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To my mother, brother

and

memory of my father

THE CHEMISTRY OF SOME
ORGANOTELLURIUM COMPOUNDS

by

ZAHRA MONSEF-MIRZAI

A thesis submitted for the Degree of
Doctor of Philosophy
in the
University of Aston in Birmingham

Department of Chemistry

September 1982

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SUMMARY

The formation of $\text{Pd}(\text{TeR})_n$ and $(\text{CuTeR})_n$ from the reaction between telluroesters and $\text{Pd}(\text{II})$ or $\text{Cu}(\text{II})$ suggested that these organotellurium reagents may be useful precursors of RTe^- ligands in reactions with transition-metal substrates.

Also the formation of telluronium salts $\text{Me}_2\text{RTe}^+\text{I}^-$ from the reaction between telluroesters and methyl iodide, together with the above, confirm the cleavage of $\text{-C}(\overset{\text{O}}{\parallel})\text{-Te}$ bonds rather than -C-Te bonds.

The formation of a carboxylic acid from the toluene solution of a ditelluride and palladium(0) complex in the presence of light and oxygen (from air) is demonstrated. When the solvent employed is p-xylene an aldehyde is formed. The reaction proceeds via the free radical, RTeO , with $\text{Pd}(\text{PPh}_3)_4$ as a catalyst. It has also been shown that the oxidation of aldehydes to carboxylic acids is catalysed by ditelluride.

Spin trapping experiments with $\text{PhCH}=\text{N}(\text{O})\text{Bu}^t$ (phenyl-t-butyl-nitrone) have provided evidence that the oxidative addition of an alkyl halide ($\text{RX}=\text{MeI}$, Bu^nBr , $\text{Bu}^{\text{sec}}\text{Br}$, Bu^tBr , $\text{BrCH}_2\text{-CH}=\text{CHCH}_2\text{Br}$, and $\text{Br}(\text{CH}_2)_4\text{Br}$) to diphenyltelluride and reductive elimination of CH_3SCN from $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$ proceeds via radical pathways. A mechanism is proposed for oxidative addition which involves the preformation of a charge transfer complex of alkyl halide and diphenyltelluride. The first step is the formation of a charge transfer complex, and the initial product of the oxidative addition is a "covalent" form of the tellurium(IV) compound. When the radical R is more stable, Ph_2TeX_2 may be the major tellurium(IV) product.

The reaction of RTeNa ($\text{R}=\text{p-EtOC}_6\text{H}_4$, Ph) with organic dihalides $\text{X}_2(\text{CH}_2)_n$ ($n=1,2,3,4$) affords telluronium salts ($n=3,4$; $\text{X}=\text{Cl}$, Br) the nature of which is discussed. For $n=1$ ($\text{X}=\text{Br}$, I) the products are formulated as charge transfer complexes of stoichiometry $(\text{RTe})_2(\text{CH}_2)_n\cdot\text{CH}_2\text{X}_2$. For $n=2$, elimination of ditelluride occurs with the formation of an alkene.

Some ^{125}Te Mössbauer data are discussed and it is suggested that the unusually low value of Δ ($7.58 \text{ mm}\cdot\text{s}^{-1}$) for $(\text{p-EtO}\cdot\text{C}_6\text{H}_4\cdot\text{Te})_2(\text{CH}_2)_2\text{CH}_2\text{Br}_2$ relates to removal of 5s electrons from the spare pair orbital via the charge transfer interaction. ^{125}Te Mossbauer data for $(\text{p-EtO}\cdot\text{C}_6\text{H}_4)\text{Te}(\text{CH}_2)_4\text{Br}$ are typical of a tellurium (IV) compound and in particular Δ is in the expected range for a telluronium salt. The product of the reaction of $\text{Na Te}(\text{C}_6\text{H}_4\cdot\text{OEt})$ with 1,3-dibromopropane is, from the Mössbauer data, also a telluronium salt.

Key Words

Telluronium salts
Telluride

Tellurium
Ditelluride

Telluroester

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This work was carried out between 1978 and 1981
at the University of Aston in Birmingham.
It has been done independently and has not been
submitted for any other degree.

Monsef
Zahra Monsef-Mirzai

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CHAPTER ONE

INTRODUCTION

INTRODUCTION

Tellurium, atomic number 52, is regarded as a "typical" element of the VIth main group of the periodic table, which includes oxygen, sulphur, selenium and polonium. The atoms are but two electrons short of an inert gas configuration. The elements of this group are classed as non-metals, but there is a steady increase in electropositive character with increasing atomic weight. The first member of the group, oxygen, differs markedly from the other elements. Sulphur shows resemblances to selenium and to a certain extent tellurium. However sulphur is entirely non-metallic whereas from selenium onwards there is increasing metallic character. There is a general similarity between the chemistry of selenium and tellurium. Some evidence of metallic character for selenium appears in the formation of a few basic salts in which the element might be regarded as having some cationic properties. This trend becomes rather more obvious with tellurium. The ionic lattice of TeO_2 is an example of the more metallic character of tellurium, which is not observed in sulphur dioxide and selenium dioxide. The properties of selenium and tellurium lie between those of the non-metals, oxygen and sulphur, and those of the decidedly more metallic polonium which is, for instance, a conductor of electricity.

Like sulphur and selenium, tellurium has a number of oxidation states in even numbers from -2 to +6 but rarely occurs in nature in the elemental state. Co-ordination numbers of 2,3,4,5,6,7 or even 8 are possible.

In general it appears that tellurium and its compounds are less toxic than selenium¹, although there are exceptions to this rule.

In industry tellurium is usually not very hazardous. Nevertheless, care must be exercised where the element or its compounds are used. The garlic odour of the breath is a good indication of the absorption of tellurium into the human body. The garlic smell is caused by a volatile tellurium compound, dimethyltelluride.

A relatively large amount of tellurium is found in fresh garlic buds². Wet ashed garlic (*allium sativum*) contains 71-73 ppm tellurium but with dry ashed garlic (450°C) no tellurium is detected, so presumably the tellurium in garlic is in a volatile compound. Certainly this plant accumulates tellurium from soil².

Since its discovery tellurium has found many industrial uses², for example:

(a) in the vulcanizing of rubber, where it increases resistance to heat, abrasion, and ageing,

(b) in bacteriology, as the tellurite diagnostic test for diphtheria,

(c) as an additive to cast iron, steel, and copper, to improve surface resistance to wear and corrosion,

(d) as a colouring agent in the glass industry,

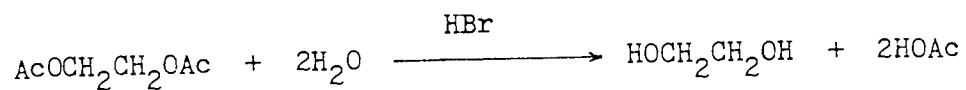
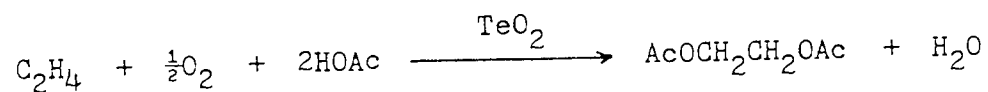
(e) formerly therapeutic uses were as sedatives, in the treatment of syphilis, and to reduce night sweats in phthisis,

(f) some tellurium isotopes are used in medicine in the treatment of thyroid gland diseases,

(g) as a catalyst in the chemical industry e.g. liquid³ tellurium has been found to catalyze the dehydrogenation of several polynuclear hydrocarbons. Also⁴ TeCl_4 and TeBr_4 are active compounds in catalyst systems for the dehydrogenation and dehydrohalogenation of several cyclic hydrocarbons and halogenated

cyclic hydrocarbons,

(h) tellurium is used as a catalyst in the oxyacetylation of ethene ⁵ :



i.e.



(i) dialky tellurides are effective as oxidation inhibitors in lubricating oils,

(j) cadmium telluride ⁶ is used as an X-ray detector in computer assisted tomography.

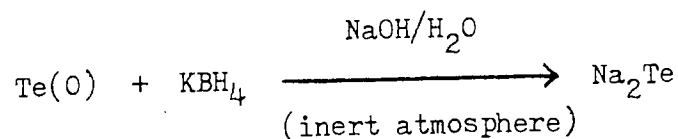
Tellurium compounds have a large history⁷ of utility as addenda in conventional silver halide photographic emulsions. More recently a wide variety of co-ordination complexes and organometallic derivatives of Te(II) and Te(IV) have been investigated as reagents in imaging processes. Images are produced by heating an exposed organo-tellurium compound, such as $(\text{PhCOCH}_2)_2\text{TeCl}_2$ with a photoreductant in a binder.

1.1 Oxidation States of Tellurium

Tellurium can be found with the following oxidation states :

1.1.1 Tellurium(-II)

Tellurium completes the krypton configuration by forming the Te^{2-} ion. This ion exists only in the salts of the most electropositive elements, e.g. sodium salts. Also it is an example of the non-metallic behaviour of this element. The reduction of elemental tellurium to Te(-II) can be effected by KBH_4 in aqueous sodium hydroxide.



1.1.2 Tellurium(0)

Reaction of triphenyl-phosphine and tetraphenylarsonium tellurocyanate in acetonitrile in the presence of LiClO_4 gives an adduct $(\text{Ph}_3\text{P})_2\text{Te}^8$. Crystallographic analysis shows the presence of linear $\text{Ph}_3\text{P}-\text{Te}\dots\dots\text{PPh}_3$ units with C_3 axial symmetry containing one "normal" (2.27-2.42 Å) and one long (3.38-3.95 Å) P-Te bond. IR and Raman spectra of the adduct complement the X-ray studies regarding the general shape of the molecule. The adduct is formally a Te(0) derivative.

1.1.3 The 1/2, 1/3, 2/3 and +1 Oxidation States of Tellurium

The reaction of tellurium with concentrated sulphuric acid to yield a red solution, reported in 1798⁹, was one of the first recorded properties of this element. Tellurium also forms red or yellow solutions in related acidic media such as oleum, sulphur trioxide and fluoro-sulphuric acid. These colours have previously been attributed to the compound 'TeSO₃'. Only recently has it been shown by conductimetric, cryoscopic and spectroscopic investigations that polyatomic cations of tellurium in formal oxidation states of + 1/3, + 1/2, + 2/3 and + 1 are responsible for these coloured solutions¹⁰. These solvent systems of high acidity thereby serve the dual purpose of oxidizing the tellurium and stabilizing the highly electrophilic polycations. The same tellurium species are obtained by reducing TeCl_4 with Te in fused NaAlCl_4 .

1.1.3.1 The + 1/2 Oxidation State

The ion Te_4^{2+} is responsible for the red colour solutions of

tellurium in fluorosulphuric acid, sulphuric acid and oleum^{11,12}. Red solids containing this cation such as $\text{Te}_4^{2+}(\text{SO}_3\text{F}^-)_2$, $\text{Te}_4^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$ and $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$ can be prepared by oxidizing tellurium with $\text{S}_2\text{O}_6\text{F}_2$, SbF_5 and AsF_5 respectively in liquid SO_2 ^{13,14}.

Alternatively, the red solids $\text{Te}_4^{2+}(\text{AlCl}_4^-)_2$ and $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ have been obtained from $\text{Te}-\text{TeCl}_4-\text{AlCl}_3$ melts^{15,16}. X-ray diffraction studies on single crystals of the last two compounds have demonstrated that the Te_4^{2+} ion lies on a centre of symmetry and is almost square planar¹⁷. The tellurium-tellurium distance of 2.66 Å is significantly shorter than the tellurium-tellurium distance of 2.86 Å within the spiral chain in elemental tellurium.

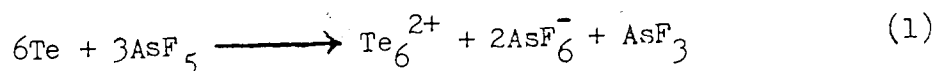
^{125}Te and ^{123}Te n.m.r spectra of the series of compounds $[\text{Te}_n\text{Se}_{4-n}]^{2+}$ ($n=1-4$) in the $\text{Te}-\text{Se}-\text{oleum}$ system have been studied^{18,19}. The square planar Te_4^{2+} cation exhibits, along with the main Te resonance line, both cis and trans $^{125}\text{Te}-^{123}\text{Te}$ coupling satellites whose component lines have relative intensities of 2:1 respectively. The Te_4^{2+} species is found to high field with respect to other ^{125}Te resonances when Se atoms are present. There is a progressive downfield shift with the replacement of Se atoms for Te atoms. This is consistent with the higher electronegativity of Se than that of Te, the Se atoms withdrawing the electrons from Te more strongly, leading to a deshielding of the Te nucleus. The chemical shifts from Te_4^{2+} to $[\text{TeSe}_3]^{2+}$ are very large because of the large paramagnetic contribution to the shielding term.

1.1.3.2 The + 1/3 Oxidation State

If tellurium is treated with a stoichiometric amount of^{14,19}

AsF₅ dissolved in liquid SO₂, a grey solid of empirical composition Te₃AsF₆ is formed. The infrared spectrum of the solid and the ¹⁹F n.m.r spectrum of an acetone solution showed the presence of the AsF₆⁻ ion. The compound is diamagnetic and therefore probably Te₆²⁺(AsF₆⁻)₂. It is concluded that the compound Te₃AsF₆ contains a polyatomic cation of tellurium Te_{3n}ⁿ⁺ in which tellurium is in the + 1/3 oxidation state.

During phase studies of the Te-TeCl₄-AlCl₃ system, hexagonal crystals of the related black compound (Te₃AlCl₄)_n have been isolated. Density^{15,21} measurements and unit-cell dimensions suggest a value of 1 or 2 for n, hence these compounds most probably contain Te₆²⁺ or Te₁₂⁴⁺ ions. Assuming that the cation is Te₆²⁺, its formation from tellurium and AsF₅ is described by the equation (1).



¹²⁵Te and ⁷⁷Se, n.m.r studies of the Te₂Se₄²⁺ and Te₃Se₃²⁺ species have been reported¹⁹. In the case of Te₂Se₄²⁺ the n.m.r spectra show one Te resonance and three Se resonances. The respective intensities of the component lines are 2:1:1. This, with the Se-Se and Se-Te spin-spin coupling patterns indicate that the structure in solution may be as shown in figure (1a). Similarly in the case of Te₃Se₃²⁺ observation of ¹²⁵Te and ⁷⁷Se n.m.r spectra show two Te resonances, in the ratio 2:1 and two Se resonances, in the ratio 2:1. The Se-Se and Se-Te spin-spin coupling patterns are in accordance with a solution structure such as shown in figure(1b). Again as shown previously for + 1/3 oxidation state

species, when the number of electronegative Se atoms increase, from $\text{Te}_3\text{Se}_3^{2+}$ to $\text{Te}_2\text{Se}_4^{2+}$, the ^{125}Te nucleus tends to become more deshielded.

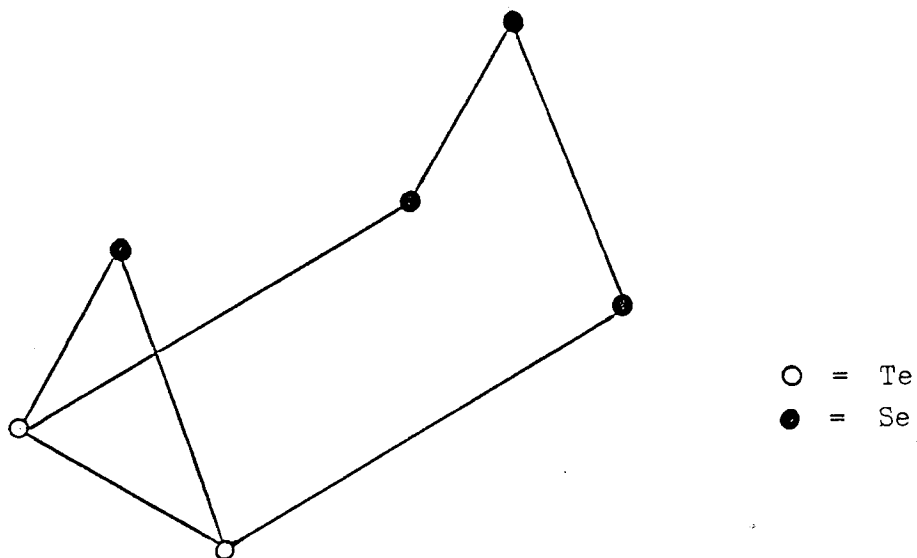


Figure (1a)

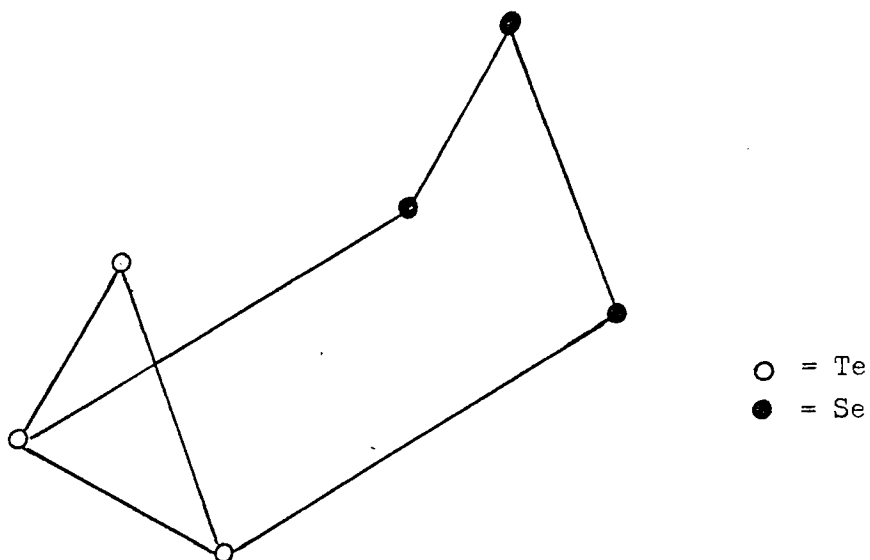


Figure (1b)

Generally both, ^{125}Te and ^{77}Se nuclei in cations where the oxidation state is $+1/3$ are found to be more shielded than ^{125}Te and ^{77}Se nuclei in cations where the oxidation state is $+1/2$. Over a period of time the $+1/3$ oxidation state species may, under suitable conditions, be oxidized to $+1/2$ oxidation state species of the type $\text{Te}_{4-n}\text{Se}_n^{2+}$, which is shown by a deshielding of the ^{125}Te and ^{77}Se nuclei.

