0791</td>
</tr>
<tr>
<td>RWF</td>
<td>0.0852</td>
</tr>
</tbody>
</table>
obtained from Ibers and Hamilton (57).

The structure was solved by the direct method using 130 reflections (E > 1.2) with the program SHELX and assuming the lower symmetry space group Pn\bar{a}1a. Iodine and germanium atoms were found from the E-map from the solution with the best overall figure of merit and the carbon atom was obtained by the difference Fourier synthesis. No attempt was made to include H atoms in the refinement as they were not visible in the final difference Fourier map.

Upon refinement of the structure by the full matrix least squares method, a mirror symmetry was found to be present in the molecule. Hence, the space group Pnma was subsequently used. The choice was confirmed by successful structure refinement and convergence was obtained at R = 0.0791 and R_{wF} = 0.0852 for 653 unique "observed (I > 3\sigma(I))" reflections using equations (1.6) and (1.7) respectively.

\[
R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad (1.6)
\]

\[
R_{wF} = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}
= \left[ \frac{\sum w \Delta^2}{\sum w|F_o|^2} \right]^{1/2} \quad (1.7)
\]

In the final two cycles of refinement, the largest shift/error ratio was 0.1, and the final difference map had a few
peaks with intensities up to 2.0 eÅ⁻³, which were unconnected to the molecule and were without any chemically feasible connectivity. These peaks probably arose because absorption correction could not be effectively applied for the following reasons:

(i) due to the irregular shape of the crystal, an accurate measurement of the crystal was not possible,
(ii) the crystal size was unusually large and
(iii) the absorption coefficient was large due to the presence of three iodine atoms in the molecule. The function

\[(|F_o| - |F_c|)^2\]

was minimized during the least squares refinement. Unit weights (w) were used in the initial stages and in the final stages, a weighting scheme of the form:

\[w = \frac{1}{\sigma^2|F_o| + pF_o^2}\]  

was employed with a final p value of 0.0096. A few low angle reflections were found to be affected by secondary extinction. An empirical isotropic extinction parameter, x, was used employing the equation:

\[F_c = F_o (1 - 0.0001x (F_o^2 / \sin \Theta))\]

and refined to a value of 0.00247.

Final fractional coordinates and thermal parameters for non-hydrogen atoms are given in Table 1.3 and interatomic distances and bond angles in Table 1.4. Figure 1.4 illustrates the unit cell packing. A list of calculated and observed
Table 1.3 Final fractional coordinates and thermal parameters for non-hydrogen atoms of MgGeI₃ with standard deviations in parentheses

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.02478(3)</td>
<td>0.2500</td>
<td>0.6399(1)</td>
<td>0.0892(12)</td>
<td>0.0831(14)</td>
<td>0.0374(10)</td>
<td>0.0</td>
<td>-0.0058(6)</td>
<td>0.0</td>
</tr>
<tr>
<td>(2)</td>
<td>0.2848(2)</td>
<td>0.4429(1)</td>
<td>0.3651(1)</td>
<td>0.0877(10)</td>
<td>0.0599(9)</td>
<td>0.0660(10)</td>
<td>0.0102(5)</td>
<td>-0.0009(5)</td>
<td>-0.0147(5)</td>
</tr>
<tr>
<td>He</td>
<td>0.1289(3)</td>
<td>0.2500</td>
<td>0.4518(1)</td>
<td>0.0505(11)</td>
<td>0.0495(11)</td>
<td>0.0379(11)</td>
<td>0.0</td>
<td>-0.0029(7)</td>
<td>0.0</td>
</tr>
<tr>
<td>Ne</td>
<td>-0.1722(33)</td>
<td>0.2500</td>
<td>0.4443(23)</td>
<td>0.045(10)</td>
<td>0.078(15)</td>
<td>0.096(20)</td>
<td>0.0</td>
<td>-0.005(10)</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 1.4 Interatomic distances (Å) and angles (°)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-I(1)</td>
<td>2.502(2)</td>
<td>I(1)-Ge-I(2)</td>
<td>107.4(1)</td>
</tr>
<tr>
<td>Ge-I(2)</td>
<td>2.497(2)</td>
<td>I(2)-Ge-I(2)*</td>
<td>107.1(1)</td>
</tr>
<tr>
<td>Ge-C</td>
<td>1.92(2)</td>
<td>I(1)-Ge-C</td>
<td>110.5(2)</td>
</tr>
<tr>
<td>I....I'</td>
<td>4.238(2)</td>
<td>I(2)-Ge-C</td>
<td>112.1(4)</td>
</tr>
</tbody>
</table>

symmetry equivalent position: *x, .5-y, z.
Figure 1.4 Packing diagram showing the contents of the unit cell
structure factors is available as supplementary material.

1.3.3 Discussion

The structure determination shows that MgGeI₃ has a distorted pseudo-tetrahedral geometry. The exact symmetry of the molecule is m (1y axis); deviations from the idealised C₃ᵥ symmetry are very small and insignificant as can be seen from Table 1.4. A comparison of the bond angles and distances of MgGeI₃ with the other trihalides of the series, as shown in Table 1.5, reveals that XGeX and CGeX bond angles are very similar for X = Br and I, although there is a clear trend of an increase in XGeX angle and decrease in CGeX angle along the series fluoride to iodide. According to Bent's rule (58-60) "more electronegative substituents 'prefer' hybrid orbitals having less s-character". This would predict that the FGeF angle should be less than the IGeI angle with the chlorides and bromides falling in between. The trend is clear but small suggesting that the effective difference in electronegativities of the halogens is less than expected when attached to germanium. This was proposed in ESCA studies of the halogeno(methyl)germanes (61). It should be pointed out that even with the largest halogen, the XGeX angle is less than 109° whereas the CGeX angle is larger than 109°. The average Ge-I distance of 2.500(2) Å is in good agreement with 2.48(3) and 2.50(3) Å in GeI₄ (30,31), 2.51(2) and 2.52(1) Å
in $\text{C}_2\text{H}_2\text{GeI}_2$ (29), 2.48 and 2.49 Å* in $\text{C}_4\text{H}_4\text{Ge}_2\text{I}_4$ (32),
2.490(1) Å in $\text{Ge}_4\text{S}_6\text{I}_4$ (26) and 2.559(1) Å in $\text{Ge}_4\text{Ph}_8\text{I}_2$ (27).
The Ge-I distances quoted for the compounds $\text{Ge}_4\text{S}_6\text{I}_4$ and
$\text{Ge}_4\text{Ph}_8\text{I}_2$ were obtained through crystal structure studies
while those quoted for the compounds $\text{C}_2\text{H}_2\text{GeI}_2$, GeI$_4$ and
$\text{C}_4\text{H}_4\text{GeI}_4$ were obtained through electron-diffraction studies.
By contrast the Ge-I bond, also obtained through electron-
diffraction, is much longer in GeI$_2$ (28) with reported
distances of 2.82, 2.88 and 3.14 Å.* The molecules in the
crystal are essentially independent with the shortest inter-
molecular I...I' distances of 4.238(2) Å being comparable
to the van der Waals distance of 4.30 Å.

* Standard deviation were not given in the original papers.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
<th>Ge-C</th>
<th>Ge-X</th>
<th>X-Ge-X</th>
<th>C-Ge-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeGeF₃</td>
<td>(23)</td>
<td>1.904(2)</td>
<td>1.714(2)</td>
<td>105.5(2)</td>
<td>113.2(6)</td>
</tr>
<tr>
<td>MeGeCl₃</td>
<td>(24)</td>
<td>1.893(10)</td>
<td>2.132(4)</td>
<td>106.4(7)</td>
<td>112.3(9)</td>
</tr>
<tr>
<td>MeGeBr₃</td>
<td>(25)</td>
<td>1.889(32)</td>
<td>2.276(2)</td>
<td>107.1(4)</td>
<td>111.6(3)</td>
</tr>
<tr>
<td>MeGeI₃*</td>
<td>this work</td>
<td>1.92(2)</td>
<td>2.500(2)</td>
<td>107.2(1)</td>
<td>111.3(6)</td>
</tr>
</tbody>
</table>

*mean values
CHAPTER TWO

REACTIONS OF TELLURIUM (IV) CHLORIDES

WITH SOME

ORGANOSILANES
2.1 INTRODUCTION

The elements of the Group VI of the Periodic Table, sulfur, selenium, tellurium, and polonium are collectively referred to as the chalcogens. These elements have outer electronic configurations of $\text{ns}^2\text{np}^4$, and thus it is not surprising that their chemistry is predominantly non-metallic with a gradually increasing metallic character progressing down the group. The trend is most clearly shown in the decreasing electronegativity, specific resistivity and first ionisation potential of the elements as the atomic number increases in the group.

Of the various organic compounds of chalcogens, the most widely studied class is that of organosulfur. Organoselenium chemistry has been studied mostly as an extension of organosulfur chemistry and it has been used mainly for comparison between sulfur and selenium. Compared to organoselenium chemistry not much is known about the organotellurium field. The first reactions of tellurium (IV) compounds with organic substrates were studied as early as 1826 by Berzelius (62). These organic derivatives have been reviewed by Day [1928] (63), Morgan [1935] (64), Nesmeyanov [1945] (65), Rheinboldt [1955] (66), Abrahams [1956] (67), Campos [1960] (68), Petragnani and Campos [1967] (69), Abel and Armitage [1967] (70), Irgolic and Zingaro [1970] (71), Cooper [1971] (72) and Irgolic [1974-1980] (73-79).

Most of the above work has been carried out from the
point of view of synthetic utility. Several authors have reported results where TeCl₄ and RTeCl₂ are known to act both as chlorinating and tellurating agents (73, 80-91). For example, TeCl₄ reacts with olefins to give monochloro or dichloro derivatives as the major products via addition (80-85), while with aromatic compounds bearing activating substituents, it gives para substituted RTeCl₃ and R₂TeCl₂ via electrophilic aromatic substitution (86-91). Campos and Petragnani (83) found that when TeCl₄ was added to cyclohexene, trichloro(2-chlorocyclohexyl)tellurium was obtained.

\[
\text{Cl}(-) \text{TeCl₃} + \frac{\text{Olefin}}{\text{TeCl₃} + \text{Cl}^-}
\]

\[
\text{Cl}^- \text{TeCl₃} \rightarrow \text{Cl}^- \text{H} \quad \text{TeCl₃} \quad \text{H} \quad \text{TeCl₃}
\]

(I)

\[
\text{Cl}^- \text{H} \quad \text{TeCl₃} \quad \text{H} \quad \text{TeCl₃}
\]

(2.1)

The mechanism, probably via a cyclic telluronium ion intermediate (I), gives rise to racemic trans products. The reaction, however, cannot be considered general since some simple olefins do not react with TeCl₄ while others by reduction produce elementary tellurium. Later work (82) done with equimolar proportions of TeCl₄ and 2,2-diphenyl-penten-4oic.
acid (II, \( R = \text{C}_6\text{H}_5 \)) produced a white viscous residue from which no definite compound was isolated. On the other hand, when molar ratios of 2:1 were used, dichloro(di-[5-(2,2-diphenyl-4-valerolactone)]tellurium (IV) was formed.

\[
\begin{align*}
\text{TeCl}_4 + \text{CH}_2=\text{CH}-\text{CH}_2 & \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2 \text{Cl-Te-CH}_2-\text{CH}-\text{CH}_2 \\
(\text{II}) & \rightarrow (\text{III})
\end{align*}
\]

\[
(\text{II}) + (\text{III}) \rightarrow \begin{align*}
\text{CH}_2-\text{CH}-\text{CH}_2 \text{Te-CH}_2-\text{CH}-\text{CH}_2 \\
\text{R} \text{C} \text{C} \text{C} \text{Cl} \text{Cl} \\
\text{O} \text{C} \text{C} \text{R} \text{R}
\end{align*}
\]

(IV) (2,2)

The result was in accordance with the increased reactivity of double bonds activated by carboxyl participation, since the possible trichloride intermediate (III) reacted with excess of the unsaturated compound producing the dichloride (IV).

\( \text{TeCl}_4 \) and \( R\text{TeCl}_3 \) also react with arylsilanes to give para substituted condensation products if the substituent on the aromatic ring is activating (92).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3 + \text{TeCl}_4 & \xrightarrow{12 \text{ h}} \text{I}_2 \text{ h} \text{toluene} \\
p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{TeCl}_3 + \\
- \text{HCl} & \quad (p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4)_2\text{TeCl}_2
\end{align*}
\]

(2.3)
When the silyl substituent is directly bonded to the phenyl ring, electrophilic aromatic substitution at the ipso position occurs (93).

\[
RC_6H_4SiMe_3 + TeCl_4 \xrightarrow{-Me_3SiCl} RC_6H_4TeCl_3 \quad (2.4) \\
RC_6H_4SiMe_3 + R'C_6H_4TeCl_3 \xrightarrow{-Me_3SiCl} RC_6H_4TeCl_2C_6H_4R' \quad (2.5)
\]

In the above equations, \( R = 4-\text{CH}_3, \text{H}, 3-\text{CH}_3 \text{ and } 4-\text{Br} \).

As an extension of the reactions performed between organosilanes and tellurium (IV) chlorides (92, 94), we describe in this chapter, the reactions of various organosilanes with tellurium (IV) chlorides where the tellurium compounds are reduced in the process of chlorinating the organosilanes.

2.2 INSTRUMENTATION AND PHYSICAL METHODS

(a) Infrared Spectroscopy (IR): Procedures were as described in section I.2.4(a).

(b) Proton Nuclear Magnetic Resonance Spectroscopy (NMR): Other than the fact that the solutions were sometimes made with CDCl\textsubscript{3} and not only CCl\textsubscript{4}; there were no further changes made to the procedures described in section I.2.4(b).

(c) Melting points (mp): Procedures were as described in section I.2.4(c).

(d) Vapor pressure (VP): The vapor pressures of volatile liquids were determined as in section I.2.4(d) while the vapor pressure of solids can be calculated according to
equation (2.6)

$$\log p = 0.05223 \frac{a}{T} + b$$  \hspace{1cm} (2.6)

where \( p \) is the pressure in mm of mercury of the saturated vapor at the absolute temperature \( T \) and \( a \) and \( b \) are constants listed by Weast (39).

(e) Boiling points (bp) were obtained by extrapolation of log \( \rho \) vs. \( 1/T \) plots (\( \rho \) = vapor pressure, \( T \) = temperature) (38) and the simple distillation method (95).

2.3 THE PREPARATION AND PURIFICATION OF STARTING MATERIALS

As in section 1.2.5, the compounds listed below were either commercially available or had known preparative routes. They were considered "starting materials" as our primary interest was not associated with their preparation. Where more than one source was available, the order was that of experimental convenience.