1.1.3.3 The $+2/3$ Oxidation State

A well known example of the $+2/3$ oxidation state is the cation Te_6^{4+} ¹⁹. ^{125}Te n.m.r studies of this cation in solution, including an observation of ^{125}Te - ^{123}Te spin-spin coupling patterns, suggests that the structure may be, as shown in figure (2), a trigonal prism¹⁹.

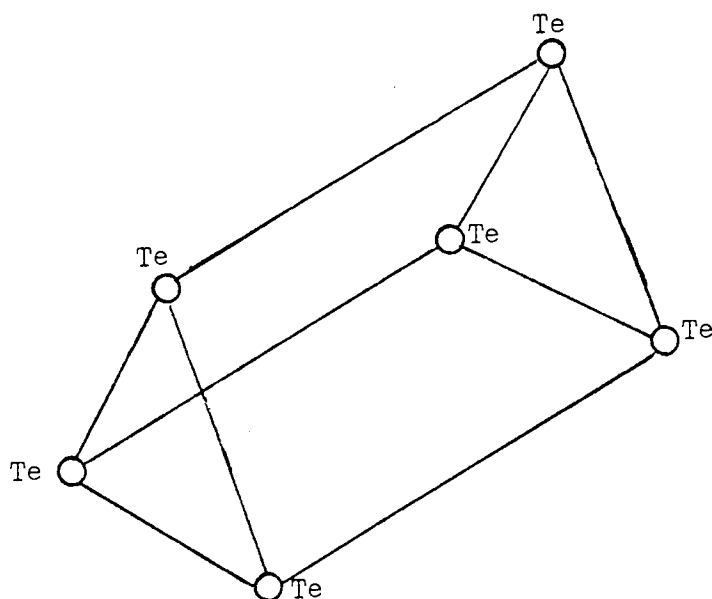


Figure (2). The structure of the Te_6^{4+} cation

This structure is in agreement with crystal structures of $\text{Te}_6(\text{AsF}_6)_4 \cdot 2\text{AsF}_3$ and $\text{Te}_6(\text{AsF}_6)_4 \cdot 2\text{SO}_2$ compounds in the solid state²⁰ from X-ray

crystallography.

It may be assumed that a series of other $+ 2/3$ oxidation state cations of the general formula $\text{Te}_{6-n}\text{Se}_n^{4+}$ ($n=1-6$) may be possible.

The relationship between the structure of $\text{Te}_2\text{Se}_4^{2+}$, $\text{Te}_3\text{Se}_3^{2+}$ 19,20 and possible structures for Te_n^{n+} and Te_6^{2+} is of interest. The first two have boat-shaped six-membered rings with one cross-ring bond forming a three-membered Te_3 or Te_2Se ring as shown in figure (3).

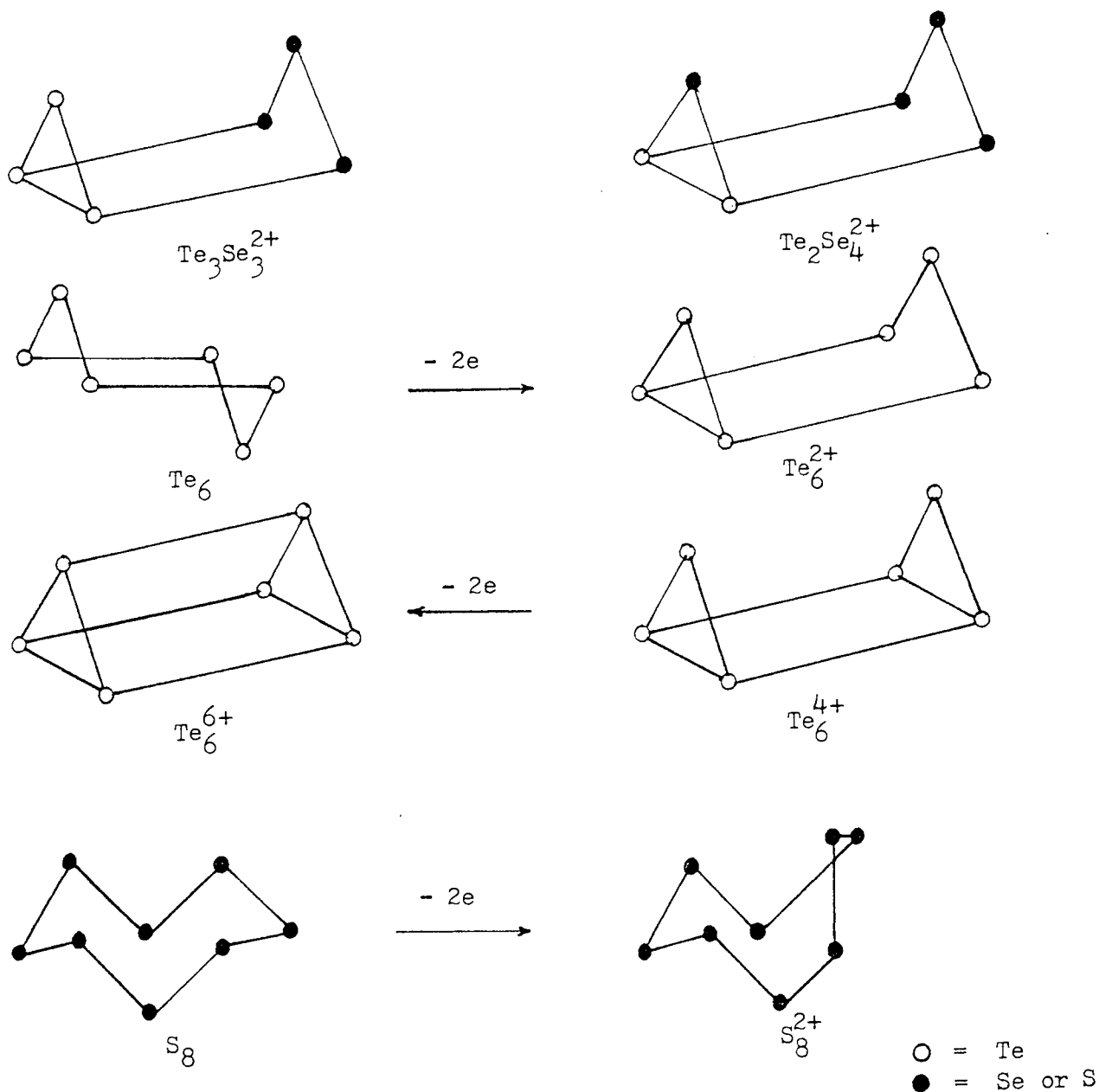


Figure (3). Structures related to Te_6^{4+}

It seems reasonable to assume that Te_6^{2+} might have the same structure. Removal of an electron pair then leads to the formation of an additional bond to complete the second Te_3 triangle to give Te_6^{4+} .

It is interesting to note^{18,19} that Te in the + 2/3 oxidation state has a higher electron density than Te in the + 1/2 and + 1/3 oxidation states. This is shown through a greater n.m.r shielding of Te nuclei in the + 2/3 oxidation state than in the + 1/2 and + 1/3 oxidation states.

1.1.3.4 The + 1 Oxidation State

The red Te_4^{2+} cation may be further oxidized to a yellow species, containing tellurium in the + 1 oxidation state¹⁴. Magnetic measurements showed the solid compound to be diamagnetic and the infrared spectrum showed that it contains the SbF_6^- ion. Cryoscopic measurements on Te_n^{n+} in fluorosulphuric acid have shown that the cation is not Te_2^{2+} but could not distinguish between Te_4^{4+} , Te_6^{6+} and Te_8^{8+} . TeCl_4 , however, is reduced by elementary tellurium to Te_2^{2+} in KAlCl_4 melts when the latter are buffered to a fairly high chloride activity with ZnCl_2 - KCl , as shown by spectrophotometric measurements. Possible structures for these cations have been proposed²¹ and are illustrated in figure (4).

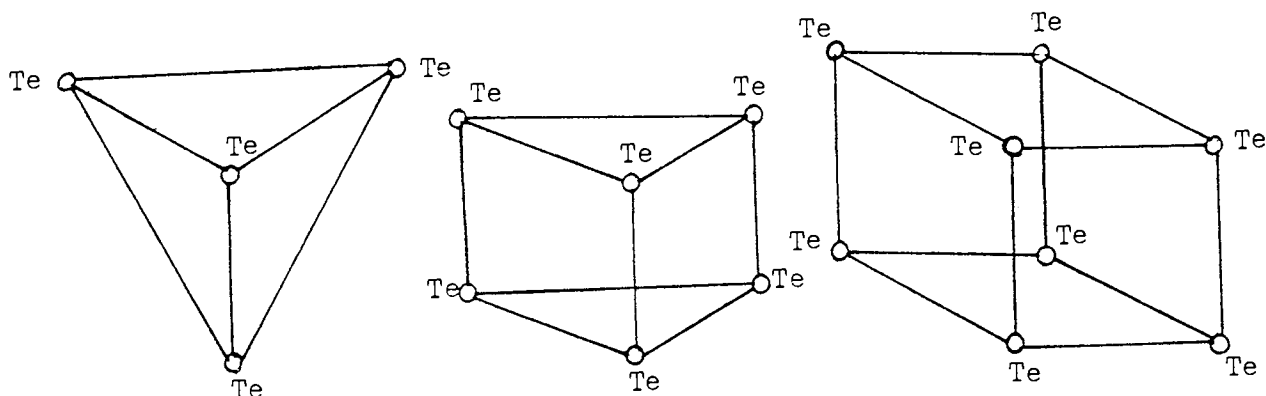


Figure (4). Proposed structures for the ions Te_4^{4+} , Te_6^{6+} , Te_8^{8+}

1.1.4 Tellurium(II)

The compounds included in oxidation state(II) are the tellurides R_2Te or TeX_2 ($X=Cl, Br, I$) and tellurenylhalides $RTeX$. Ditellurides exhibit oxidation state(I) but it is convenient to include them here, since the evidence of Mössbauer spectroscopy²² indicates that the electronic environment of tellurium in ditelluride is very similar to the tellurium in telluride.

Tellurium(II) compounds are often two co-ordinate, but can be four co-ordinate.

The structure of tellurium dibromide in the vapour phase, from Rogers and Spurr's electron diffraction study²³ in 1947, is shown in figure (5). The Te-Br bonds are 2.51 \AA , which agrees with the sum of the covalent single bond radii, and the Br-Te-Br angle is 98° .

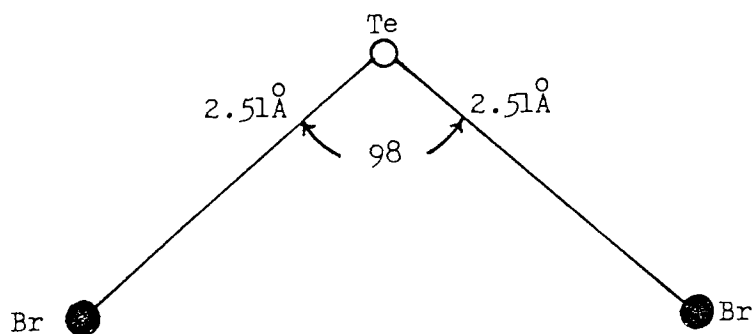


Figure (5). The tellurium dibromide molecule.

In the molecule of *o*-formylphenyltellurenyl bromide²⁴ the Te(II) atom has a bipyramidal geometry, if the two lone pairs are considered. However, the Te...O distance to the carbonyl oxygen atom is long

(2.31 Å) and makes only a small contribution to the overall bonding scheme. This is illustrated in figure (6) below.

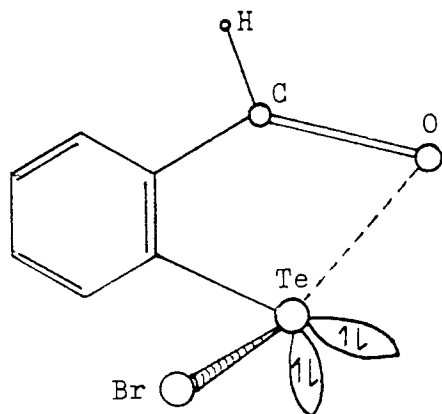


Figure (6)

The C=O distance of 1.283 Å is consistent with this interpretation. The Te-Br and Te-C distances are 2.618 Å and 2.08 Å, respectively.

The crystal and molecular structure of diphenylditelluride²⁵ $C_{12}H_{10}Te_2$ has been determined by X-ray crystallography and is shown in figure (7). The molecule has a non-planar configuration and the planes of the benzene rings are inclined at an angle of 20.1°. The Te-Te bond length is 2.712 Å. The average of the observed Te-C bond distances is 2.115 Å.

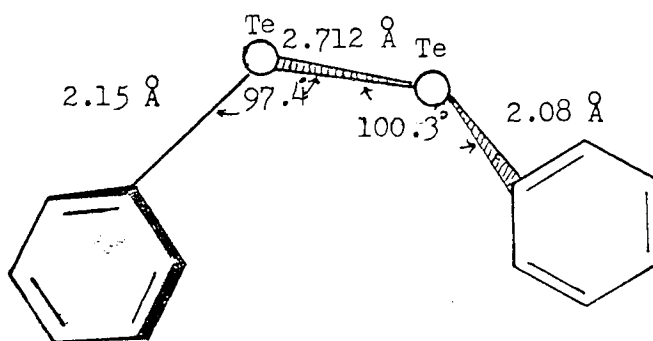


Figure (7)

The crystal and molecular structures of several three co-ordinated complexes of divalent tellurium have been reported^{26,27}.

The crystal structures²⁸ of $C_6H_5Te(su)_2Cl$, phenylbis(selenourea)-tellurium(II) and $C_6H_5Te(tu)_2Cl$ phenylbis(thiourea)tellurium(II) chloride are shown in figures (8) and (9). In each of the two structures the tellurium atom is three co-ordinated, being bonded to one phenyl carbon atom and, in directions nearly perpendicular to the Te-C bond, to two selenourea selenium atoms in figure (8), and to two thiourea sulphur atoms in figure (9), and to two thiourea sulphur atoms in figure (9).

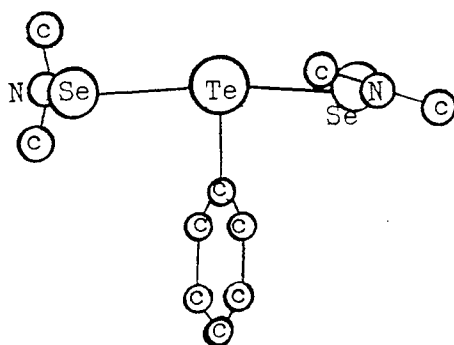


Figure (8). Phenylbis(selenourea)tellurium(II) cation, as seen normal to the plane through the co-ordination group.

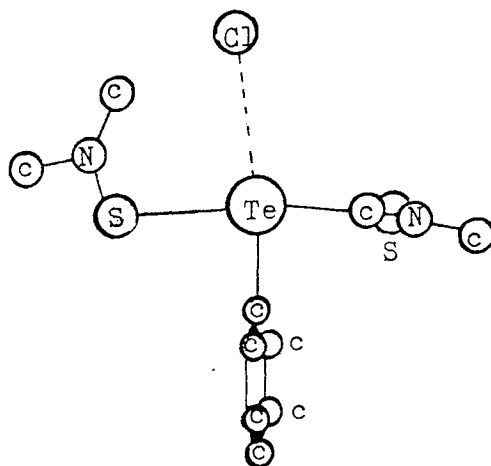


Figure (9). Phenylbis(thiourea)tellurium(II) chloride, as seen normal to the plane through the co-ordination group.

1.1.5 Tellurium(IV)

Structures of tetravalent tellurium compounds are well known. The most common co-ordination of atoms around Te(IV) in the solid state is that shown in figure (10)²⁹.

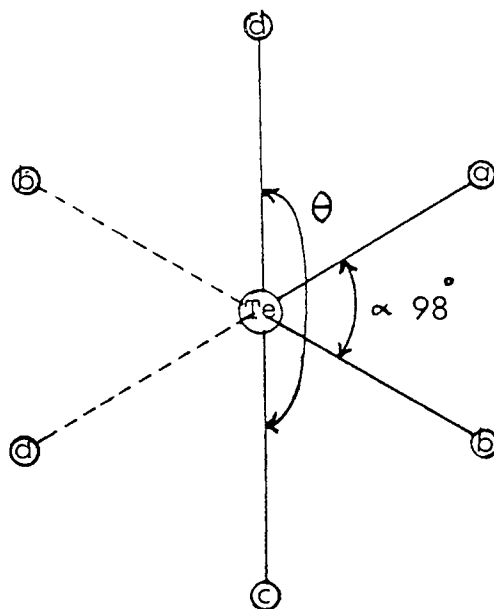


Figure (10). Common co-ordination of atoms around Te(IV) in crystals.

In compounds of the type R_2TeX_2 where R is an organic group and X is a halogen, two distinct structural forms are known, α - and β -types.

The crystal structures of Me_2TeCl_2 ³⁰, Ph_2TeBr_2 ³¹, α - Me_2TeI_2 ³² are similar, and have been described as distorted tetrahedral, distorted trigonal bipyramidal, and distorted octahedral, depending on the significance attributed to intermolecular attractions and the mixing of p-electron density with the 5s electrons. Low frequency i.r and Raman

spectra of many diaryl tellurium dihalides are consistent with Ψ -trigonalbipyramidal structures in which the halogens occupy the axial position³³.