2.3.1 The Purification of Solvents

All solvents used during the present investigation were purified as described by Vogel (40).

Acetonitrile, \( \text{CH}_3\text{CN} \): To the sample of commercial \( a \) acetonitrile, about half of its volume of water was added followed by anhydrous potassium carbonate until the aqueous layer was saturated. The lower carbonate layer was run off and the upper layer was distilled over phosphorus pentoxide. The fraction
coming out between 79-82°C was collected and stored over molecular sieves. IR (96); NMR (97); VP (39).

**Benzene, C₆H₆**: Commercial benzene was stirred repeatedly with about 15% of its volume of concentrated sulfuric acid until the acid layer turned colorless. After each stirring, the mixture was allowed to settle and the lower layer of acid was drawn off. Benzene was then shaken thrice with water, twice with 10% sodium carbonate solution and finally with water to remove any unreacted carbonate. It was then dried by storing it over anhydrous calcium chloride. The resulting sample of benzene was refluxed over sodium metal for 2 h and distilled. The fraction obtained at 80-81°C/740 mm Hg was collected and stored over sodium wire. IR (96); NMR (97); VP (39).

**Carbon tetrachloride, CCL₄**: Prepared as in section 1.2.5.

**Ether, C₂H₅OC₂H₅**: The commercial sample of diethylether was washed with water to remove any alcoholic content, then kept overnight over anhydrous calcium chloride. It was distilled over phosphorus pentoxide and stored over sodium wire in well stoppered bottles. IR (96); NMR (97); VP(39).

**Methanol, CH₃OH**: Commercial methanol was treated with quick lime and kept for 2-3 days. It was then distilled and the distillate was refluxed with a few grams of clean and dry magnesium turnings and a small amount of iodine. The mixture was warmed on a water bath until the iodine disappeared. The product was then distilled discarding the
first 25ml of the distillate. IR (96); NMR (97); VP (39).

**Petroleum ether**: Commercial[^b,c] petroleum ether was kept overnight over anhydrous calcium chloride and then distilled over phosphorus pentoxide. The fraction distilling between 40-60°C was collected and stored over sodium wire.

**Tetrachloroethane, C₂H₂Cl₄**: The commercial[^b] sample was warmed on a steam bath with 8% of its volume of concentrated sulfuric acid and stirred mechanically for 30 min. The upper layer was decanted and the process was repeated until the acid layer became almost colorless. It was then distilled in steam, dried with anhydrous calcium chloride and distilled. The fraction with bp I45-I47°C was collected. IR (96); NMR (97); VP (39).

**Toluene, CH₃C₆H₅**: Commercial[^a] toluene was purified by stirring several times with 10% of its volume of concentrated sulfuric acid. The lower acidic layer was removed and the process was repeated until the acid layer became colorless or very pale yellow on standing. The acid was removed by shaking the organic layer with water. The toluene layer was then treated with 10% sodium carbonate solution, washed again with water and finally dried over anhydrous calcium chloride. Then it was distilled and stored over sodium wire for use in well stoppered bottles. IR (96); NMR (97); VP (39).
Commercial Suppliers:

a. The British Drug Houses Ltd., Poole, Dorset, Eng.
c. J.T. Baker Chemical Co., Phillipsburg, N.J.

2.3.2 The Preparation and Purification of Reagents

Except for the organosilanes and tellurium (IV) chloride which were used without further purification; all other reagents were purified as described by Brauer (98).

\text{Bis(p-dimethylsilyl)benzene, } p(\text{Me}_2\text{Si})_2\text{C}_6\text{H}_4: \text{commercial}^a; \text{ stored and used as supplied. Purity checked by IR and NMR (99).}

\text{Calcium chloride, } \text{CaCl}_2: \text{commercial}^b; \text{stored and used as supplied.}

\text{Chloroform, } \text{CHCl}_3: \text{commercial}^c; \text{purified and stored at RT. IR (96); NMR (97); VP (39).}

\text{Diethylsulfate, } \text{Et}_2\text{SO}_4: \text{commercial}^b; \text{purified and stored at RT. IR (96); NMR (97).}

\text{Dimethylphenylsilane, } \text{PhMe}_2\text{SiH: commercial}^a; \text{stored and used as received. IR (100,101); NMR (102); VP (39).}

\text{Diphenylsilane, } \text{Ph}_2\text{SiH}_2: \text{commercial}^a; \text{stored and used as supplied. IR (96); NMR (97).}

\text{Ethoxybenzene (phenetole), } \text{EtOPh: Prepared using the Williamson's method (103) for the preparation of ethers which was particularly well adapted for the preparation of mixed ethers. The method consisted essentially in the reaction between the}
sodium salt of an alcohol or a phenol and an alkyl halide or sulfate. In the preparation, phenol was dissolved in aqueous alkali and treated with diethyl sulfate:

$$\text{PhOH} + \text{NaOH} \rightarrow \text{PhONa} + \text{H}_2\text{O} \quad (2.7)$$

$$\text{PhONa} + \text{Et}_2\text{SO}_4 + \text{NaOH} \rightarrow \text{PhOEt} + \text{EtOH} + \text{Na}_2\text{SO}_4 \quad (2.8)$$

Diethyl sulfate constituted a much cheaper source of ethyl groups than bromide or iodide, which could also be used in the above reaction. With the latter reagents the reaction should be performed under anhydrous conditions.

In the actual preparation itself, phenol (30g, 0.32mol) was dissolved in 10% sodium hydroxide (130ml). Diethyl sulfate (55ml) and 10% sodium hydroxide (250ml) were added from separate vessels in small portions with constant stirring. The addition required approximately 30min and was so regulated that both reagents were added at the same fractional rate. The mixture was then heated under a reflux condenser with constant stirring on a boiling water bath for 1 h. Phenetole was then extracted from the reaction mixture with ether and the ether solution was dried over anhydrous sodium sulfate. After removal of the ether, the phenetole was purified by distillation. Bp 172°C, lit. (103) 172°C; IR (104); NMR (105); VP (39).

**Iodine, I₂**: Prepared as in section 1.2.5.

**Magnesium, Mg**: commercial; stored and used as supplied. VP (39).
Methoxybenzene (anisole), MeOPh: commercial$^a$; purified and stored at RT. IR (96); NMR (97); VP (39).

Methylidiphenylsilane, Ph$_2$MeSiH: commercial$^a$; stored and used as supplied. IR (I00, I06); NMR (I06, I07); VP (39).

Methylphenylsilane, PhMeSiH$_2$: commercial$^a$; stored and used as supplied. IR (I08, I09); NMR (I07).

Phenol, PhOH: commercial$^c$; purified and stored at RT. IR (96); NMR (97); VP (39).

Phenylsilane, PhSiH$_3$: commercial$^a$; stored and used as supplied. IR (IIO); NMR (I07, I11, I12).

Potassium carbonate, $K_2CO_3$: commercial$^b$; stored and used as supplied.

Sodium hydroxide, NaOH: commercial$^b$; stored and used as supplied.

Tellurium (IV) chloride, TeCl$_4$: commercial$^d$; stored and used as supplied. VP (39).

Tetraphenylditin, Ph$_4$Sn: commercial$^d$; stored and used as supplied. IR (96); NMR (97).

Trihexylsilane, (n-C$_6$H$_{15}$)$_3$SiH: commercial$^a$; stored and used as supplied. IR (96); NMR (97).

Sulfuric acid, H$_2$SO$_4$: commercial$^e$; stored and used as supplied.

Commercial Suppliers:


c. Merck, Sharpe and Dohme Ltd., Montreal, P.Q.

2.3.3 The Preparation of Organotellurium Compounds

2.3.3(a) Dichloro(diaryl)tellurium

Although dihalogeno(diorgano)tellurium could be produced in quantitative yields by the halogenation of organic tellurides in carbon tetrachloride or carbon disulphide (73,II5) the method used proved to be very time consuming

\[ \text{R}_2\text{Te} + \text{X}_2 \rightarrow \text{R}_2\text{TeX}_2 \]  \hspace{1cm} (2.9)

and involved the preparation of terribly bad smelling intermediate tellurides.

Dihalogeno(diaryl)tellurium could also be prepared by several other methods. Rust (II6) and Rohrbaech (II7) claimed that the direct reaction of certain aromatic compounds such as p-methoxy and p-ethoxy benzenes with tellurium (IV) chloride yielded dichloro(diaryl)tellurium. Morgan and Drew (II8) on reinvestigation of the above reaction concluded that mixtures of both the di- and trichlorides were produced. Drew, Morgan and Kellet (88,90,II8) showed that when the aromatic rings consisted of electron withdrawing substituents, such as alkoxy and phenoxy groups, the reaction in warm chloroform proceeded very smoothly to the trichloride in almost quantitative yields.

\[ \text{TeCl}_4 + \text{RO} - O - \text{H} \rightarrow \text{RO} - O - \text{TeCl}_3 + \text{HCl} \]  \hspace{1cm} (2.10)
The reaction went further producing the dichloride, when excess of the aromatic compound was used and the reactants were heated to higher temperatures (150-180°C) for prolonged periods without any solvent (88,90).

\[
\text{TeCl}_4 + \text{n-RO-}\text{H} \xrightarrow{150-180^\circ\text{C}} \text{(RO-)}_2\text{TeCl}_2
\]  

(2.11)

The major problem in the above method was that a pure compound could not be obtained without going through the process of a number of recrystallisations.

The reaction between benzene diazonium chloride and tellurium in acetone in the presence of chalk yielded dichloro(diphenyl)tellurium in very poor yield (~2%) (119). Sandin and coworkers (120) reacted diphenyliodonium chloride and finely divided tellurium metal. The contents were refluxed

\[
[\text{Ph}_2\text{I}]^+\text{Cl}^- \xrightarrow{\text{Br}_2} \text{Ph}_2\text{TeBr}_2
\]  

(2.12)

in n-propyl alcohol and after several hours, the unchanged tellurium was filtered off. The evaporation of the filtrate and addition of bromine afforded dibromo(diphenyl)tellurium. However, the yield (~1%) was so low that the only form of identification carried out was that of a melting point determination.

Approximately a decade ago, Pant(121) successfully employed the redistribution reaction between tetraphenyllead and tellurium (IV) chloride for the simple preparation of
dichloro(diphenyl)tellurium and trichloro(phenyl)tellurium. Also, Chadha et. al. (I22) showed that when tetraorganotin or halogeno(triorgano)tin reacted with tellurium (IV) halides, the tin compound converted to the more stable dihalogeno(di-organo)tin. In the above process, tellurium (IV) halides changed first to the corresponding trihalogeno(organo) tellurium and then to the dihalogeno(diorgano)tellurium derivatives (I23). These observations were consistent with the re-distribution reactions shown below involving tin (I24):

\[
2R_2SnX \rightarrow R_2SnX_2 + R_4Sn \quad (2.13)
\]

\[
2RSnX_3 \rightarrow R_2SnX_2 + SnX_4 \quad (2.14)
\]

where it was found that if trihalogeno(organo)tin or halogeno-(triorgano)tin were stored for some time, they gradually converted to the dihalogeno(diorgano) species.

\textbf{Dichloro(di-p-methoxyphenyl)tellurium, (p-MeOPh)\textsubscript{2}TeCl\textsubscript{2}}: \mbox{}

Dichloro(di-p-methoxyphenyl)tellurium was prepared by the method of Burstall and Sugden (I25) with certain modifications. Tellurium (IV) chloride (I5g, 0.056mol) and anisole(30g, 0.28 mol) were added to a flask and the temperature was slowly raised to 100°C. The contents were refluxed in vacuum at 100°C for approximately 12 h. Then they were allowed to cool down. The crude dark red product obtained was dissolved in benzene and the solution was passed through an alumina column
to remove the colored impurities. The eluent was also benzene.

The clear solution which was collected contained dichloro-(di-p-methoxyphenyl)tellurium. On reducing the volume of the solution and adding petroleum ether, a white precipitate of dichloro(di-p-methoxyphenyl)tellurium was obtained. This was recrystallised using a chloroform-petroleum ether mixture.

Mp I83-I84°C, lit. (88) I8I-I82°C. IR (I26) in cm⁻¹: 2950s, I580m, I570w, I490m, I455s, I400vw, I378m, I295m, I260s, I175m, I120w, I057w, I020m, I000vw, 822w, 812m, 801w, 790w, 720w, 580w, 504w, 478vw, 320w, 268vw, 255vw, 250w. NMR (I27): § Ph 7.17ppm (dd, 2H, ortho), 7.98ppm (dd, 2H, meta); § MeO 3.78ppm (s, 3H).

Dichloro(di-p-ethoxyphenyl)tellurium, (p-EtOPh)₂TeCl₂:

Dichloro(di-p-ethoxyphenyl)tellurium was prepared in exactly the same manner as dichloro(di-p-methoxyphenyl)tellurium.

The only change made in obtaining (p-EtOPh)₂TeCl₂ was that phenetole, instead of anisole, was used to react with tellurium (IV) chloride. Mp 109°C, lit. (I18) 108°C. IR (I26) in cm⁻¹: 2970w,sh, 2955s, 2820m, I542m, I450m, I433s, I363w, I343m, I275w, I245w, I210s, II90w,sh, II65w, II32m, III4w, I035vw, I005vw, 980vw, 965vw, 823m, 798m, 740m, 710m, 680w, 645w, 450w, 435w. NMR (I27): § Ph 7.09ppm (dd, 2H, ortho), 7.88ppm (dd, 2H, meta); § Me I.40ppm (t,3H); § CH₂O 4.10ppm (q, 2H).
Figure 2.1 The infrared spectrum of (p-MeOPh)₂TeCl₂ (Nujol)
Figure 2.2 The NMR spectrum of (p-MeOPh)$_2$TeCl$_2$
**Dichloro(diphenyl)tellurium, Ph₂TeCl₂:**

Dichloro(diphenyl)tellurium was prepared using Chadha's method (122,123). Although dichloro(diphenyl)tellurium could be obtained by refluxing chloro(triphenyl)tin and trichloro(phenyl)tellurium in toluene for approximately 3 h,

\[
\text{Ph}_3\text{SnCl} + \text{PhTeCl}_3 \xrightarrow{\text{reflux}} \text{Ph}_2\text{SnCl}_2 + \text{Ph}_2\text{TeCl}_2
\]

(2.15)

it was more conveniently prepared by reacting tetraphenyltin and tellurium (IV) chloride in toluene at room temperature. The trichloro(phenyl)tellurium produced was converted to dichloro(diphenyl)tellurium by allowing the reaction mixture

\[
\text{Ph}_4\text{Sn} + \text{TeCl}_4 \xrightarrow{\text{reflux}} \text{Ph}_2\text{SnCl}_2 + \text{Ph}_2\text{TeCl}_2
\]

(2.16)

to reflux for approximately 3 h. Unlike the latter method which was simple, the former method involved the preparation of starting materials such as chloro(triphenyl)tin and trichloro(phenyl)tellurium.