In the case of $(\text{CH}_3)_2\text{TeCl}_2$ the Cl-Te-Cl angle is slightly less than 180° , the Te-Cl bonds are bent slightly towards the Te-C bonds and away from the lone pair, as would be expected. In $(\text{C}_6\text{H}_5)_2\text{TeBr}_2$ where a deviation from the ideal angle of 180° has been recorded the angle between the axial bond is slightly greater than 180° , the axial bonds are bent slightly away from the equatorial bonds and towards the lone pair these are illustrated in figures (11) and (12) respectively.

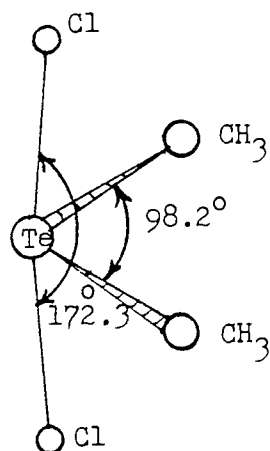


Figure (11). $(\text{CH}_3)_2\text{TeCl}_2$

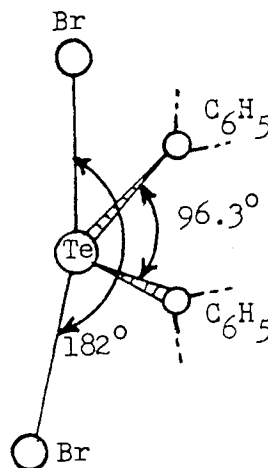


Figure (12). $(\text{C}_6\text{H}_5)_2\text{TeBr}_2$

A straight application of modern structural considerations³⁴ would suggest that the Me_2TeI_2 molecule possesses a trigonal-bipyramidal arrangement around the tellurium atom with the non-bonding electron pair in an equatorial position. In fact, dimethyltellurium diiodide exists

in α and β forms which were originally classified as cis and trans isomers of a square-planar structure. Further chemical evidence³⁵ suggested that the α form had the covalent structure Me_2TeI_2 while the β form had the ionic structure $(\text{Me}_3\text{Te})^+(\text{MeTeI}_4)^-$. Although optical crystallographic data for both forms³⁶ and preliminary X-ray measurements for the α form have been reported,³⁷ Einstein et.al³⁸ have reported the detailed crystal structure of the β form, confirming the suggested ionic formulation shown in figure (13).

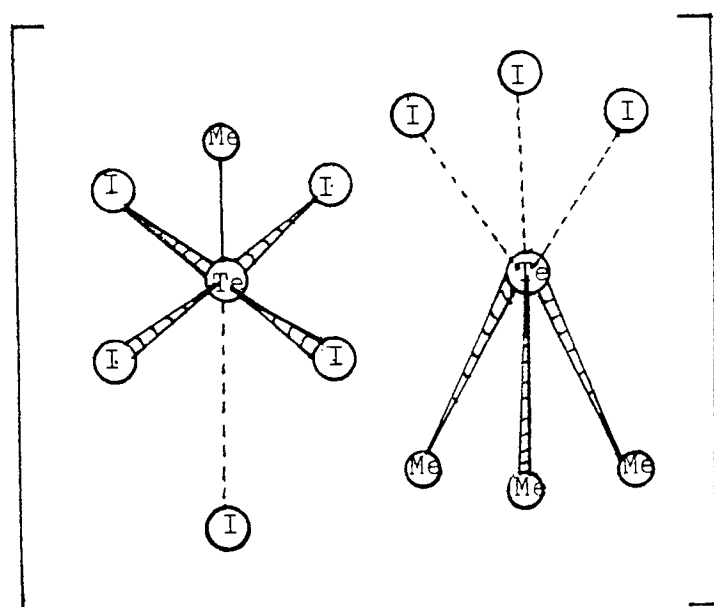


Figure (13)

The monoclinic crystals are built up from trigonal pyramidal Me_3Te^+ cations with the Te-C bond length equal to 2.07 Å and the C-Te-C angle equal to 95 degrees, and from square pyramidal MeTeI_4^- anions with a Te-C bond length at 2.15 Å and Te-I bond lengths 2.84-2.98 Å. The ions are bridged by four weak Te....I interactions (distances 3.84, 3.88, 3.97 and 4.00 Å) which complete a distorted octahedral environment around each tellurium ion, the non-bonding electron pair presumably completing

a tetrahedral configuration in the Me_3Te^+ cation and occupying the sixth position of an octahedron in the anion MeTeI_4^- . Einstein et.al³² have carried out a structure determination of the α form in order to investigate its nature and also to compare it with the ionic form shown in figure (14).

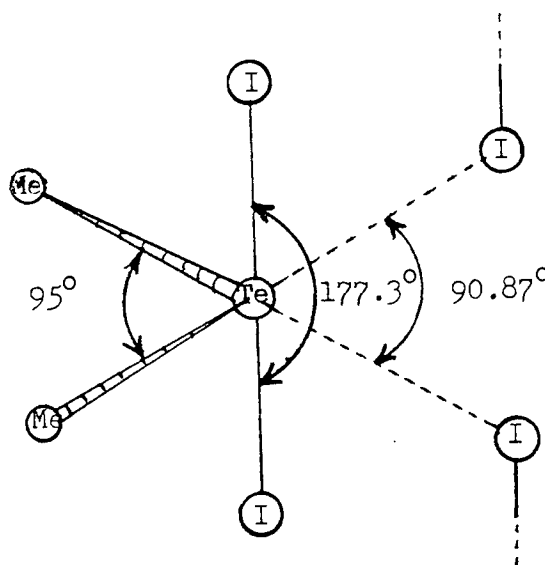


Figure (14)

Each tellurium atom has a distorted octahedral environment with iodine atoms in a trans-arrangement, two methyl groups cis-to each other, and two contacts from iodine atoms attached to neighbouring molecules.

Intramolecular Te-I bond lengths range from 2.85 to 2.99 Å and Te-C bond lengths range from 2.10 to 2.16 Å. The intermolecular Te.....I contacts range from 3.659 to 4.03 Å.

A number of tetramethylthiourea complexes of the general formula $\text{RTeX}_3(\text{tmtu})$ (where R=Me or Et; X=Cl, Br, or I; or R=p-MeO. C_6H_5 , X=Cl) have been prepared³⁹ as moisture-sensitive crystalline solids. The

complexes are monomeric in CHCl_3 solution and i.r data suggest a square pyramidal form [figure(15)] with sulphur co-ordinated tetramethylthiourea.

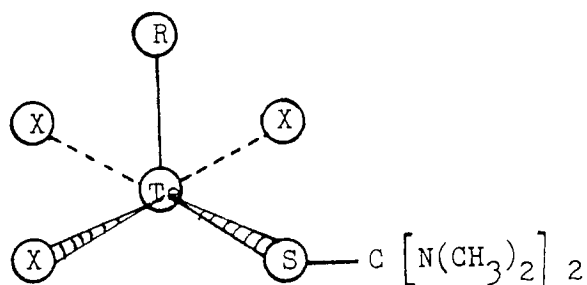


Figure (15)

The reaction⁴⁰ of TeBr_2 with cycloheptene in ethanol, however, produced cis-2-ethoxycycloheptyltribromotellurium(IV), $[\text{2}(\text{TeBr}_3\text{C}_7\text{H}_{12}\text{OC}_2\text{H}_5)]$. The crystal structure of this compound has been determined by X-ray crystallography and is illustrated in figure (16).

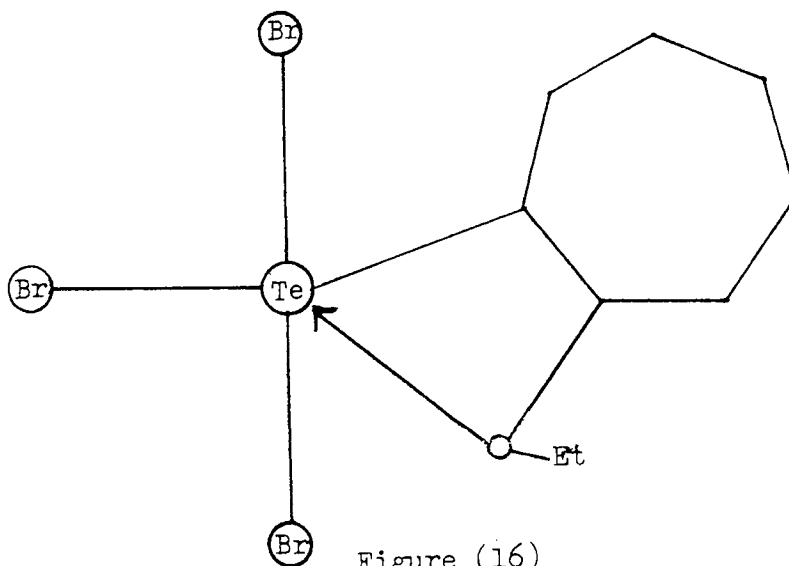


Figure (16)

The oxygen atom of the ethoxy group acts as an internal

Lewis base donating a pair of electrons to the tellurium atom. The tellurium atom therefore is now a five co-ordinate species with an additional lone pair of electrons. Consequently the structure is a distorted octahedron.

The crystal and molecular structures of trans-tetrabromo- and trans-tetrachloro-bis(tetramethylthiourea)tellurium(IV) have been studied⁴¹. As in other 6-co-ordinated Te^{IV} species, the unshared electron pair appears to play no detectable role in determining the disposition of the ligands around the central atom so that the configuration is regularly octahedral as shown in figure (17).

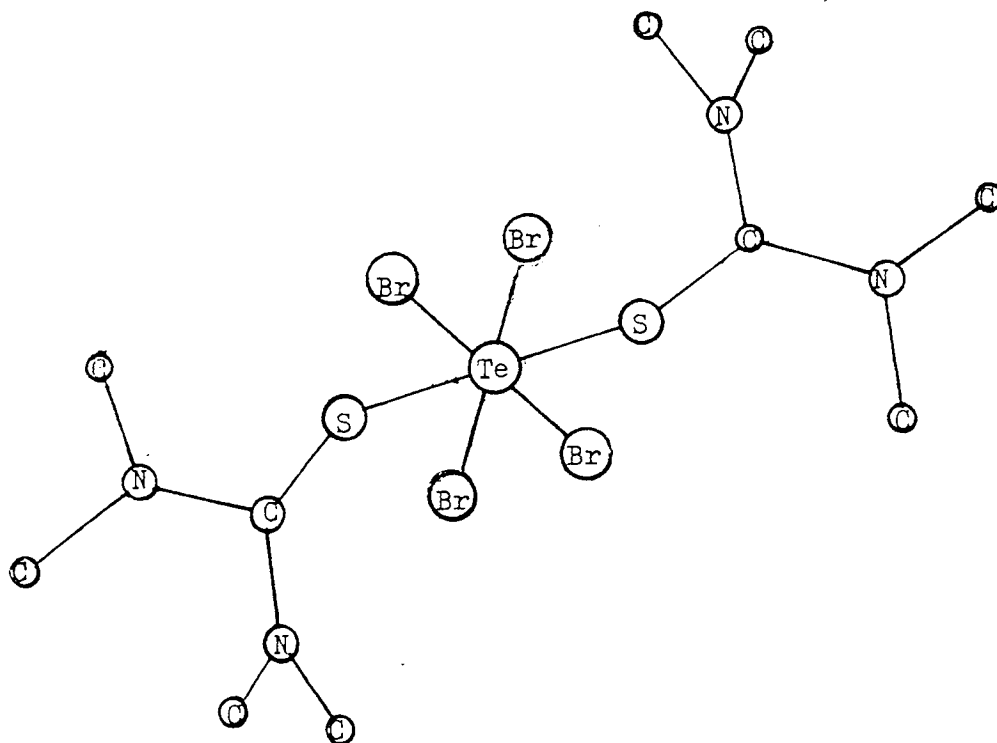


Figure (17). The molecular structure of tetrabromobis(tetramethylthiourea)tellurium(IV)

Crystal structures of the tellurium complexes $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Ph}$,⁴² $\text{Te}(\text{Et}_2\text{NCS}_2)_4$ ⁴³ and $\text{Te}(\text{OC}_4\text{H}_8\text{N}.\text{CS}_2)_4$ ⁴⁴ show that the tellurium atom has seven and eight co-ordination respectively. The structure having co-ordination number seven is a distorted pentagonal bipyramid (figure(18)). The central tellurium atom is bonded to all six sulphur atoms in the molecule and to a carbon atom in the phenyl group.

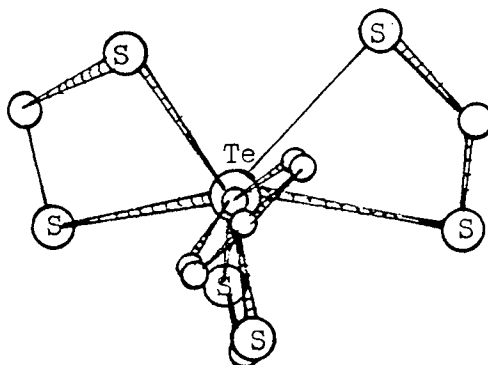


Figure (18). The $(\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Ph})$ molecule

The $\text{Te}(\text{OC}_4\text{H}_8\text{N}.\text{CS}_2)_4$ molecule Te atom is found to be eight co-ordinated by sulphur atoms in a dodecahedral D_{2d} arrangement. The dodecahedral TeS_4 group has a structure similar to that found for the corresponding group in tetrakis(diethyldithiocarbamato)tellurium(IV)⁴⁵ and thus the lone pair of electrons in the valency shell of the central

Te atom is essentially stereochemically inert. $\text{Te}(\text{Et}_2\text{NCS}_2)_4$ forms flat, prismatic orange crystals. The asymmetric unit comprises two crystallographically independent but very similar molecules. The central tellurium atom is bonded to all eight sulphur atoms in each molecule in a slightly distorted dodecahedral configuration. A dodecahedron can be visualized as two interleaving planar trapezoids at right angles to each other. The average co-ordinations within a trapezoid for $\text{Te}(\text{OC}_4\text{H}_8\text{NCS}_2)_4$ and $\text{Te}(\text{Et}_2\text{NCS}_2)_4$ are shown in figures (19) and (20) respectively.

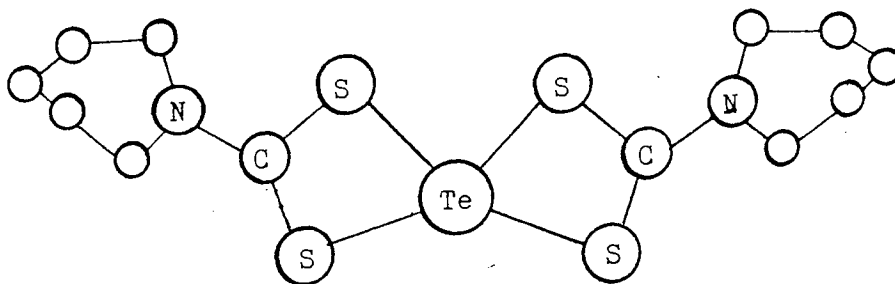


Figure (19)

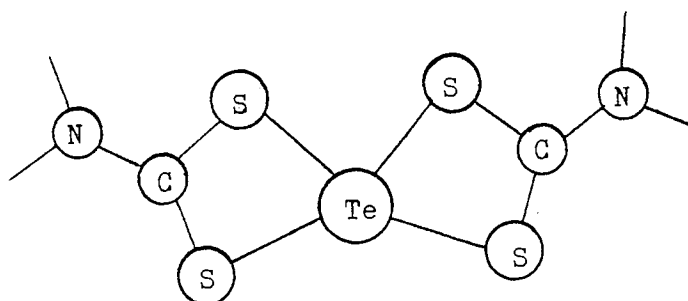


Figure (20)

1.2 Organotellurium Compounds

These compounds are classified into the following :

R_2Te_2 , R_2Te , R_2TeX_2 , $RTeX_3$, R_3TeX and R_4Te .

1.2.1 R_2TeX_2

Organic tellurides form adducts of 1:1 molecular composition with halogens, and many of these can be isolated as crystalline solids.



^{125}Te Mössbauer⁴⁶ data for a number of aryl tellurium dihalides have been investigated. The isomer shifts for the dihalides are more positive than those of the diorganotellurides and this is consistent with the halogen ligands removing predominantly 5p electron density from the tellurium. However within a given series of dihalides the isomer shift does not change significantly with increasing electronegativity of the halogen. For example, the derivatives $(p-MeOC_6H_4)_2TeX_2$ ($X=F, Cl, Br, I$) all have the same isomer shift within experimental error.

The quadrupole splittings for the dihalides clearly lie in the order $F > Cl > Br > I$ for the $(p-MeOC_6H_4)$ derivatives for example. This is consistent with an increasing 5p orbital imbalance about the tellurium as the electronegativity of the halogen increases.

The structure⁴⁷ of phenoxotellurium 10,10-diiodide, $C_{12}H_8OTeI_2$ has been determined by X-ray crystallography and is shown in figure (21). The I-Te-I angle is 176.44° . Tellurium also forms weak bonds with iodine in each

of two neighbouring molecules with Te....I distances of 3.739 and 3.788 Å. The tellurium-carbon bond angle is 91.5° .