In the actual preparation, tetraphenyltin (4.4g, 0.01 mol) and tellurium (IV) chloride (2.8g, 0.01mol) were refluxed in toluene (50ml) for 3 h. After filtering out the small amount of insoluble matter present, petroleum ether was added until a white precipitate was formed. The precipitate was then filtered, dried and recrystallised from methanol to give dichloro(diphenyl)tellurium. Mp 159°C, lit. (119) 159°C; IR (128) in cm⁻¹: 3025w, 1570w, 1475m, 1433s, 1420w, sh,
I387w, 3327m, I304w, I270w, I207 m, II59m, sh, II50w, I095w, I066m, I057m, sh, I052m, I015m, 994s, 974w, 923w, 824w, 747s, 737vs, 688s, 682s, 656w, 606vw, 464m, 455s, 287m, 271m.
NMR (I29): δ Ph 7.59 ppm (m, 3H), 8.24 ppm (m, 2H).

2.3.3(b) **Trichloro(aryl)tellurium**

Trihalogeno(organo)tellurium could be prepared by the action of elemental halogens on organic ditellurides (I30-I32).

\[
R-\text{Te-Te-R} \xrightarrow{3X_2} 2R\text{TeX}_2
\]  
(2.17)

The intermediate organic ditellurides could be synthesised from sodium ditellurides and organic halides. Trihalogeno-(aryl) tellurium could also be prepared by several other methods. As mentioned in the previous section, the direct interaction of certain aromatic compounds with tellurium (IV)chloride always yielded a mixture of trichloro(aryl)tellurium and dichloro(diaryl)tellurium (II8). Such reactions were possible only when the ring consisted of electron withdrawing substituents such as alkoxy, phenoxy or carbonyl groups (88,I33,I34).

In the preparation of trihalogeno(aryl)tellurium from halogeno(aryl)mercury (I35-I38), it was found that the

\[
\text{RHgCl} + \text{TeCl}_4 \xrightarrow{\text{dioxane, reflux}} \text{RTeCl}_3 + \text{HgCl}_2, \text{dioxane}
\]  
(2.18)
separation of the mercuric chloride was facilitated by carrying out the reaction in dioxane with which it formed a solid adduct. The trichloro(aryl)tellurium was then obtained from the solution by distilling off the solvent in vacuum. The product however remained contaminated with the mercury compounds which were found as side products (I39).

**Trichloro(p-methoxyphenyl)tellurium, p-MeOPhTeCl₃:**

p-MeOPhTeCl₃ was prepared by Morgan and Kellet's method (88). Tellurium (IV) chloride (20g, 0.075mol), anisole (24g, 0.22mol) and dry chloroform (30ml) were heated on a water bath for approximately 2 h. The mixture became yellowish-red even in the cold, but, on warming hydrochloric acid gas was evolved and the condensation product crystallised to a mass of yellow needles. Recrystallisation from boiling chloroform gave trichloro(p-methoxyphenyl)tellurium.

Mp 190°C, lit. (88) 190°C. IR (I29) in cm⁻¹: 3040w, 1600w, 1572s, 1480s, 1433m, 1402w, 1300s, 1260s, 1178s, 1052s, 1048s, 1032w, 1015w, 820s, 800s, 780w, 720s, 692w, 500s, 470w, 323s, 295s, 262w, 252w, 230w. NMR (I40): δ Ph 7.16ppm (dd, 2H, ortho), 8.35ppm (dd, 2H, meta); δ MeO 3.80ppm (s, 3H).

**Trichloro(p-ethoxyphenyl)tellurium, p-EtOPhTeCl₃:**

Trichloro(p-ethoxyphenyl)tellurium was prepared in exactly the same manner as trichloro(p-methoxyphenyl)tellurium. Instead of heating anisole with tellurium (IV) chloride and dry chloroform, phenetole was used. Mp 182°C, lit. (II8) 183°C. IR (I29) in cm⁻¹: 2975w, 2840m, 1578w, 1510vw, 1480w, 1455m,
I370m, I298vw, I280w, I242m, II70m, I091w, I028m, 900w, 810vw, 790m, 775vw, 700w, 482m, 380vw, 340vw, 320w, 300m. NMR (127): 
$^1$H Ph 7.13 ppm (dd, 2H ortho), 8.32 ppm (dd, 2H, meta); $^1$H Me 
I.42 ppm (t, 3H); $^1$H CH$_2$O 4.23 ppm (q, 2H).

**Trichloro(phenyl)tellurium, PhTeCl$_3$:**

Trichloro(phenyl)tellurium was prepared using Chadha's method (122,123). Although trichloro(phenyl)tellurium could be obtained by the action of chloro(triphenyl)tin on tellurium (IV) chloride, it was more conveniently prepared by the action of tetraphenyltin on tellurium (IV) chloride. Both

$$\text{Ph}_2\text{SnCl} + \text{TeCl}_4 \xrightarrow{\text{rt}} \text{Ph}_2\text{SnCl}_2 + \text{PhTeCl}_3$$  \hspace{1cm} (2.19)

the above reactions were carried out in toluene at room temperature.

For the preparation of trichloro(phenyl)tellurium from tetraphenyltin and tellurium (IV) chloride, a mixture of tetraphenyltin (4.3g, 0.01mol) and tellurium (IV) chloride (2.7g, 0.01mol) in toluene (50ml) was stirred for about 2 h at room temperature. The insoluble precipitate, which was formed was filtered, dried and recrystallised from acetonitrile-tetrachloroethane (1:1) mixture to give pure trichloro(phenyl)tellurium. Mp 216°C, lit. (141) 215-218°C.
IR (128) in cm⁻¹: 2900w, 2840w, 1467m, 1432m, 1366m, 1285m, 1249s, 1159m, 1098s, 1093s, 1063s, 993m, 888m, 842s, 737vs, 688s, 474vw, 463m, 311m, 305s. NMR (142): δ Ph 7.62ppm (m, 3H), 8.36ppm (m, 2H).

2.4 EXPERIMENTAL

All the reactions done in the present investigation were carried out under moisture-free conditions. Since the experimental procedures involved were similar for all the reactions, only typical reactions have been described in the sections below. Table 2.1 lists all the various reactions done between tellurium (IV) chloride and different organosilanes, Table 2.2 gives reactions of trichloro(aryl)tellurium with certain organosilanes and Table 2.3 outlines the reactions of dichloro(diaryl)tellurium with organosilanes which have been attempted. From Tables 2.1 and 2.2, it can be seen that no new products have formed. Since all the tabulated products can be found in the literature, IR and NMR references for the silicon products are given in Table 2.4 while those for the tellurium products, which have not already been described in section 2.3, are listed in Table 2.5. Also listed for both the silicon and tellurium products are bp for the corresponding liquids and mp for the solids.
2.4.1 Reactions of Tellurium (IV) Chloride with Various Organosilanes in Benzene

A typical reaction in this section would be one between tellurium (IV) chloride and diphenylsilane. In the actual reaction itself, a solution of diphenylsilane (1.60g, 8.66mmol) in benzene (10ml) was added dropwise to a stirred solution of tellurium (IV) chloride (2.33g, 8.66mmol) in the same solvent (20ml). The reaction mixture was stirred for 1/4 h and refluxed subsequently for 3 h or until the Si-H protons had disappeared from the NMR spectrum of the reaction mixture. The gas evolved was condensed in a liquid nitrogen trap and its IR spectrum was recorded. After the reaction mixture had cooled down to room temperature, the tellurium metal* which had formed during the course of the reaction was filtered off. On evaporation under vacuum, the filtrate was found to be dichloro(diphenyl)silane (2.08g, yield 95%); bp 301-305°C, lit. (99, I43) 302-305°C.

2.4.2 Reactions of Trichloro(aryl)tellurium with Some Organosilanes in Benzene

It was found that reactions of trichloro(aryl)tellurium with organosilanes proceeded in two different ways. When

*This product was confirmed by doing the analytical test (I44) for tellurium metal.
the reaction mixture was stirred at room temperature for 6-8 h, diarylditellurides and chlorinated silanes were obtained; but, when the reaction mixture was refluxed for 6-10 h, dichloro(diaryl)tellurium and chlorinated silanes were obtained along with tellurium powder. A typical reaction of each of the mentioned cases involving trichloro(p-methoxyphenyl)tellurium and diphenylsilane is described below.

(a) Diphenylsilane (1.23g, 6.68mmol) and trichloro(p-methoxyphenyl)tellurium (3.04g, 8.91mmol) were mixed in the same manner as described in section 2.4.I. The reaction was complete after 6 h when NMR spectroscopic analysis showed the absence of peaks due to the presence of Si-H in the reaction mixture. All insoluble impurities found were then filtered off and the reaction mixture was reduced to 5ml by evaporation in vacuum. The reaction mixture was then transferred to the top of a silica gel column (2x30 cm) made up with CCl₄. The column was developed with the same solvent. On evaporation, the first fraction yielded dichloro(diphenyl)silane (1.40g, yield 83%); bp 301-304°C, lit. (99, I43) 302-305°C and the second fraction gave di-p-methoxyphenylditelluride (1.18g, yield 78%); mp 55-57°C, lit. (73, 88) 56-58°C.

(b) A similar reaction was set up with diphenylsilane (1.43g, 7.75mmol) and trichloro(p-methoxyphenyl)tellurium (5.29g, 15.50mmol). The mixture was stirred for 1 h and subsequently refluxed for 8 h. When NMR spectroscopy showed the absence
of Si-H peaks at the end of the 8 h reflux, the contents were allowed to cool and the black precipitate of tellurium metal was filtered off. On standing for a few hours, a white precipitate of dichloro(di-p-methoxyphenyl)tellurium was produced. Recrystallisation of the crude residue from CH₂CN gave pure (p-MeOPh)₂TeCl₂ (2.75g, yield 85%); mp 183-184°C, lit. (88) 181-182°C. Dichloro(diphenyl)silane was recovered from the filtrate as described in section 2.4.I(a).

2.4.3. Reactions of Dichloro(diaryl)tellurium with Organosilanes in Benzene

In this section, it was found that the reactions of dichloro(diaryl)tellurium with organosilanes did not proceed to appreciable amounts even when the reactants were refluxed in the presence of a catalytic amount of AgNO₃ for 48 h.

From Table 2.3, it can be seen that 80-85% of the R₂TeCl₂ species were recovered from the reaction mixture each time. Typical reactions involving dichloro(di-p-methoxyphenyl) tellurium and triphenylsilane are described below.

(a) Triphenylsilane (2.45g, 9.40mmol) and dichloro(di-p-methoxyphenyl)tellurium (3.89g, 9.40mmol) were mixed in the same manner as described in section 2.4.I. The reaction mixture was stirred for 1 h and subsequently refluxed for 30 h. On standing, it was found that the starting material, dichloro(di-p-methoxyphenyl)tellurium (3.18g, yield 82%), was precipitated. After this was filtered off, the reaction mixture was reduced to 5ml by evaporation in vacuum and transferred
to the top of a silica gel column, identical to the one described in section 2.4.2, and the compounds present were separated. On evaporation, the first fraction yielded triphenylsilane (1.93g, yield 79%), bp 161-165°C, lit. (99) 160-165°C, the second fraction yielded chlorotriphenylsilane*, mp 90-92°C, lit. (99) 91-92°C and the third fraction yielded di-p-methoxyphenyltelluride (0.16g, yield 5%), mp 53-54°C, lit.(88,125) 53-54°C.

(b) A similar reaction was set up with triphenylsilane (2.07g, 7.96mmol), (p-MeOPh)₂TeCl₂ (3.28g, 7.96mmol) and AgNO₃ (0.51g, 2.94mmol). The reaction mixture was stirred for 1 h and subsequently refluxed for 32 h. Again the starting material di-chloro(di-p-methoxyphenyl)tellurium (2.62g, yield 80%), was precipitated when the reaction mixture was left standing. After (p-MeOPh)₂TeCl₂ was filtered off, the reaction mixture was reduced and passed through a silica gel column as described in section 2.4.2. As found in the above section, on evaporation, the first fraction yielded triphenylsilane (1.72g, yield 83%), the second fraction yielded chlorotriphenylsilane* and the third fraction yielded di-p-methoxyphenyltelluride (0.19g, yield 7%).

* So little product was obtained, only its melting point was taken; a calculation of its yield was impossible.
Table 2.1 Reactions of TeCl₄ with Organosilanes in Benzene

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants (Mole Ratio)</th>
<th>Products</th>
<th>Reflux Time (h)</th>
<th>% Yield (SP*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TeCl₄ + PhSiH₃ (1:1)</td>
<td>PhSiHCl₂ + Te</td>
<td>5.0</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>TeCl₄ + PhSiH₃ (3:2)</td>
<td>PhSiCl₂ + Te</td>
<td>6.0</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>TeCl₄ + Ph₂SiH₂ (1:1)</td>
<td>Ph₂SiCl₂ + Te</td>
<td>3.0</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>TeCl₄ + PhMeSiH₂ (1:1)</td>
<td>PhMeSiCl₂ + Te</td>
<td>4.5</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>TeCl₄ + Ph₃Si (1:2)</td>
<td>Ph₃SiCl₂ + Te</td>
<td>2.5</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>TeCl₄ + Ph₂MeSiH (1:2)</td>
<td>Ph₂MeSiCl₂ + Te</td>
<td>4.0</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>TeCl₄ + PhMe₂SiH (1:2)</td>
<td>PhMe₂SiCl₂ + Te</td>
<td>4.0</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>TeCl₄ + (n-C₆H₁₃)₃SiH (1:2)</td>
<td>(n-C₆H₁₃)SiCl₂ + Te</td>
<td>4.0</td>
<td>98</td>
</tr>
<tr>
<td>9</td>
<td>TeCl₄ + p-(Me₂HSi)₂Ph (1:1)</td>
<td>p-(Me₂ClSi)₂Ph + Te</td>
<td>2.0</td>
<td>95</td>
</tr>
</tbody>
</table>

* SP = Silicon Product.
Table 2.2 Reactions of RTeCl₃ with Organosilanes in Benzene