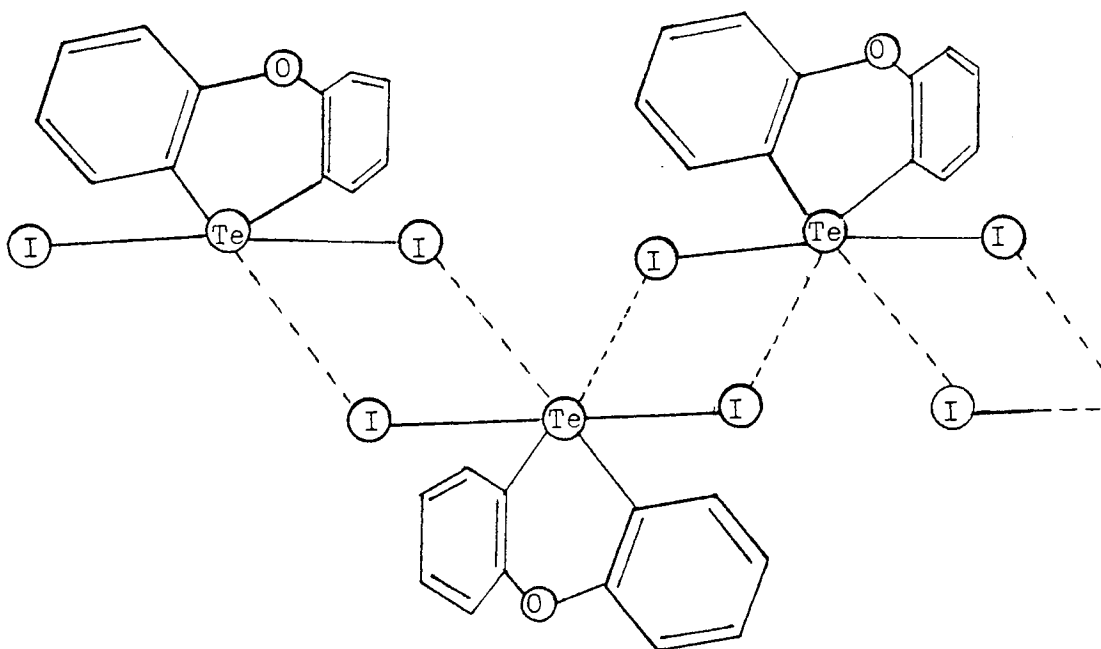


Figure (21)

In the case of 1-oxa-4-telluracyclohexane 4,4-diiodide, $C_4H_8OTeI_2$, the structure is similar as shown in figure (22).

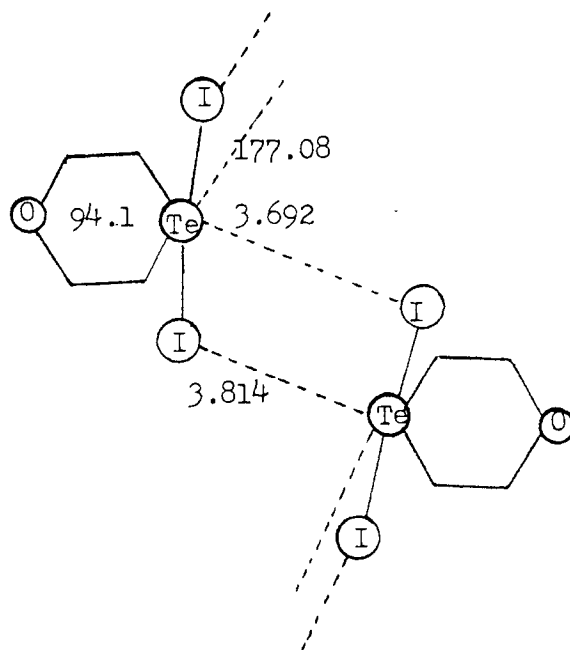


Figure (22)

1.2.2 $R\text{TeX}_3$

Spectroscopic evidence suggests that the aryltellurium(IV)-trichlorides, tribromides and triiodides are associated in the solid state⁴⁹. It is possible to consider that each structure may arise from a donor-accepter interaction between X^- and $R\text{TeX}_2^+$.

Structural studies of $C_{12}H_9\text{TeBr}_3$ ⁵⁰ and $C_{12}H_9\text{TeI}_3$ ^{51,52} have been reported. In both structures, the configuration about tellurium is found to be essentially trigonal bipyramidal with two halogen atoms in axial positions and with the third halogen atom plus a carbon atom and a pair

of electrons in the equatorial positions. Intermolecular or secondary bonding is of considerable importance in the triiodide but is almost absent in the tribromide (figures(23), (24), (25)).

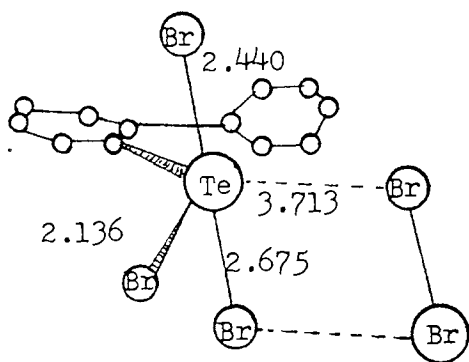


Figure (23)

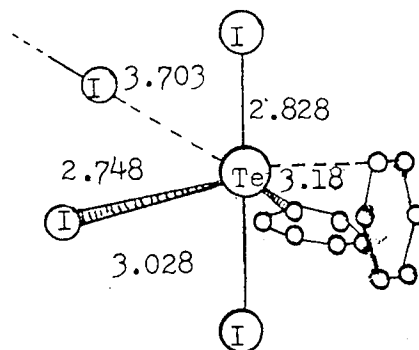


Figure (24)

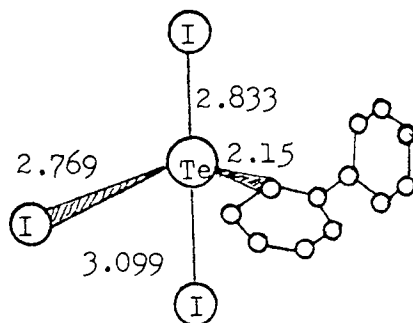


Figure (25)

In the case of the triiodide two crops of crystal forms are known, α - and β -types. The principal differences in the crystal structures of the α and β forms are in the intermolecular bonding arrangements of the heavy atoms.

Molecular weight studies⁵³ of CH_3TeCl_3 and CH_3TeBr_3 in solution suggested acceptor behaviour of these compounds. The reactions of CH_3TeCl_3 and CH_3TeBr_3 with tetramethylthiourea (tmtu) to yield 1:1 complexes also demonstrates acceptor behaviour. The reaction of RTeCl_3 , where $\text{R}=\text{CH}_3$, C_2H_5 and $p\text{-CH}_3\text{OC}_6\text{H}_4$, with SbCl_5 as Lewis acid capable of accepting halide ions to give 1:1 adducts is an example of donor behaviour.

^{125}Te Mössbauer⁴⁹ data for the trihalides, when $\text{X}=\text{Cl}$, Br , I show that the isomer shifts are more positive than those of the dihalides, consistent with the removal of predominantly p character by the halogen. However, the chemical isomer shifts for the difluorides and trifluorides are essentially the same and thus the trifluorides are significantly different from the other trihalides in this regard. This is an example of donor behaviour.

1.2.3 R_4Te

Very little structural data is available for tetraorganyl-tellurium compounds, the only example being the X-ray crystallographic study of $(\text{C}_6\text{H}_5)_4\text{Te}\cdot\text{C}_6\text{H}_6$. Ziolo⁵⁴ found a trigonalbipyramidal arrangement of four phenyl groups as shown in figure (26a). No bond angles were given, only the bond lengths for the Te-C axial as 2.3 Å and Te-C equatorial as 2.13 Å. This structure is in fact similar to that found for diorganyltellurium dihalides, for example $(\text{C}_6\text{H}_5)_2\text{TeBr}_2$ as shown in

figure (26b).

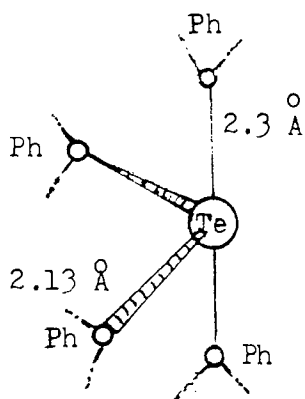


Figure (26a)

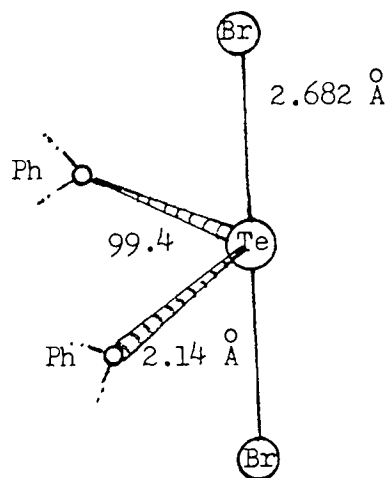
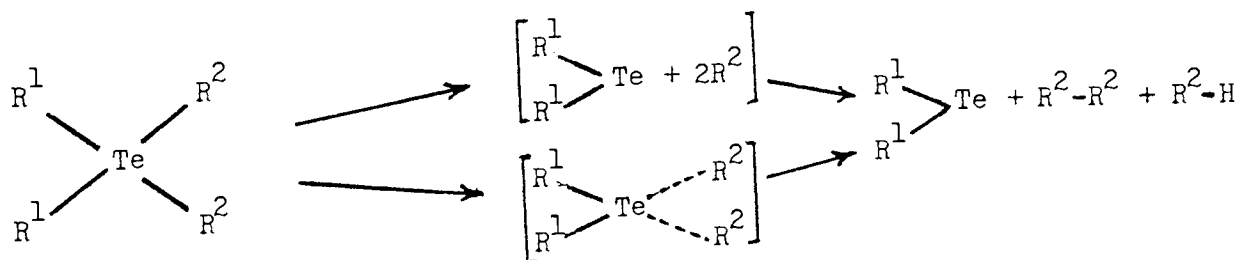
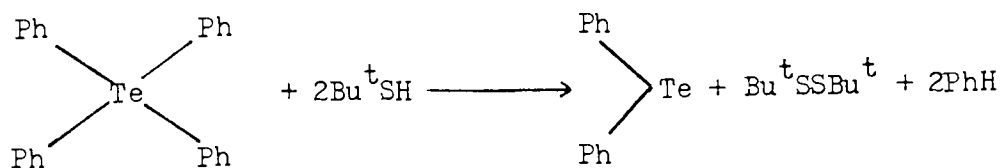


Figure (26b)

Tetra-aryltellurium⁵⁵ compounds decompose thermally to biaryls and diaryl tellurides.



Diaryl tellurides and biaryls are the major products. Tetraphenyltellurium reacts exothermically with Bu^tSH at room temperature, where it is stable thermally, to produce benzene, diphenyltelluride, and di-*t*-butyl disulphide.

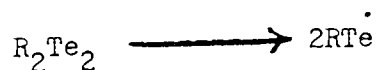


It has been concluded that tetra-aryltellurium compounds exchange ligands by a fast non-radical process prior to decomposition to diaryltellurium and biaryl. The decomposition process itself is concerted, does not involve radicals and represents an interesting procedure for the formation of carbon-carbon bonds.

1.2.4 R₂Te

Investigations of organic tellurium(II) compounds as ligands are reported. Most of information available suggests that they have a pronounced class(b) character^{56,57}.

Co-ordination complexes have involved three different species of co-ordinated ligand, the telluro group, RTe^- , the tellurides, R_2Te , and ditellurides, R_2Te_2 . The telluro group usually arises from the cleaving of Te-Te bond in ditellurides. One case has been reported where the breaking of a Te-C bond in a telluride is involved⁵⁸.



A series of metal halide complexes⁵⁹ of di-p-ethoxyphenyl telluride have been studied by Mössbauer spectroscopy with a view to interpreting it in terms of donor/acceptor properties of these compounds. The chemical isomer shift(δ) is seen, within the error of the measurement, to be very insensitive to complex formation. This implies that the p-lone pair is primarily involved in the donation to the acceptor; more particularly, significant rehybridization at tellurium may be excluded and there is no overwhelming evidence of backbonding to tellurium d-orbitals forming a significant part of the bonding.

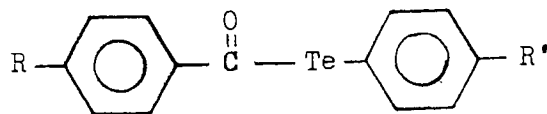
Quadrupole splittings(Δ) suggest that the drift of electrons to the Lewis acid is very small even in the most favourable case. It has been shown that an order of Lewis acidity relative to (p-EtOC₆H₄)₂Te is in the series Hg(II) > Pt(II) > Pd(II) > Cu(I).

A series of organotellurium(II) derivatives of general formula "ArCOTeAr" have been prepared and characterized chemically and spectroscopically.

These diorganotellurium(II) derivatives, in contrast to the dialkyl analogues R₂Te^{60,61} and mixed alkyl aryl derivatives RTeAr^{62,63}, which are both ligands, are isolable as stable crystalline solids⁶⁴. They are relatively low melting and soluble in a variety of organic solvents (e.g acetone, DMF, acetonitrile, benzene and chloroform).

¹³C n.m.r spectra⁶⁵ for several of the telluroesters have been determined in an attempt to correlate the chemical shift of the carbonyl carbon with the various substituents on the phenyl rings. The chemical shift data show no correlation between the Hammett σ values of the various substituents and the position of the carbonyl carbon.

¹²⁵Te n.m.r data for the telluroesters shown in figure (27) have been reported⁶⁶.



(a : R=H, R'=CH₃;

b : R=CH₃O, R'=CH₃;

c : R=C₈H₁₇O, R'=C₅H₁₁)

Figure (27)

The smaller chemical shifts for the two p-alkoxy substituted esters b and c relative to a in both series suggest that the tellurium nucleus is strongly shielded by the electron density donated by the p-alkoxy groups. It is interesting to note that both hetero-atoms are thus affected even with a carbonyl function between them and the p-alkoxy substituted aromatic ring.

The electron-impact mass spectrum⁶⁷ of one of the derivatives, PhCOTePh, has been recorded. As with diaryltellurides and diaryl-ditellurides, the molecular ion(M⁺) is present in the spectrum. Other ions visible in the spectrum are Ph₂Te⁺, PhTe⁺, Ph₂⁺, PhCO⁺ and Ph⁺.

The first report of photoreactions of telluroesters was published in 1978⁶⁸. Telluroesters Ia-f undergo photoinduced α -cleavage to give a variety of products, including elemental tellurium, ditellurides, aldehydes, and photo-Fries product^{68,69} as shown in figure (28).

Cleavage of the carbonyl-tellurium bond under ultraviolet irradiation leads to free aroyl radicals IIa-f, and telluryl radical III.

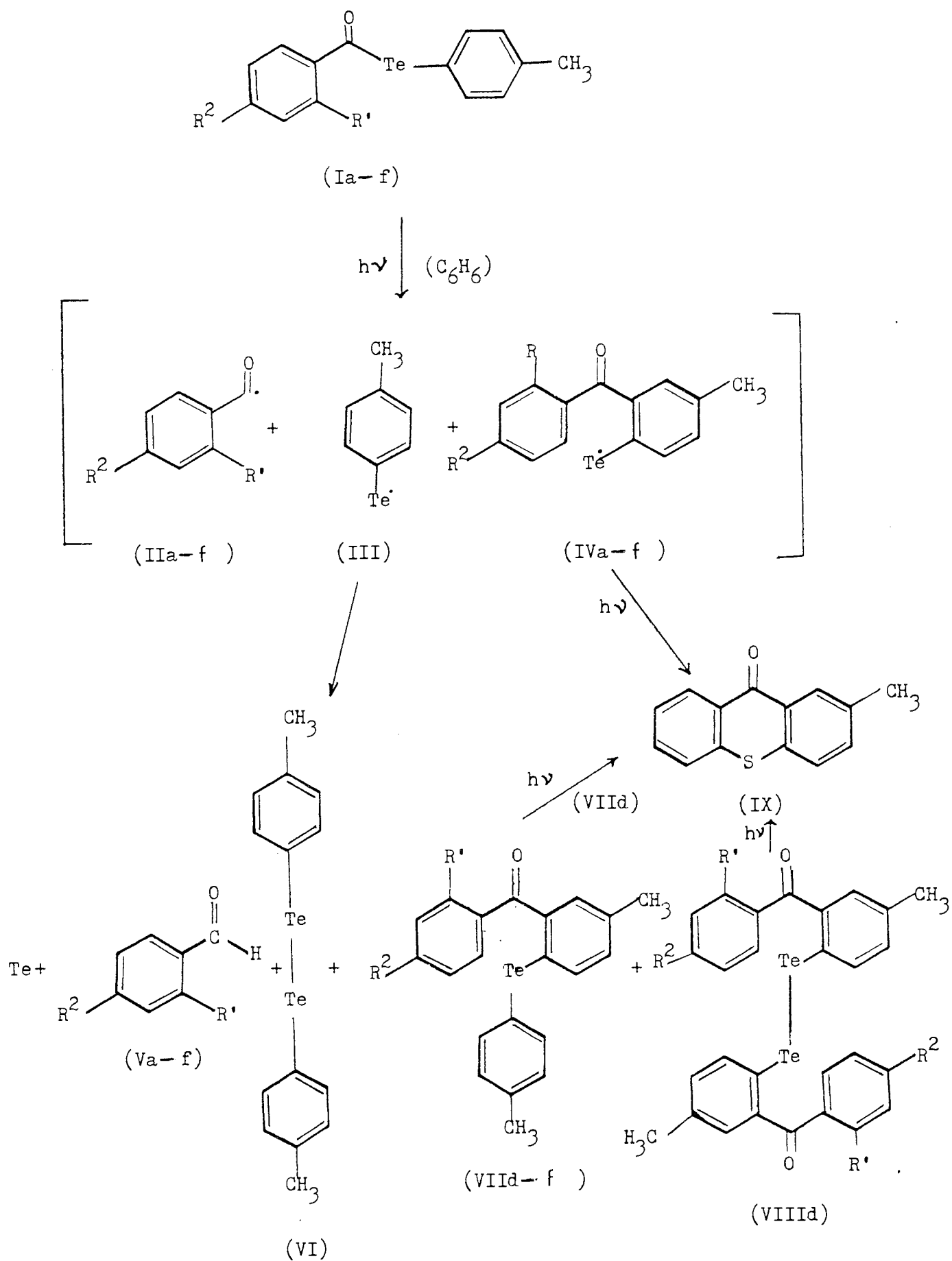


Figure (28). Photo reaction of some telluroesters.

The aroyl radicals abstract hydrogen to give the benzaldehydes Va-f. The telluryl radicals dimerize to form the ditelluride VI. In the case of the ortho-O and ortho-S substituted telluroesters Ia-f the benzophenones VIIId-f are formed as secondary products of an initial telluro-photo-Fries reaction⁶⁹. In the special case of the telluroester Ia-f six photo-products have been isolated; namely elemental tellurium, aldehyde Va-f, ditelluride VI, benzophenone VIIIdf, ditelluride VIIId, and thioxanthone IX^{68,69}. Independently, VIIId and VIIId are suitable substrates to form thioxanthone I-X on ultraviolet irradiation^{68,69}. The yields of the various products are indicated in table (1).

	R ₁	R ₂	Yields (%)					
			Te	Va-f	VI	VIIId-f	VIIId	IX
a	H	H	30	22	46			
b	H	OCH ₃	0	15	62			
c	Cl	H	19	9	49			
d	SCH ₃	H	25	13	33	2	11	22
e	SO ₂ CH ₃	H	11	6	26	10		
f	OCH ₃	H	24	21	26	6		

Table (1)

1.2.5 R₂Te₂

Diorganyl ditellurides, R₂Te₂, are convenient, stable starting materials for various tellurium compounds and metal complexes. ¹²⁵Te Mössbauer data⁷⁰ of (C₆H₅)₂Te₂ suggests that the involvement of intermolecular tellurium associations, in addition to short Te-C and Te-Te bonds, gives rise to highly coloured diarylditellurides as shown by the red coloured (C₆H₅)₂Te₂ in which the Te-Te bond is 2.7 Å and the intermolecular contacts are 4.2 Å.⁷⁰ The tellurium atoms in diorganoditellurides therefore have a higher degree of co-ordination than those in the tellurides as a result of both intra- and intermolecular bonding. The donation and movement of non-bonding valence electrons into the conductance band formed by overlap of the empty orbitals on the atoms gives rise to the orange, red or brown colours characteristic of these compounds. However, Thavornyutikarn⁷² has shown that reflectance and solution spectra of (C₆H₅)₂Te₂ are identical, hence it seems unlikely that the colour may be attributed solely to intermolecular interactions in the solids.

It has been suggested that some decompositions of diaryl ditellurides to free radicals occur in solution⁷¹. However, Thavornyutikarn⁷² concluded that the ditelluride is undissociated in organic solvents; the e.s.r spectrum of a solution of diphenylditelluride in benzene did not indicate any radical species present, and the diffuse reflectance spectrum of diphenylditelluride and visible spectrum of a solution in chloroform are similar, indicating that the species in the solid and in solution are similar.

Dance⁷³ provided the first evidence for the existence of

unsymmetric diarylditellurides, R-Te-Te-R' by the examination of a mixture of two ditellurides by mass and ^1H n.m.r spectroscopies.

Davies⁷⁴ suggested that the reaction between R_2Te_2 and the compounds $\text{Br}(\text{CH}_2)_n\text{Br}$ ($n=1, 3, 4$) produces a complex series of a new class of organotellurium compounds.

The conductivity⁷⁴ measurements in acetonitrile indicate a 1:2 species for the methylene compound, and a 1:1 species for the other compounds. The formulations shown below in figure (29) were postulated although unsupported by physical data.

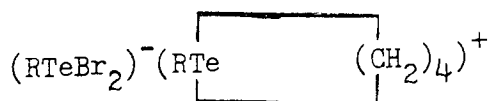
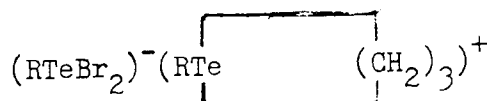
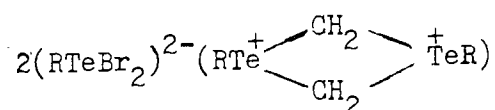


Figure (29)

Mössbauer data⁷⁴ show that the methylene compound is different from the others. They also show that there is no possibility of two tellurium sites. Analytical data give an empirical formula of

$(R\text{Te})_2(\text{CH}_2)_n\text{Br}_2$ which possibly have the polymeric structures of the type shown in figures (30a) and (30b). The methylene derivatives tend toward a telluride type compound, whereas the others tend toward a telluronium type species⁷⁴.

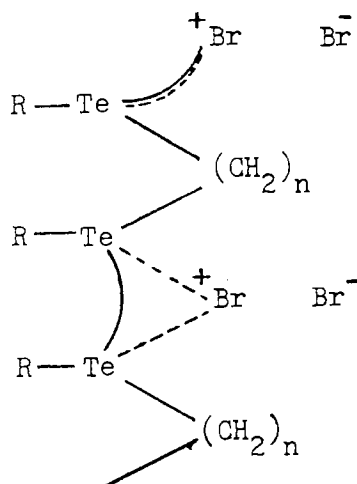


Figure (30a)

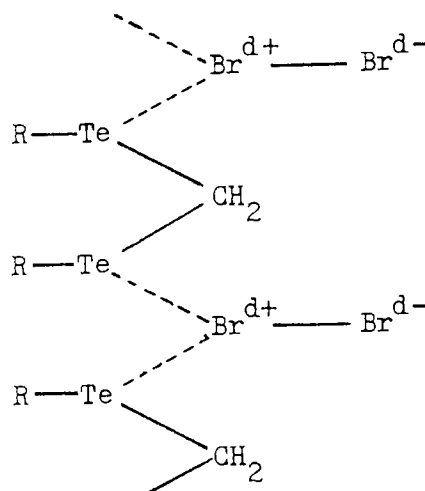


Figure (30b)

1.2.6 $(R_3\text{Te})^+\text{X}^-$

Studies on the triorganochalcogenonium salts, $R_3\text{MX}$, have shown that the salts have relatively complex structures due to weak bonding interactions between the chalcogen atom and the anion^{75,76}. It has become evident that these interactions determine the overall structural features of the compound and that the interactions are sensitive to the nature of both the chalcogen and anion^{77,53}. In addition, the structural features are influenced by the organic groups and the presence

or absence of solvent of crystallization.

The dependence of the weak-bonding interactions on the nature of the chalcogen atom can be explained by the relative positions of the chalcogens in the periodic table. Tellurium for example, with its expanded valence shell, shows higher co-ordination numbers than does selenium or sulphur. Tellurium is both five and six co-ordinate in the compound $(C_6H_5)_3TeNCS$ ⁷⁷, whereas selenium in $(C_6H_5)_3SeNCS$ is only four co-ordinate⁷⁸. Accordingly, the former salt is oligomeric while the latter is monomeric.

Triphenyltellurium chloride⁷⁹ is dimeric and predominately ionic in the solid state. Each tellurium atom is five co-ordinate with a distorted square pyramidal geometry. Two chloride ions bridge the $(C_6H_5)_3Te^+$ ions with the Te-Cl distances ranging from 3.142 to 3.234 Å.

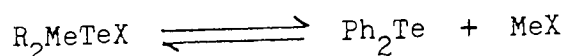
Diarylmethyltellurium salts decompose in chloroform solution⁸⁰; this behaviour is not expected from analogy with triphenyltelluronium salts, which are insoluble in chloroform, and the behaviour indicates that in solution the formulation R_2MeTe^+ is probably not a good representation for these telluronium salts.

Dance⁸⁰ attempted the preparation of telluronium ylids from suitable telluronium salts such as $Ph_2(PhH_2)Te^+Br^-$ and $Ph_2(PhCOH_2)Te^+Br^-$ by the salt method, but failed due to the rapid dissociation of the telluronium salt in chloroform solution into diphenyl telluride and organic halide⁸⁰.

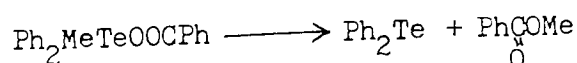
The observation⁸⁰ that diphenylbenzyl telluronium bromide decomposes in chloroform solution led to the examination of the effects of several solvents on a number of telluronium salts. Two types of salts have been studied⁸⁰, namely $Ph_2TeMe^+X^-$ where $X=Cl, Br, I, NO_3, NCS, PhCOO$ and $Ph_3Te^+X^-$ where $X=Cl, Br, I$. All the salts are soluble in

dimethylsulphoxide, but only the $\text{Ph}_2\text{TeMe}^+\text{X}^-$, where $\text{X}=\text{Cl}$, Br and I are soluble in chloroform.

Dance⁸¹ investigated the reaction of methyl iodide with an excess of diphenyltelluride (which also functioned as the solvent) and established that the formation of Ph_2MeTeI proceeded via an intermediate. Further, it has been established by ^1H n.m.r spectroscopy that, in deuteriochloroform solutions of Ph_2MeTeX the chemical shift of the methyl group attached to tellurium (identified by ^1H - ^{125}Te satellites) is significantly dependent on the anion, the following reaction occurs :

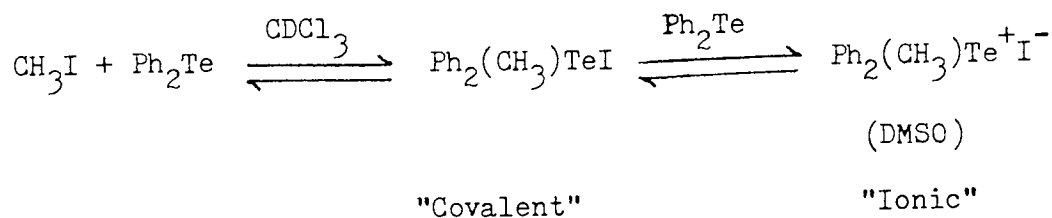


The rate of reaction decreases in the order : $\text{X}=\text{I} \rangle \text{Br} \approx \text{NCS} \rangle \text{Cl} \rangle \text{PhCOO}$. In the more polar dimethylsulphoxide (DMSO) the only compound to undergo reductive elimination is $\text{Ph}_2\text{MeTe}(\text{OOCPh})$ ⁸² as shown below :



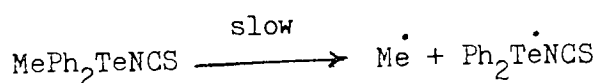
The ^1H n.m.r spectra chemical shift of the methyl-group of Ph_2MeTeI in deuteriochloroform prior to reductive elimination of MeI ($\delta=3.04$ ppm) happens to be the same as that observed for the intermediate species in the formation of the above compound. Also the final product of the reaction of MeI with excess Ph_2Te has a methyl resonance ($\delta=2.69$ ppm) identical to that observed for $\text{Ph}_2\text{MeTe}^+\text{I}^-$ in dimethylsulphoxide. The methyl resonance of $\text{Ph}_2\text{MeTe}^+\text{X}^-$ in dimethylsulphoxide is independent of X (where: $\text{X}=\text{Cl}$, Br , I , NCS) and the solutions conduct electricity. However, there is evidence of more ($\text{X}=\text{I}$) or less

(X=NCS) ion pairing. Thus combining the results of the measurements in DMSO and CDCl_3 ,

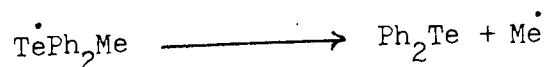
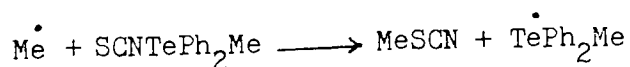


it is concluded that the telluronium salts in chloroform form a covalent compound which decomposes to give diphenyltelluride and methylhalides, and in DMSO solution the ionic form is present.

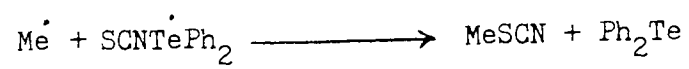
Musa⁸³ studied the chemistry of $\text{MePh}_2\text{Te}(\text{NCS})$ and found it to be ionic in the solid state and in solution (CDCl_3) as a covalent form, $\text{MePh}_2\text{Te}(\text{NCS})$, from which reductive elimination of methylthiocyanate occurs. The mechanism of the decomposition is not simple. Initially it is probable that a free radical pathway dominates, but after about 100 minutes the rate of decomposition increases. The reaction scheme may follow the below indicated route :



followed by a sequence of fast steps such as :



and a termination step :



There is evidence that the process is catalysed by diphenyltelluride.

CHAPTER TWO

GENERAL EXPERIMENTAL METHODS

GENERAL EXPERIMENTAL METHODS

To avoid duplication, those methods common to all subsequent chapters are gathered here.

2.1 Chemicals

All chemicals were obtained from commercial sources, and where necessary melting points, and other physical data were used to assess the purity of the compounds.

2.2 Solvents

Analar solvents were used when possible, otherwise reagent grades were used after distillation. Solvents used for some physical measurements, e.g. e.s.r and conductivity measurements, were purified by literature methods⁸⁴.

2.3 Melting Points

These were determined using a Gallenkamp electrically heated melting point apparatus.

2.4 Conductivity Measurements

Molar conductivity measurements in various solvents were carried out using a standard conductivity bridge, and a Mullard type

E7591 B cell with a cell constant of 1.46 with bright platinum plates.

2.5 Elemental Analysis

Micro-analysis for carbon, hydrogen, nitrogen and phosphorus was carried out by the Micro-Analytical Laboratories of the Chemistry Department of Aston University.

2.6 Infra-red Spectra

Spectra in the range $4000-250\text{ cm}^{-1}$ were recorded on a Perkin-Elmer 457 spectrophotometer. Solid state samples were examined as Nujol mulls supported between KBr plates. Some samples were also examined as KBr discs, prepared by pressing a mixture of sample and dry powdered KBr.

Solution spectra were obtained from 10% solutions in chloroform using a standard liquid cell, with chloroform as reference.

2.7 Mass Spectra

The mass spectra of all compounds were recorded on the AEI-MS9 spectrometer at 70 eV.

2.8 Electron Spin Resonance (ESR) Spectra

E.s.r spectra were determined with JEOL PE-1X electron spin resonance spectrometer operating in the X-band and calibrated with a

standard manganese(II) (line 4 g = 1.981; separation of lines 3 and 4 = 86.9 G) sample diluted with magnesium oxide. Spectra were run at room temperature.

Note

Mössbauer data were obtained at 4-K using equipment as described in reference (95). These data were obtained at Simon Fraser University, Burnaby, B. C., Canada.

CHAPTER THREE
SYNTHESIS, AND PROPERTIES OF ORGANOTELLURIUM(II)
COMPOUNDS AS LIGANDS

3.1 Introduction

The theory of acceptor/donor interactions as applied to chemical reactivity is arguably a most important concept. It enables the chemist to obtain a better understanding of such diverse topics as hydrolysis, or the bonding of carbon monoxide and oxygen to haemoglobin. Considerations of Lewis acidity and basicity are very important in the fields of heterogeneous and homogeneous catalysis. A Lewis acid is defined as any substance capable of accepting electron density, and a Lewis base as any substance capable of donating electron density. Many substances are capable of being one or the other, and some materials are capable of being both. A Lewis acid/base interaction requires co-ordination of the two so that bonding electron density is shared by both the acid (acceptor) and the base (donor).

Two systems have been reported in terms of the relative affinities of ligand atoms for metals. Metals are divided in two classes of acceptor⁵⁷ : (a) those which form their most stable complexes with bases containing as ligand atom the first element of the group (e.g N, O, F), and (b) those which form their most stable complexes with bases containing as ligand atom the second or a subsequent element (e.g P, S, Cl, Te). For class (a) the stabilities of the complexes will be $O \gg S \gg Te$; for class (b) metals $S \gg O$ but almost any sequence of S, Se and Te may occur. Class (b) metals form a triangular area in the centre of the periodic table with a somewhat diffuse border. Metals of pronounced (b) character are in the centre of this area, for example Cu(I), Rh(I), Pd(II), Ag(I), Pt(II) and Hg(II)⁸⁵. The oxidation state of the metals affects the degree of (b) character, which is strongest for transition metals in low oxidation states i.e. metals having

non-bonding d electrons, so that they are capable, in principle, of forming $d_{\pi} - p_{\pi}$ and $d_{\pi} - d_{\pi}$ bonds by donating a pair of electrons to the ligand.

Another system was based on hard and soft Lewis acids and bases⁸⁶ which relate respectively to the preceding (a) and (b) characters. The principle of hard and soft acids and bases (HSAB Principle) seems to have some value in aiding the understanding of a wide variety of chemical phenomena. The general rule for this principle is that hard acids will bind strongly to hard bases, and that soft acids will bind strongly to soft bases. A hard acid is one that binds to a base that has a large affinity for a proton. A soft acid binds to a highly polarisable or unsaturated base which has a small affinity for the proton e.g. R_2S , R_2Se and R_2Te . It is noted that it is possible for a base to be both soft and bind strongly to the proton e.g. the highly polarisable S^{2-} ion.

Organotellurium(II) compounds as ligands have not been studied extensively. The bulk of the information available suggests that they have a pronounced class (b) or softish base character⁸⁶.