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants (Mole Ratio)</th>
<th>Products</th>
<th>Temp</th>
<th>Time (h)</th>
<th>%Yield (SP*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhSiH₂⁺p-MeOPhTeCl₃</td>
<td>PhSiHCl₂⁺ (p-MeOPh)₂Te₂</td>
<td>22</td>
<td>6</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>Ph₂SiH₂⁺p-MeOPhTeCl₃</td>
<td>Ph₂SiCl₂⁺ (p-MeOPh)₂TeCl₂</td>
<td>RF⁺</td>
<td>8</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>Ph₂SiH₂⁺p-MeOPhTeCl₃</td>
<td>Ph₂SiCl₂⁺ (p-MeOPh)₂Te₂</td>
<td>22</td>
<td>6</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>Ph₂SiH₂⁺PhTeCl₃</td>
<td>Ph₂SiCl₂⁺ Ph₂Te₂</td>
<td>22</td>
<td>8</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>Ph₂SiH₂⁺p-EtOPhTeCl₃</td>
<td>Ph₂SiCl₂⁺ (p-EtOPh)₂Te₂</td>
<td>RF⁺</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>Ph₃SiH⁺p-EtOPhTeCl₃</td>
<td>Ph₃SiCl⁺ (p-EtOPh)₂TeCl₂</td>
<td>RF⁺</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>Ph₂MeSiH⁺PhTeCl₃</td>
<td>Ph₂MeSiCl⁺ Ph₂Te₂</td>
<td>RF⁺</td>
<td>7</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>(n-C₆H₁₃)₃SiH⁺p-MeOPhTeCl₃</td>
<td>(n-C₆H₁₃)₃SiCl⁺ (p-MeOPh)₂TeCl₂</td>
<td>RF⁺</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>Ph₂MeSiH⁺PhTeCl₃</td>
<td>Ph₂MeSiCl⁺ Ph₂Te₂</td>
<td>22</td>
<td>6</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>p-(Me₂HSi)₂Ph⁺p-MeOPhTeCl₃</td>
<td>p-(Me₂SiCl)₂Ph⁺ (p-MeOPh)₂Te₂</td>
<td>22</td>
<td>8</td>
<td>95</td>
</tr>
</tbody>
</table>

* SP = Silicon Product.  
+ RF = Reflux.
Table 2.3  Reactions of $R_2TeCl_2$ with Organosilanes in Benzene

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants (Mole Ratio)</th>
<th>Reflux Time(h)</th>
<th>% $R_2TeCl_2$ Unreacted</th>
<th>% Yield ($R_2Te$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$(p$-MeO$Ph)_2TeCl_2$ + $Ph_3SiH$ (1:1)</td>
<td>30</td>
<td>82</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Rx*1 + Catalytic amount of AgNO$_3$</td>
<td>32</td>
<td>80</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>$Ph_2TeCl_2$ + $Ph_3SiH$ (1:1)</td>
<td>46</td>
<td>85</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Rx*3 + Catalytic amount of AgNO$_3$</td>
<td>48</td>
<td>85</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>$(p$-MeO$Ph)_2TeCl_2$ + $PhSiH_3$ (1:1)</td>
<td>33</td>
<td>83</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>Rx*5 + Catalytic amount of AgNO$_3$</td>
<td>40</td>
<td>80</td>
<td>6</td>
</tr>
</tbody>
</table>

* Rx = Reaction Mixture.
Table 2.4 IR and NMR References for the Silicon Products

<table>
<thead>
<tr>
<th>No</th>
<th>Chlorosilanes</th>
<th>Bp(99) (°C)</th>
<th>IR</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Mp(99) if solid)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>PhMe$_2$SiCl</td>
<td>50</td>
<td>(108,109)</td>
<td>(150)</td>
</tr>
<tr>
<td>2</td>
<td>PhSiHCl$_2$</td>
<td>65-66</td>
<td>(145)</td>
<td>(145,151)</td>
</tr>
<tr>
<td>3</td>
<td>Ph$_2$SiCl$_2$</td>
<td>II3-II4</td>
<td>(146)</td>
<td>(152)</td>
</tr>
<tr>
<td>4</td>
<td>(n-C$<em>6$H$</em>{13}$)$_3$SiCl</td>
<td>I54-I55</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>5</td>
<td>Ph$_2$MeSiCl</td>
<td>I20-I25</td>
<td>(147)</td>
<td>(153)</td>
</tr>
<tr>
<td>6</td>
<td>PhSiCl$_3$</td>
<td>201</td>
<td>(146,148)</td>
<td>(154)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(149)</td>
</tr>
<tr>
<td>7</td>
<td>PhMeSiCl$_2$</td>
<td>205-206</td>
<td>(108,109)</td>
<td>(155)</td>
</tr>
<tr>
<td>8</td>
<td>Ph$_3$SiCl</td>
<td></td>
<td>(146)</td>
<td>(156)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(91-92)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>p-(Me$_2$ClSi)$_2$Ph</td>
<td>-</td>
<td>c</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(88-90)*</td>
<td></td>
</tr>
</tbody>
</table>

a IR(cm$^{-1}$): 2905s, I510s, I505s, I403m, I373m, I360vw, sh, I337w, I305vw, I290w, I250m, I230m, I220w, I180s, I070vs, br, 990m, 965m, 884w, 835m, 787vs, br, 762vs, br, 715vs, br, 498m, 405w, 375w.

b NMR: & C$_6$H$_{13}$ I.30ppm (m) and 0.88ppm (m).

c IR(cm$^{-1}$): 3030w, 2975s, 2860s, I460m, I405w, I377m, I263s, I242s, II32s, I070vs, br, I014w, 875w, 820s, 775vs, br, 728w, 690vw, 660w, 650w, 628vw, 497s, 420s.

d NMR: & Ph 9.51ppm (g, 4H), & Me 0.32ppm (s, 12H).

* Recrystallised from ethanol-petroleum ether, mp 88-90°C, lit. (157) 87°C.
Figure 2.3 The infrared spectrum of \((n-C_{2}H_{13})_{2}SiCl\) (Nujol)
Figure 2.4 The infrared spectrum of p-(Me₂SiCl)₂Ph(Nu₁ο₁)
<table>
<thead>
<tr>
<th>No.</th>
<th>$R_2Te_2$</th>
<th>$Mp(^{\circ}C)$</th>
<th>IR</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(p$-MeO$Ph)_2Te_2$</td>
<td>55-57</td>
<td>(I58)</td>
<td>(I27)</td>
</tr>
<tr>
<td>2</td>
<td>$(p$-EtO$Ph)_2Te_2$</td>
<td>108-109</td>
<td>(I58)</td>
<td>(I27,I59)</td>
</tr>
<tr>
<td>3</td>
<td>Ph$_2Te_2$</td>
<td>66-67</td>
<td>(I28)</td>
<td>(I60)</td>
</tr>
</tbody>
</table>
2.5 RESULTS AND DISCUSSION

A typical reaction between TeCl$_4$ and an organosilane can be written as:

$$\text{Ph}_2\text{SiH}_2 + \text{TeCl}_4 \xrightarrow{\text{benzene, reflux}} \text{Ph}_2\text{SiCl}_2 + \text{Te} + 2\text{HCl}$$

All the reactants in Table 2.I were refluxed in benzene for 2-6 h and the completion of each reaction was detected by the absence of a Si-H proton chemical shift in the NMR spectrum of the respective reaction mixture. The evolution of two equivalents of HCl gas was confirmed by performing the reaction on a vacuum line (described in section I.2.I) where the gas could be trapped using a liquid nitrogen bath (-196°C) and its IR spectrum recorded. There was no indication of the evolution of hydrogen gas as reported in the reaction between TeCl$_4$ and Et$_3$SiH (161) where the products were Et$_3$SiCl and hydrogen with only a trace amount of HCl gas present. Other silanes reacted in a similar manner to diphenylsilane under slightly different conditions, all of which are given in Table 2.I. Pure chlorosilanes were obtained when the tellurium powder was filtered off. It was found that when any excess of TeCl$_4$ was used in the reaction, it became difficult to separate the chlorosilanes from the reaction mixture because of the slow deposition of tellurium metal from TeCl$_2$ which is probably an intermediate in the reduction.
of TeCl₄ to tellurium.