Chatt and Venanzi⁸⁷ found in the bridged complexes of Pd(II), PdL_2Cl_4 , ($L = R_2S, R_2Se, R_2Te$) that when L is an R_2S group, the complex could be more easily isolated than in the case of R_2Se or R_2Te . They report that the stabilities fall in the order $R_2S \rangle R_2Se \rangle R_2Te$. In the corresponding Pt(II) complexes, PtL_2Cl_4 , those having $L = R_2Te$ are more easily isolated than the R_2Se derivatives. This suggests an order of stabilities $R_2S \rangle R_2Te \rangle R_2Se$ ⁸⁸. The difference in the sequence of the stabilities is explained on the basis of relative size of the orbitals involved in forming co-ordinate σ bonds. Thus, Pd(II)

and Se are comparable in size, as are Pt(II) and Te. Subsequent studies⁸⁹ on the vibrational spectra of co-ordination compounds of the type MX_2Y_2 where $\text{M} = \text{Pd(II)}$ or Pt(II) ; $\text{X} = \text{Cl, Br or I}$ and $\text{Y} = \text{Me}_2\text{S, Me}_2\text{Se or Me}_2\text{Te}$, have shown that the relative bond order follows the sequence $\text{M-Cl} \rangle \text{M-Br} \rangle \text{M-I}$ and $\text{M-S} \rangle \text{M-Se} \rangle \text{M-Te}$. The inverse order $\text{M-Te} \rangle \text{M-Se}$ suggests strong π bonding between Pt and Te rather than nonbonded interactions. Subtle effects on the internal modes of vibrations of the donor molecules, R_2S , R_2Se and R_2Te have been reported⁹⁰ in the cis, trans and bridged halide complexes of Pd(II) and Pt(II).

Mercury(II) compounds co-ordinate readily with telluride ligands and a wide range of mercuric halide complexes have been prepared^{91,92}. The ^{125}Te Mössbauer parameters for the complexes $\text{R}_2\text{Te.HgX}_2$ (where $\text{R} = \text{Ph, p-EtOC}_6\text{H}_4$, $\text{X} = \text{Cl, Br, I}$) indicate that in all cases the tellurium atom is present in an environment similar to that in a triorganotellurium⁹³ salt (c.f. $\text{Ph}_3\text{Te}^+\text{Cl}^-$). The parameters do not appear to be influenced by the choice of halogen, indicating that the type of bonding at tellurium is largely invariant within the series. It is suggested that they are of the type $(\text{R}_2\text{Te}^+-\text{HgX})\text{X}^-$.

Spectroscopic data indicated that the complex $\text{p-EtOC}_6\text{H}_4\text{TeHgCl}$ has the structure as shown below in figure (31).

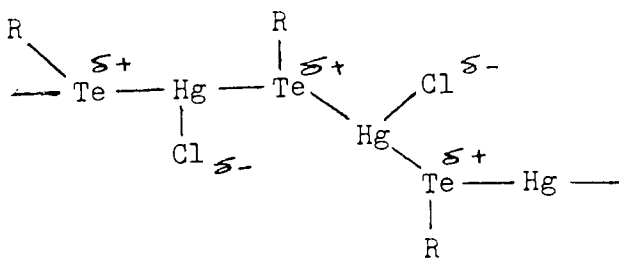


Figure (31)

This structure is similar to those suggested for $(p\text{-EtOC}_6\text{H}_4\text{Te})_2\text{Hg}$;⁹³ the presence of the electronegative Cl ligand would aid in the transfer for some degree of positive charge to the tellurium, resulting in a stronger Te-Hg bond in this compound than in $(\text{EtOC}_6\text{H}_4\text{Te})_2\text{Hg}$.

Both aliphatic and aromatic diorganoditellurides give compounds with CuCl or CuBr of stoichiometry $\text{R}_2\text{Te}_2\cdot\text{CuX}$ ⁹⁴. ¹²⁵Te Mössbauer line-widths of Copper(I) halide derivatives of diorganoylditellurides are relatively narrow. Low χ^2 values were obtained for two line spectra. Hence no clear evidence could be obtained for two quadrupole doublets, implying that the two tellurium atoms present in these complexes are in similar environments.

Quadrupole splitting data was interpreted in terms of Townes-Dailey theory⁹⁵. It is assumed that donation is mainly from the p-orbitals so that complex formation will lower the electron population of the p_z orbital and hence decrease the quadrupole splitting factor. The stronger the interaction, the greater the decrease in the splitting factor. These complexes only give slightly decreased quadrupole splittings compared with the unreacted ditelluride implying that there is only a weak interaction between the Cu(I) ion and the tellurium ligand. Also, i.r spectroscopic studies go some way to substantiating the evidence of Mössbauer spectroscopy, as presented above, in that both Te atoms are weakly co-ordinated to Cu(I) and that the halide ligands are bridging. A structure that accommodates the available data is shown schematically in figure (32).

Dimeric⁹⁶ compounds of the general formula $[\text{Pd}(\text{TeR})_2(\text{PPh}_3)]_2$ have been isolated containing both bridging and terminal R-Te groups from the reaction of $(\text{PPh}_3)_4\text{Pd}$ and R_2Te_2 . This is demonstrated in figure (33).

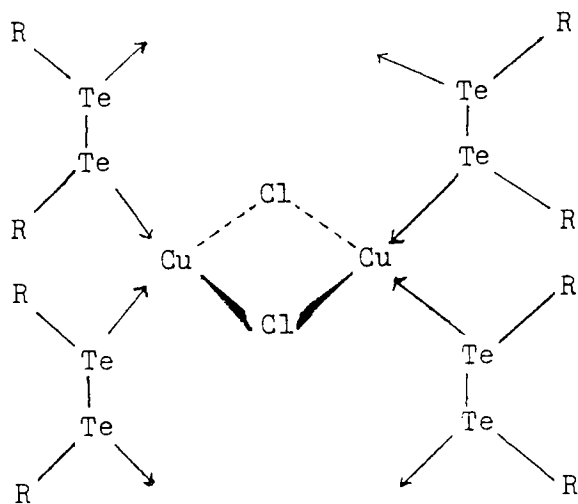


Figure (32)

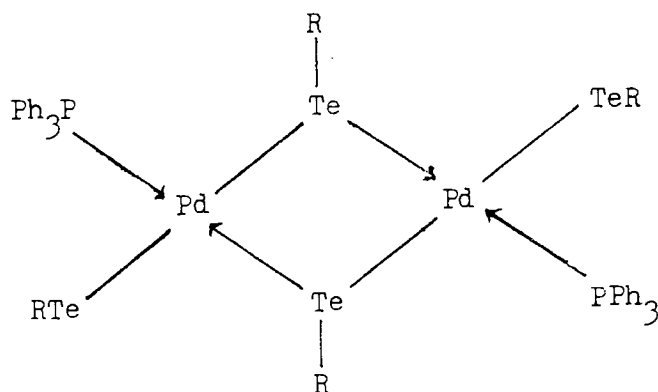
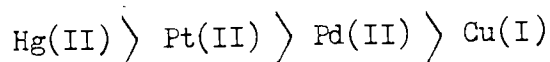


Figure (33)

As mentioned previously (chapter one, section 1.2.4) Mössbauer studies of the formation of a complex between the telluride, $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}$, as a Lewis base, and a metal halide, as a Lewis acid, indicate that the Te p-electron lone pair is primarily involved in the donation to the acceptor. Also, the electron drift from Te to the metal atom of the Lewis acid is small and decreases with metal atom in the order,



Of interest is the co-ordination chemistry of tellurium ligands with harder metals. This would enable an extension of the Mössbauer work of Davies⁵⁹. Instead of using simple telluride R_2Te , the telluro-ester $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Te}-\text{R}'$ is employed. The telluroester can act both as a hard (C=O) and a soft (Te) Lewis base which may hopefully complex with metals such as Cu(II), Ni(II) etc.

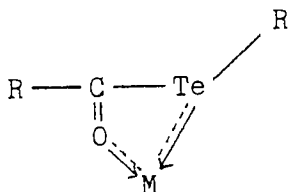
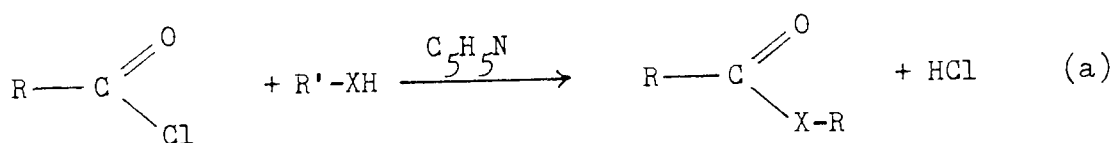


Figure (34)

It is noted from the figure (34) that the ligand may be bidentate (similar to a carboxylate) and resulting complexes may be of some

structural interest.

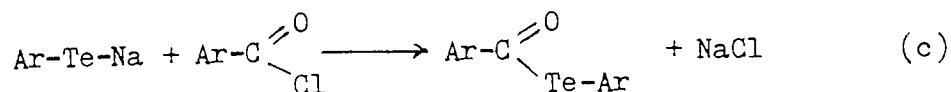
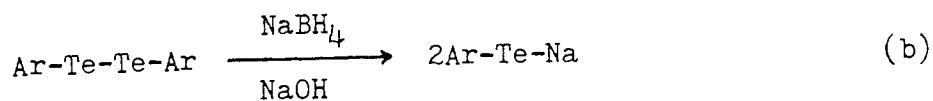
The classical preparation of an ester, by reaction between an acid chloride and an alcohol or a phenol in the presence of an organic base, is a general one and can also be used for the preparation of thioesters and selenoesters, giving products in excellent yields in a short time⁶⁴.



R= alkyl or aryl

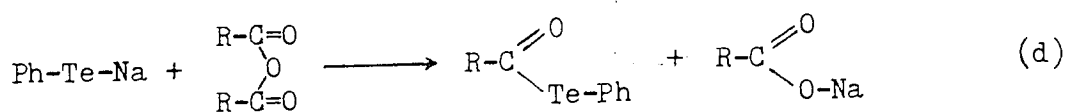
X= O, S and Se

Unfortunately, the analogous reaction in organotellurium chemistry is not applicable, owing to the extreme instability of tellurophenol-type compounds. A modification of the general procedure has therefore been used⁶⁴, and the mixed aryl derivatives, $\text{ArCOTeAr}'$, have been prepared by the reaction sequence in equations (b) and (c)



The reduction of the aromatic ditellurides (reaction b) by sodiumborohydride in a basic alcohol/water medium gives, quantitatively, the corresponding sodium tellurophenolate. The addition of differently substituted aromatic acid chlorides to this reaction medium yields diaromatic telluroesters with variable yields. The final step is accompanied by several secondary reactions, primarily re-formation of the diarylditelluride. However, a 10-20% excess of the aromatic acid chloride is generally sufficient to retard these unwanted processes. The telluroesters formed by this method are stable in the reaction medium and can be easily isolated in pure form after only one recrystallization from an organic solvent.

To form an aryl aliphatic telluroester, the above reactions (b,c) using an acid chloride, are not very good. However, if the aliphatic acid anhydride is used the yield is better;



(R= aliphatic)

The condensation reaction (d) between Ph-Te-Na and the aliphatic anhydrides has been applied with success to the preparation of telluroesters.

3.2 Experimental

Synthesis of Telluroesters and their Reaction with a Variety of Metal Salts

3.2.1 Preparation of (p-ethoxyphenyl)tellurium trichloride

(p-EtOPh)TeCl₃ and bis(p-ethoxyphenyl) ditelluride

(p-EtOPh)₂Te₂

(p-EtOPh)TeCl₃ was prepared by refluxing tellurium tetrachloride, phenetole and chloroform. m.p. 182 °C (lit.⁹⁷, 182-183 °C). The diarylditelluride was obtained by reduction of the trichloride at 0°C with potassium metabisulphite (K₂S₂O₅). m.p. 105-106 °C (lit.⁹⁷, 107-108 °C).

(Found % : C, 38.2, H, 3.70. Calc. for C₁₆H₁₈O₂Te₂ % : C, 38.6, H, 3.60).

3.2.2 Preparation of Diphenylditelluride (Ph₂Te₂)

(Ph₂Te₂) was prepared by the method of Gunther⁹⁸ using a mixture of tellurium tetrachloride, aluminium trichloride and dry benzene to give phenyltellurium trichloride (PhTeCl₃). Reduction of the trichloride with sodium metabisulphite gave (Ph₂Te₂).

The resulting product was recrystallized from ethanol to give pure diphenylditelluride as a crystalline solid.

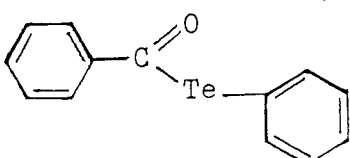
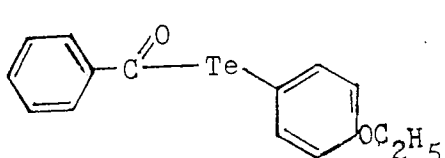
Variation in colour was noted between samples from different preparations, for which analytical data are given in table (3).

3.2.3 Preparation of Telluroesters (RCO.TeR')

These derivatives were prepared by the reaction of benzoyl chloride with NaTeR'.⁶⁴ All compounds gave satisfactory analysis and had melting points and spectroscopic data (e.g. IR) in good agreement with those reported in the literature⁶⁴. Infrared spectrum is shown in figure(35)

(C₆H₅CO.TeC₆H₄.OEt-p) was prepared by a similar method to that described above using bis(p-ethoxyphenyl)ditelluride. Recrystallization from 20-40° petroleum ether, with the addition of a little benzene, gave the pure compound. Analytical data are given in table (2).

Table (2) Analytical Data for R'TeCO R Derivatives

Compounds	m.p °C	Found		Calculated	
		%C	%H	%C	%H
	58-60 lit (64)	50.4	3.20	50.4	3.29
	49-50 Figure (36)	50.8	4.00	50.9	3.96

3.2.4 Preparation of Tetrakis(triphenylphosphine)palladium(0) (a slight modification of a literature⁹⁹ method was used)

A mixture of palladium dichloride (17.7 g, 0.1 mol), triphenylphosphine (131 g, 0.5 mol) and 1200 ml of dimethyl sulphoxide was placed in a three-necked, 400 ml, round-bottomed flask equipped with a magnetic stirring bar and a dual-outlet adapter. A rubber septum and a vacuum system were connected to the outlets. The system was then placed under nitrogen with provision for pressure relief through a mercury bubbler. The yellow mixture was heated by means of an oil bath with stirring until complete solution occurred (about 140°C). The bath was then taken away, and the solution was rapidly stirred for approximately 15 minutes. Hydrazine hydrate (20 g, 0.4 mol) was then rapidly added over one minute.

A vigorous reaction took place with evolution of nitrogen. The dark solution was then immediately cooled in a water bath; crystallization began to occur at about 125°C. At this point the mixture was allowed to cool naturally. After the mixture had reached room temperature it was filtered under nitrogen. The resulting solid was washed successively with two 50 ml aliquots of ethanol and two 50 ml aliquots of ether. The product was dried by passing a slow stream of nitrogen through the funnel overnight. The product was stored under nitrogen in an ampoule.

3.2.5 Preparation of Palladium(II) Derivatives

Dichlorobis(benzonitrile)palladium(II) $\left[\text{Pd}(\text{PhCN})_2\text{Cl}_2 \right]$ was prepared by Doyle's method¹⁰⁰. This was then reacted with

bis(p-ethoxyphenyl)telluride to give trans-dichlorobis di(p-ethoxyphenyl) telluride palladium(II), $\text{Pd} \left[\left(\text{p-OEtPh} \right)_2 \text{Te} \right]_2 \text{Cl}_2$ (m.p = 125 °C). The bromo-complex trans-dibromobis di(p-ethoxyphenyl)telluride palladium(II), $\text{Pd} \left[\left(\text{p-OEtPh} \right)_2 \text{Te} \right]_2 \text{Br}_2$ was obtained by metathesis using an excess of sodium bromide (m.p = 105 °C).

3.2.6 Preparation of Copper(I) Chloride

The copper(I) chloride was obtained by the literature method¹⁰¹. Copper(I) chloride was stored under nitrogen.

3.2.7 Preparation of Thallium(III) Chloride

Chlorine was bubbled through a suspension of thallium(I) chloride in dry acetonitrile until a clear solution was obtained. The solution was flushed with nitrogen to remove excess chlorine and crystallization allowed to take place. This procedure yielded anhydrous thallium(III) chloride.

3.2.8 Reaction of Telluroesters with Metal Salts

(A) With Thallium(III) Chloride

PhCOTe.Ph (0.06 g, 2 mmol) was dissolved in acetonitrile (25 ml). Thallium(III) chloride (1 mmol) in acetonitrile (25 ml) was added to the above solution. The reaction mixture was stirred at room temperature for 2 hours. The resulting white precipitate was filtered and dried in

vacuo over P_4O_{10} . From an examination of the precipitate it was found to be $TlCl$ (m.p = over $360^\circ C$).

(B) With Copper(I) Chloride

$(PhCO.TeC_6H_4OEt-p)$ (0.7 g, 2 mmol) was dissolved in acetonitrile (35 ml). A solution of anhydrous copper(I) chloride (0.01 g, 1 mmol) in acetonitrile (15 ml) was slowly added through a dropping funnel. After complete addition of the copper(I) chloride solution, the reaction mixture was left stirring for two hours at room temperature. A brown precipitate was obtained. The resulting solid was collected and dried in vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

The reaction mixture smelt strongly of benzoyl chloride.

(C) With Copper(II) Chloride

$(PhCO.TeC_6H_4.OEt-p)$ (0.7 g, 2 mmol) was dissolved in ethanol (75 ml). A solution of anhydrous copper(II) chloride (0.13 g, 1 mmol) in acetonitrile (25 ml) was added dropwise. The mixture was stirred for two hours at room temperature. The resulting orange precipitate was collected and dried in vacuo over P_4O_{10} (m.p = $130^\circ C$).

(D) With Nickel(II) Chloride

$(PhCO.TePh)$ (0.6 g, 2 mmol) was dissolved in ethanol (25 ml). A solution of anhydrous nickel(II) chloride (0.13 g, 1 mmol)

in ethanol (15 ml) was added through a dropping funnel. After complete addition of the nickel(II) chloride solution, the mixture was stirred for five hours at room temperature and left to stand for 24 hours. The resulting orange precipitate was filtered and dried in vacuo over P_4O_{10} (m.p = 46 °C). Its infrared was identical to that of ^{the} telluroester (PhCOTePh).

(E) With $(PhCN)_2PdCl_2$

$(PhCN)_2PdCl_2$ (0.38 g, 1 mmol) was dissolved in toluene (100 ml) and the mixture filtered. $(PhCO.TeC_6H_4OEt-p)$ (0.7 g, 1 mmol) was added to the above solution. A red brown solution was obtained. The reaction mixture was stirred for five hours at room temperature. The brown product was washed with ethanol and ether and dried under vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

(F) With $Pd\left\{\left(p-EtOPh\right)_2Te\right\}_2Br_2$

$Pd\left\{\left(p-EtOPh\right)_2Te\right\}_2Br_2$ (1 g, 1 mmol) was dissolved in toluene (50 ml). A solution of $(PhCO.TeC_6H_4OEt-p)$ (0.7 g, 1 mmol) in dry toluene (50 ml) was added giving a red brown solution. The reaction mixture was stirred for five hours. The brown precipitate was filtered and dried in vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

(G) With $Pd(Ph_3P)_4$

(i) Tetrakis(triphenylphosphine)palladium(0) (1.15 g, 1 mmol)

in dry toluene (30 ml) was added to $(C_6H_5CO)_2TeC_6H_4OC_2H_5$ (0.7 g, 2 mmol) in dry toluene (20 ml). The resulting solution was stirred in the absence of light at room temperature for four hours. The dark brown product was filtered and dried in vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

(ii) Tetrakis(triphenylphosphine)palladium(0) (1.15 g, 1 mmol) in nitrogen saturated toluene (30 ml) was added to $(C_6H_5CO)_2TeC_6H_4OC_2H_5$ (0.7 g, 2 mmol) in nitrogen saturated dry toluene (20 ml). The resulting solution was stirred under an atmosphere of nitrogen for six hours at $45^\circ C$. The brown solid was filtered and dried in vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

(iii) Tetrakis(triphenylphosphine)palladium(0) (1.15 g, 1 mmol) in nitromethane (25 ml) was added to $(PhCO)_2TePh$ (0.35 g, 1 mmol) in nitromethane (15 ml). The reaction mixture was left at room temperature for two hours. The resulting light brown precipitate was filtered and dried in vacuo over P_4O_{10} . Analytical data and melting point are given in table (4).

3.2.9 Reaction Between $C_2H_5OC_6H_4Te-C(=O)-Ph$ and CH_3I

$(C_6H_5CO)_2TeC_6H_4OEt-p$ (3.5 g, 0.01 mol) was dissolved in dry toluene (25 ml). CH_3I (0.5 ml) was added to the above solution. The reaction mixture was allowed to stand at room temperature for 24 hours. Needle yellow crystals were precipitated. The product was filtered and dried in vacuo over P_4O_{10} . Analytical data and melting point are given

in table (4). The major features of the mass spectra are gathered into table (5).

3.2.10 New Reaction of Ditellurides and Palladium(0)

$(PPh_3)_4Pd$ (0.6 g, $\frac{1}{2}$ mmol) was dissolved in toluene (20 ml). Ph_2Te_2 (0.2 g, $\frac{1}{2}$ mmol) in toluene (10 ml) was added to the above solution. The resulting solution was left under normal laboratory conditions for one week after which it was filtered, and the resulting filtrate was left for a further week. Concentration on a rotary evaporator gave white crystals.

The above reaction was repeated under various condition.

- (i) In the presence of fluorescent light.
- (ii) In the presence of visible (ordinary) light.
- (iii) In the presence of uv light.

In all cases the progress of the above reactions was monitored using physical methods during the period of the reactions.

Also, the reactions were repeated in p-xylene and using $(p-EtOC_6H_4)_2Te_2$ instead of Ph_2Te_2 . In each case the product solutions were filtered, and the filtrates were concentrated on a rotary evaporator. Results are listed in tables (6,7).

3.2.11 Reaction Between Ditellurides and a Range of Aldehydes

R_2Te_2 (R=Ph, $p-C_2H_5OC_6H_4$) (0.1 mmol) was dissolved in various solvents (20 ml) (benzene, toluene, hexane and p-xylene).

RCHO (R=CH₃, C₂H₅CH₂, C₆H₅ and CH₃-CH=CH₂) (0.1 mmol) was added to the above solution and the reaction mixtures were left in various light situations (visible, uv, fluorescent) for different time periods. Results are given in tables (8-12).

3.2.12 Reaction Between Ph₂Te₂ and Toluene

Ph₂Te₂ (0.4 g, 1 mmol) was dissolved in toluene (30 ml). The solution was left at room temperature in the presence of visible light for four weeks. A white precipitate was obtained, filtered and dried. Infrared analysis showed absorption due to a (Te-O) group. The filtrate was concentrated and its infrared spectrum showed absorption due to the C=O group.

3.2.13 Reaction Between Pd(Ph₃P)₄ and Toluene

Tetrakis(triphenylphosphine)palladium(0) (1.15 g, 1 mmol) was dissolved in toluene (50 ml). The solution was left at room temperature in the presence of visible light for four weeks. A white precipitate was obtained, filtered and dried. Its infrared spectrum is consistent with the compound (Ph₃PO).

3.2.14 Reaction of Diorganyl Tellurides with Thallium(III) Chloride and Thallium(III) Bromide

I- With Thallium(III) Chloride

R_2Te ($R=Ph, p-EtOC_6H_4$) (1 mmol) was added to a solution of thallium(III) chloride (1 mmol) in acetonitrile (30 ml), while the reaction mixture was stirring at room temperature. A white precipitate was isolated immediately upon the addition. From an examination of the precipitate it was found to be $TlCl$ (m.p= over $360^\circ C$). The filtrate was concentrated on a rotary evaporator. From the infrared spectrum it was found to be (R_2TeCl_2).

II- With Thallium(III) Bromide

The procedure was identical to that for thallium(III) chloride. A parallel observation was made, with isolation of $TlBr$ and (R_2TeBr_2)

3.2.15 Reaction of Diorganylditellurides with Thallium(III) Chloride and Thallium(III) Bromide

I- With Thallium(III) Chloride

R_2Te_2 ($R=Ph, p-EtOC_6H_4$) (1 mmol) was added to a solution of thallium(III) chloride in acetonitrile (30 ml), while the reaction mixture was stirred at room temperature for two hours, after which a grey precipitate (m.p = $99^\circ C$) was obtained, the infrared spectrum of which was identical to that of R_2Te_2 . The above reaction was repeated under nitrogen and in the absence of light. Elemental tellurium was isolated.

II- With Thallium(III) Bromide

A similar reaction was carried out as above except with thallium(III) bromide. A parallel observation was made, with isolation of R_2Te_2 .

3.3 RESULTS

The analytical data for the complex formed between diphenylditelluride and palladium(0) are given in table (6).

Formation of aldehyde or acid from the reaction between diphenylditelluride and palladium(0) in different solvents and under different conditions are given in table (7).

The infrared spectra of all solid state compounds were examined as KBr discs and solution spectra were obtained from a thin film between CsI discs. All spectra are in the range $4000-250\text{ cm}^{-1}$.

The infrared spectrum of tolualdehyde produced from the reaction between diphenylditelluride and palladium(0) in p-xylene is represented in figure (38).

The infrared spectrum of benzaldehyde produced from the reaction between diphenylditelluride and palladium(0) in toluene is represented in figure (39).

The infrared spectrum of benzoic acid produced from the reaction between diphenylditelluride and palladium(0) in toluene is represented in figure (40).

The infrared spectrum of triphenylphosphine produced from the reaction between palladium(0) and toluene is represented in figure (41).

Results of the reactions between ditellurides and various aldehydes in different solvents are given in tables (8-12).

Table (3) Analytical Data for Ph_2Te_2

Colour	* _{m.p} °C	Found		Calculated
		%C	%H	
red-yellow	60	37.0	2.50	C = 34.8
yellow	58	36.5	2.60	
orange-yellow	57-58	38.7	2.60	
orange yellow	58	36.8	2.90	
orange	63	35.1	2.60	H = 2.41
red-orange	58	37.3	2.60	
red-orange	62	34.0	2.30	
bright orange	58	38.4	2.70	

*(lit.⁹⁸ m.p = 65 °C)

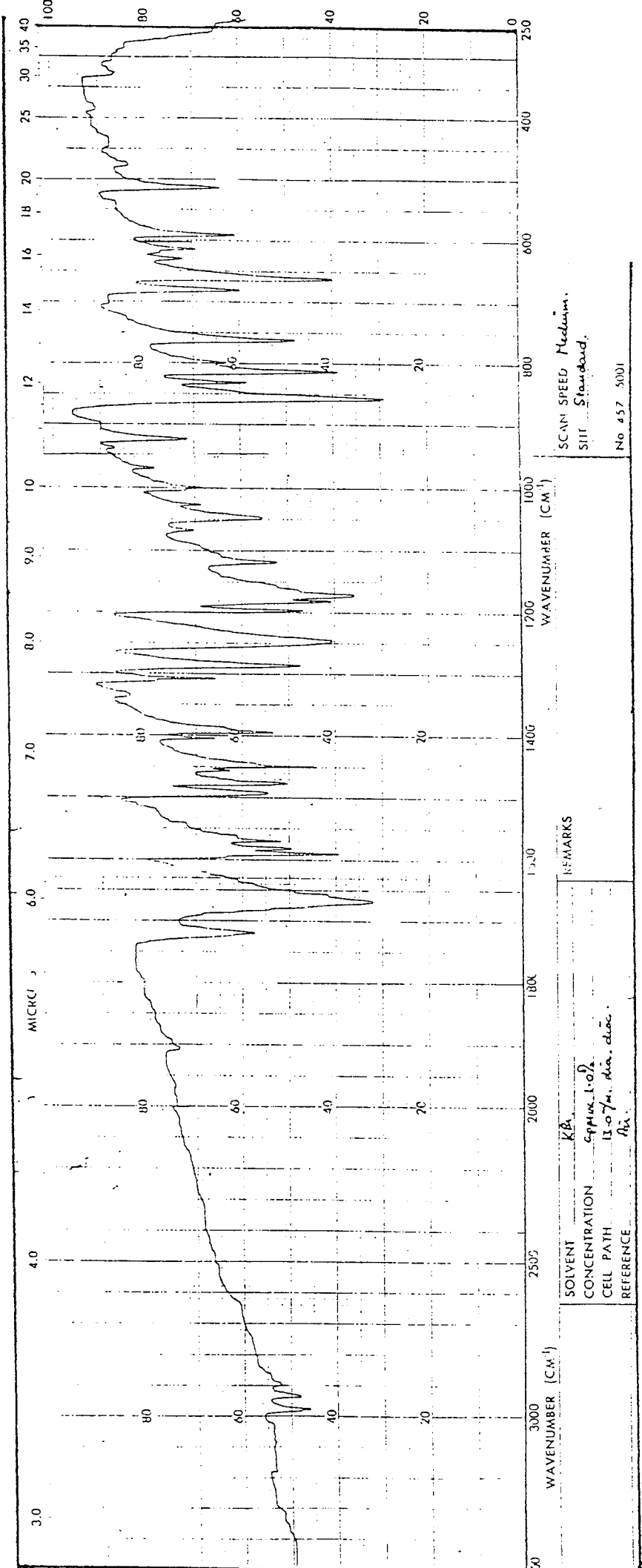


Figure (35) Infrared spectrum of Ph-C(=O)-Te-C₆H₄OEt-p

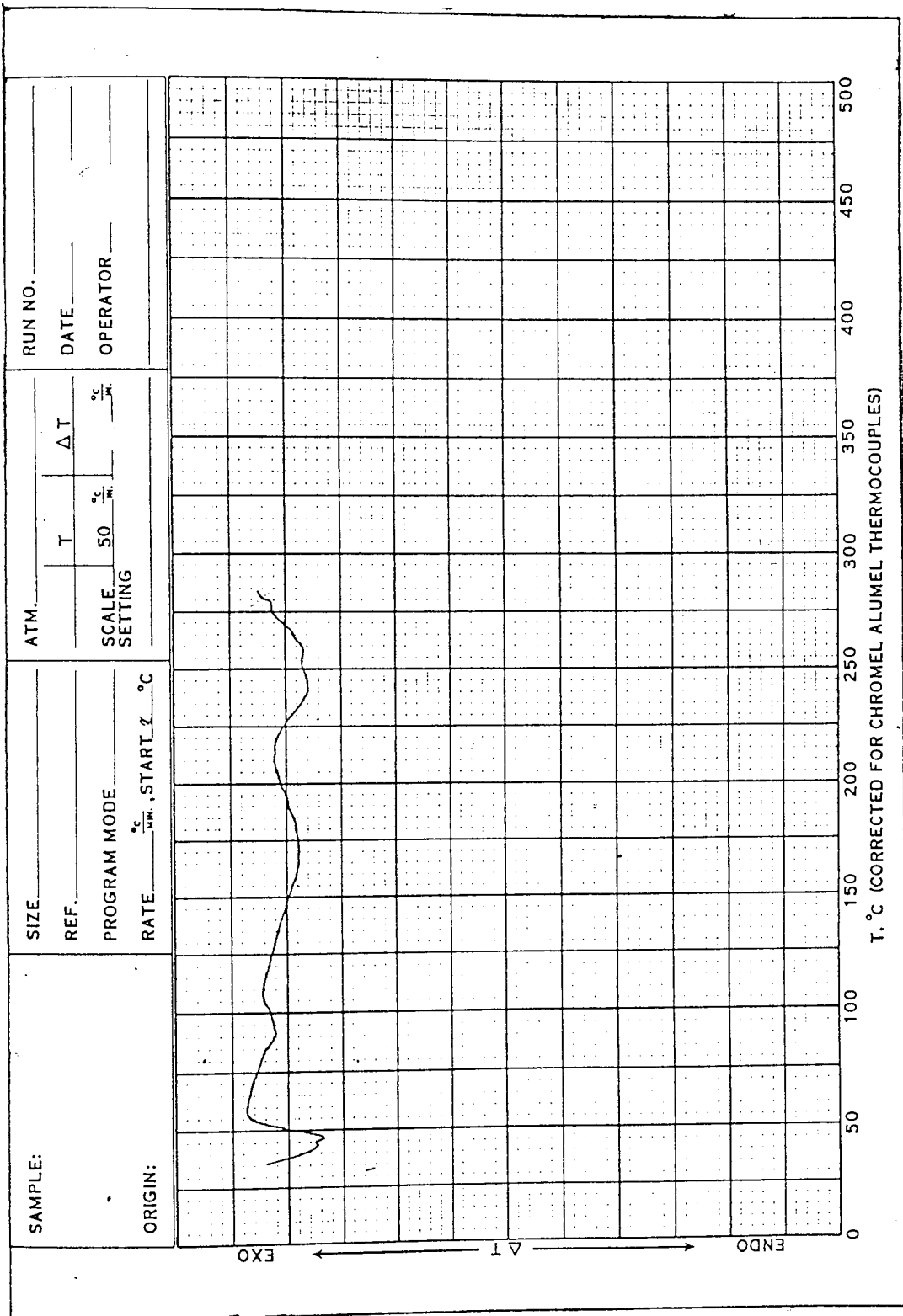


Figure (36) Melting curve of $\text{Ph-C-Te-C}_6\text{H}_4\text{OEt-p}$

Table (4) Elemental analysis of the complex formed between the telluroester
 $(\text{PhCOTeC}_6\text{H}_4\text{OEt})$ are given reactants.