\[
\text{TeCl}_4 \rightarrow \text{TeCl}_2 \rightarrow \text{Te}
\]  

(2.22)

As can be seen from section 2.4.2, the reactions between organosilanes and trichloro(aryl)tellurium were carried out in two different ways. It was found that when the reactants were stirred at room temperature for approximately 6-8 h, diarylditellurides along with the chlorinated silyl products were obtained. A representative reaction can be written as:

\[
3\text{Ph}_2\text{SiH}_2 + 4\text{p-MeOPhTeCl}_3 \xrightarrow{\text{stir, 6h}} 3\text{Ph}_2\text{SiCl}_2 + 2(\text{p-MeOPh})_2\text{Te}_2 + 6\text{HCl}
\]

(2.23)

On the other hand, when the reaction mixture was refluxed for 6-10 h, dichloro(diaaryl)tellurium and chlorosilanes were obtained. The reaction should then be written as:

\[
\text{Ph}_2\text{SiH}_2 + 2\text{p-MeOPhTeCl}_3 \xrightarrow{\text{reflux, 8h}} \text{Ph}_2\text{SiCl}_2 + (\text{p-MeOPh})_2\text{TeCl}_2 + \text{Te} + 2\text{HCl}
\]

(2.24)

As with the reactions with TeCl₄, the completion of the reaction was monitored by NMR spectroscopy and the evolution of HCl gas was confirmed by IR spectroscopy. The experimental details of the various reactions of RTeCl₃ with organosilanes are summarised in Table 2.2. Of the many examples studied, only the reaction between p-EtOPhTeCl₃ and Ph₂SiH₂ needed
4 h of refluxing to perform the reaction according to equation (2.23). In the reactions according to equation (2.23), the products were separated by simple column chromatography because they were both highly soluble in benzene even at low temperatures. Since all the products are known compounds, they were identified by mixed mp with the authentic samples (73, 99) or by comparing their IR and NMR spectra with those of the authentic samples. When the reaction conditions were not carefully controlled, for example, not stirred or refluxed for the appropriate length of time or the mole ratios of the reactants were incorrect, then a mixture of products was obtained which included partially or fully chlorinated silyl products.

Equations (2.23) and (2.24) show that the reaction between RTeCl$_3$ and organosilanes proceed in two steps since it is known that R$_2$Te$_2$ species react with RTeCl$_3$ to give R$_2$TeCl$_2$ and tellurium on refluxing in toluene (162). Thus, in the first step RTeCl$_3$ is reduced to R$_2$Te$_2$ while in the second step the R$_2$Te$_2$ that is formed apparently reacts with the unreacted RTeCl$_3$ on refluxing to give R$_2$TeCl$_2$.

It is interesting to note that RPhTeCl$_2$ species (R = C$_{12}$H$_{25}$, C$_9$H$_{19}$) are reduced to RPhTe and RH by Ph$_3$SnH (144). The analogous reactions of organosilanes with R$_2$TeCl$_2$ (e.g. PhSiH$_3$ or Ph$_2$SiH with Ph$_2$TeCl$_2$ or (p-MeOPh)$_2$TeCl$_2$) in benzene did not yield appreciable amounts of R$_2$Te even when the reactants were refluxed in the presence of AgNO$_3$ for 48 h.
Table 2.3 gives the experimental details of all such reactions done. Also, there was no indication of the evolution of chlorine gas during the course of the reactions (equations (2.21), (2.23) and (2.24)). It should also be noted that the conversion of TeCl$_4$ to TeCl$_2$ and tellurium metal does not occur below 500°C (I63).

2.6 MECHANISTIC CONSIDERATIONS

The relationship between the structures of TeCl$_4$, RTeCl$_3$ and R$_2$TeCl$_2$ species in both the solid state and liquid state (in solution in organic solvents in this case) is not clear, but, the determination of the crystal structure of TeCl$_4$ shows that one of the Te-Cl bonds is longer and hence would be presumably weaker than the rest (I64). Thus in the presence of organic solvents (I65), it would be reasonable to assume that the species can be depicted as Cl$_3$Te($\delta^+$)-Cl($\delta^-$). It is also apparent that the Si-H bond is polarised as $\equiv$Si($\delta^+$)-H($\delta^-$) (I00,I66) so that the classical four-center transition state (I67) can be involved arising from nucleophilic substitution on tellurium and electrophilic substitution on silicon.

$$
\equiv\text{Si}(\delta^+)-\text{H}(\delta^-) \quad \equiv\text{Si}...\text{H} \quad \equiv\text{Si} \quad \rightarrow \quad + (\text{HTeCl}_3) \rightarrow
$$

Cl($\delta^-$)--($\delta^+$)TeCl$_3$  Cl...TeCl$_3$  Cl

$$
\rightarrow \quad \text{HCl} + \text{TeCl}_2
$$

(2.25)
Any HTeCl$_3$ formed would be extremely unstable and would immediately decompose to HCl and TeCl$_2$. Tellurium dichloride is an unstable compound in organic solvents and is known to disproportionate to tellurium metal and TeCl$_4$ (I68) which would then react again.

Again, the determination of the crystal structures of RTeCl$_3$ species such as PhTeCl$_3$ (I69) and p-MeOPhTeCl$_3$ (I70) leads to the conclusion that one of the Te-Cl bonds is weakened because it acts as a bridge between two RTeCl$_3$ molecules. Also, RTeCl$_3$ species are known to form complexes of the type RTeCl$_2^+$(SbCl$_6^-$) (I71) and (RTeCl$_2$)$_2^+(MC_6H$_5^-$)$^2-$, M = Sn, Te (I72). Thus a similar mechanism involving the reaction of RCl$_2$Te(S+)—Cl(S−) and =Si(S+)—H(S−) would give RHTeCl$_2$.

This would be expected to dissociate to HCl and another reactive and unstable (I62) intermediate, RTeCl. Two of those species either react with a Si-H bond involving probably a more complex mechanism to form R$_2$Te$_2$ or disproportionate on refluxing to give R$_2$TeCl$_2$ and tellurium metal (I62).

In contrast to both the TeCl$_4$ and RTeCl$_3$ species, there is no unique Te-Cl bond in R$_2$TeCl$_2$ species. The determinations of the crystal structures of the R$_2$TeCl$_2$ species (55,92,169, 173,174) including Ph$_2$TeCl$_2$ (I70) and (p-MeOPh)$_2$TeCl$_2$ (I73) show that while weak secondary interactions hold together two or four molecules, the chlorine atoms always occupy the identical apical positions of a trigonal bipyramidal structure. Furthermore, no stable R$_2$TeCl$_2^+$ species is known so that it is
perhaps not so surprising that very little reaction occurs between the $R_2TeCl_2$ and the $≡Si-H$ species.
REFERENCES


(b) Program used for centering reflections, auto-indexing refinement of cell parameters, axial photographs
and data collection were those described in:
"Syntex P2 1 Operations Manual", R.A. Sparks Ed.,
analytical Instruments, Cupertino, CA (1973).


137. L. Reichel, E. Kirschbaum, Ann., 52B, 211 (1936); CA, 32, 6718 (1937).


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