Reactant	Complex	m.p (°C)	Found%			Required%		
			C	H	P	C	H	P
$(\text{PPh}_3)_4\text{Pd}$	$(\text{PPh}_3)_2\text{Pd}(\text{TeR}')_2$ $\text{R}'=\text{C}_2\text{H}_5\text{OC}_6\text{H}_4$	165 d.c	56.0	4.4	5.3	55.3	4.3	5.5
$[(\text{PhCN})_2\text{PdCl}_2]$	$[\text{Pd}(\text{TeR}')_2]_n$ $\text{R}'=\text{C}_2\text{H}_5\text{OC}_6\text{H}_4$	145	31.8	3.1	—	31.8	3.0	—
$\text{Pd}[(p\text{-OEtPh})_2\text{Te}]_2\text{Br}_2$	$[\text{Pd}(\text{TeR}')_2]_n$ $\text{R}'=\text{C}_2\text{H}_5\text{OC}_6\text{H}_4$	155	31.9	3.1	—	31.8	2.9	—
ClCu	$(\text{CuTeC}_2\text{H}_5\text{OC}_6\text{H}_4)_n$	300	30.5	2.9	—	30.7	2.8	—
CH_3I	$\text{R}(\text{CH}_3)_2\text{Te}^+\text{I}^-$ $\text{R}=\text{C}_2\text{H}_5\text{OC}_6\text{H}_4$	150	29.6	3.8	—	29.6	3.6	—



Table (5) Mass spectroscopic data for $\text{Me}_2(\text{p-EtOC}_6\text{H}_4)\text{Te}^+\text{I}^-$
 (a relative to ^1H ^{12}C ^{130}Te ^{127}I ^{16}O)

Ions	m/e	R.I
$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}^+(\text{Me})_2$	281	9
$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}^+\text{Me}$	266	100
$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}^+$	251	97
$\text{HOC}_6\text{H}_4\text{Te}^+\text{Me}$	238	6
$\text{OC}_6\text{H}_4\text{Te}^+\text{Me}$	237	45
$\text{HOC}_6\text{H}_4\text{Te}^+$	223	99
MeTe^+	145 (? isotope pattern masked)	27
MeI^+	142	100
I^+	127	100
$^+\text{OC}_6\text{H}_4$	92	98
$\text{C}_2\text{H}_5\text{O}^+$	45	27
C_2H_5^+	29	100

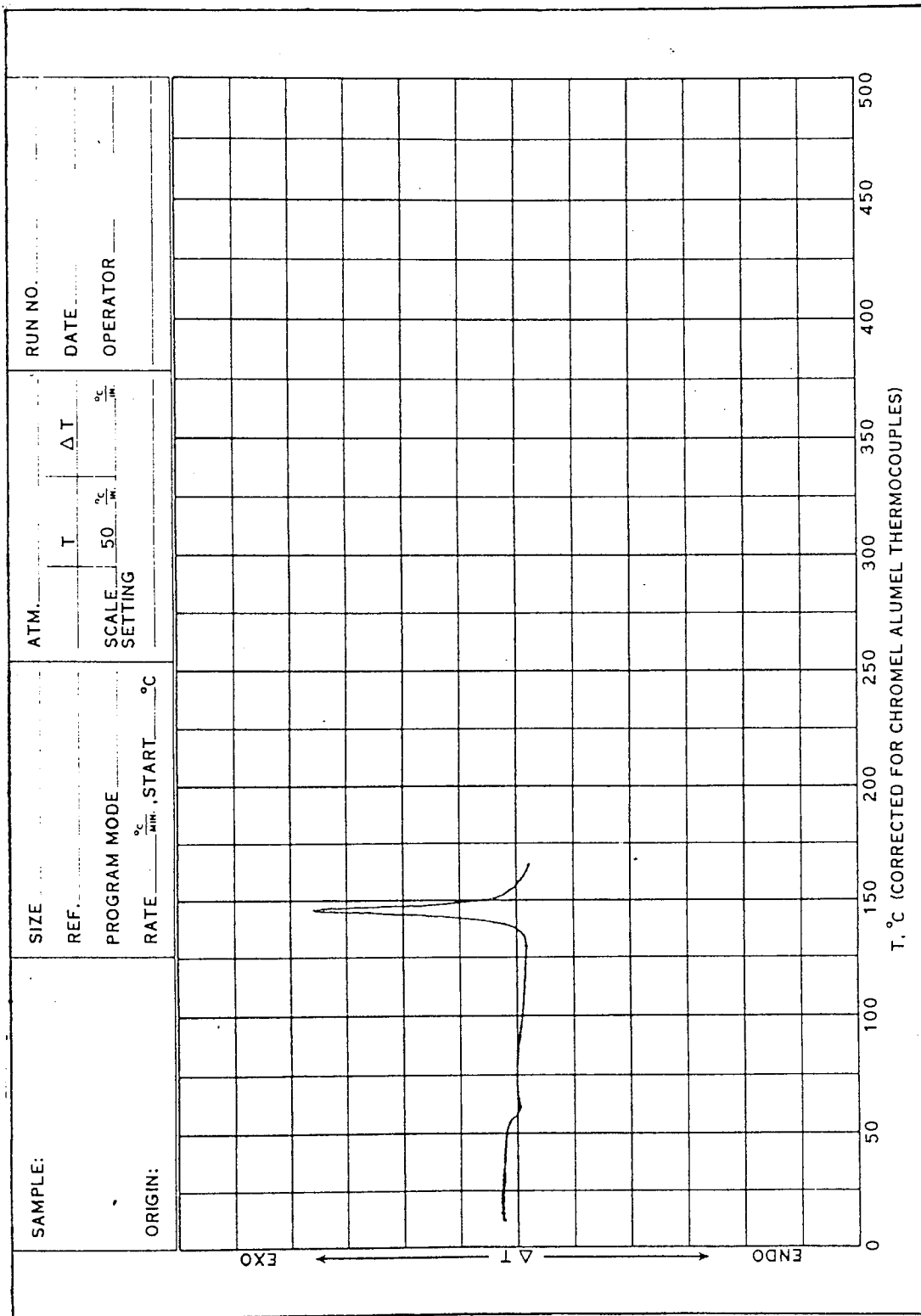


Figure (37) Decomposition curve of $[\text{Pd}(\text{TeR})_2]_n$
 $\text{R} = (\text{P-EtOC}_6\text{H}_4)$.

Table (6) Elemental analysis of the complex formed between diphenylditelluride (Ph_2Te_2) and [tetrakis(triphenylphosphine)palladium(0)] $[(\text{PPh}_3)_4\text{Pd}]$

Reactant	Complex	Found%			Required%			m.p ($^{\circ}\text{C}$)
		C	H	P	C	H	P	
$(\text{PPh}_3)_4\text{Pd}$		45.9	3.0	5.2	46.4	3.2	5.0	145

Note:

When bis(p-ethoxyphenyl)ditelluride was used, mixture of $[\text{Pd}(\text{TeR}')_2]_n$ and $[\text{Pd}(\text{PPh}_3)_2(\text{TeR}')_2]$ complexes were formed.

Table (7) Reaction between diphenylditelluride and palladium(0)

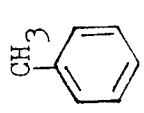
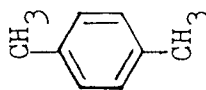
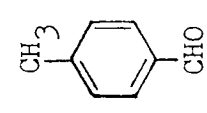
Solvent	Radiation	Situation	Time of Reaction and Product	Infrared Spectra Data
Toluene 	Visible	Open to the atmosphere	After one week the brown precipitate was filtered. The filtrate was left for six days and white crystals were obtained.	The infrared spectrum of the white crystals was identical to that of benzoic acid. The brown solid was shown to be a palladium complex (table (6))
"	Fluorescent tube	Closed to the atmosphere	After one week the brown precipitate was filtered. The filtrate was left for a further two weeks.	The infrared spectrum of the filtrate was identical to that of toluene.
"	Visible	"	"	"

Table 7 (Continued)

Solvent	Condition		Time of Reaction and Product	Infrared Spectra Data
	Radiation	For which oxygen was bubbled through		
 (p-xylene)	Visible	20 min.	After ten days the brown precipitate was obtained. The solution was then concentrated.	The infrared spectrum of concentrated solution was identical to that of p-tolualdehyde. Figure (38)  The brown solid was shown to be a palladium complex (table (6))
//	Fluorescent tube	25 min.	//	//
//	uv	10 min.	After five days the brown precipitate was obtained. The solution was then concentrated	//

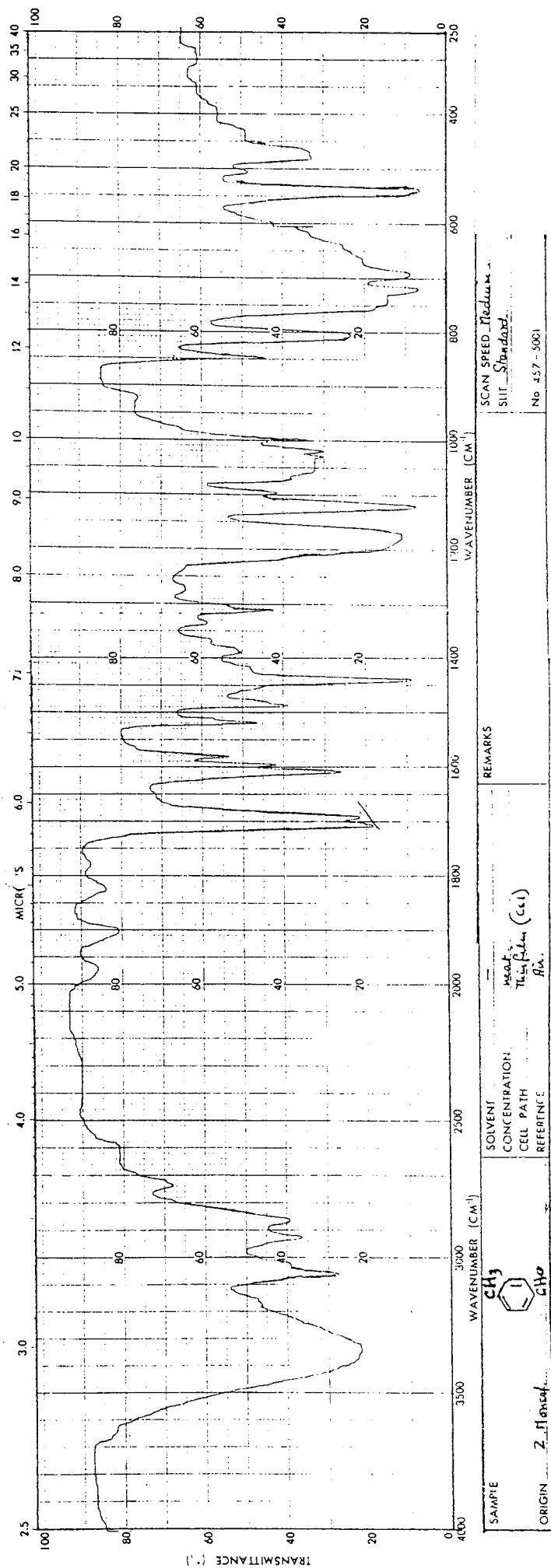


Figure (38) Infra-red spectrum of the species produced from the reaction between diphenylditelluride and palladium(0) in p-xylene

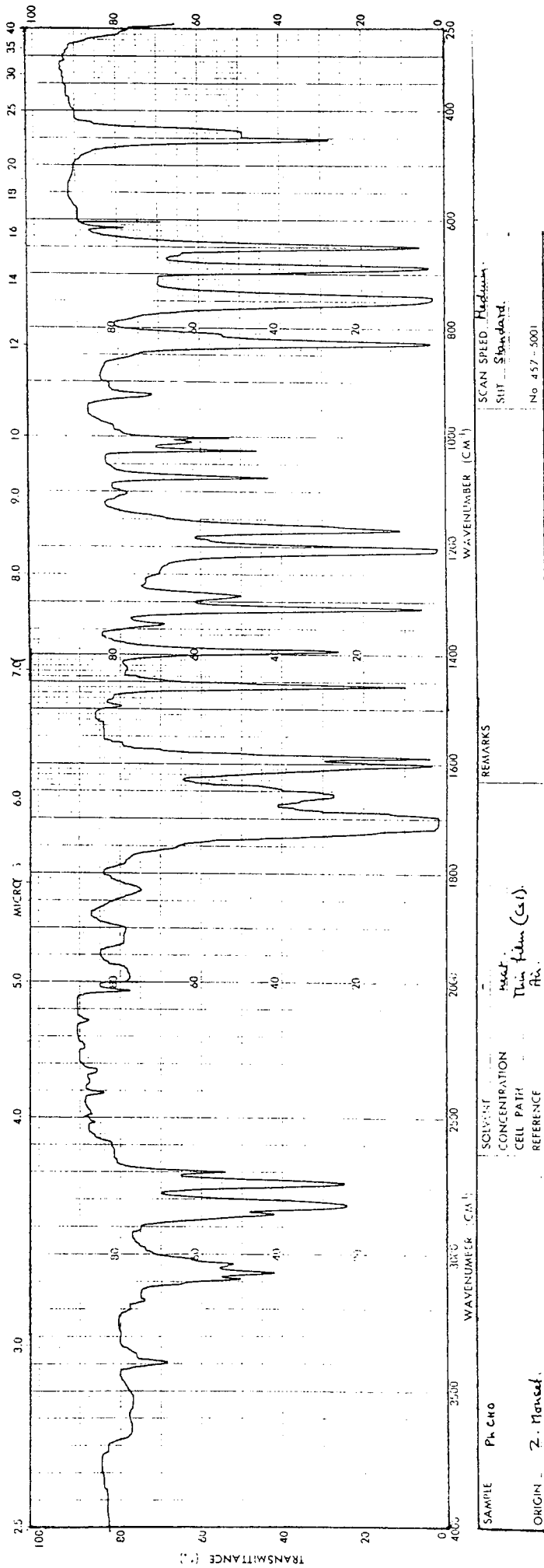


Figure (39) Infra-red spectrum of the species produced from the reaction between diphenylditelluride and palladium(0) in toluene

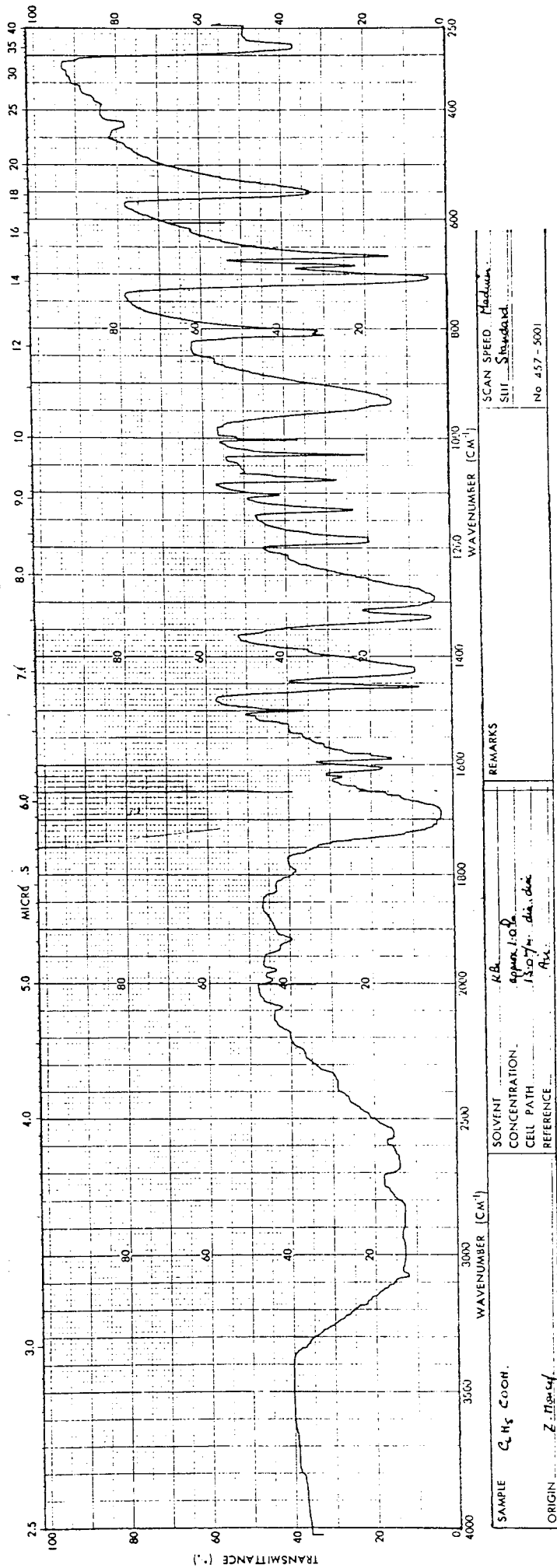


Figure (40) Infra-red spectrum of the species produced from the reaction between diphenylditelluride and palladium(0) in toluene

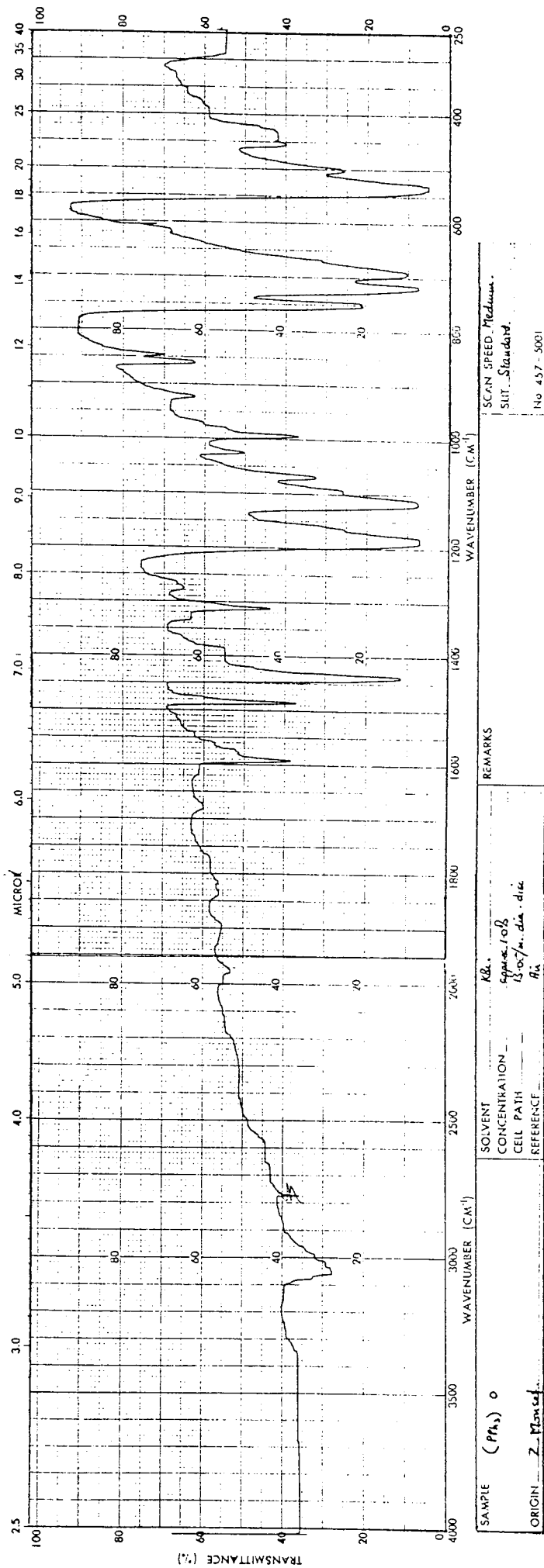


Figure (41) Infra-red spectrum of the species produced from the reaction
 palladium(0) and toluene

Table (8) Reaction between diphenylditelluride (Ph_2Te_2) and acetaldehyde (CH_3CHO) at room temperature

Solvent	Condition		Time of Reaction and Product	Infrared spectra Data
	Radiation	Time for which oxygen was bubbled through		
Benzene	uv	20 min.	After two days the solution became colourless. This solution was left for two days, brown crystals were obtained.	The brown crystals gave i.r evidence for a Te-O and >C=O bonds. The solution showed absorption due to >C=O in acetic acid.
Benzene	Fluorescent tube	15 min.	After three days a cream solid was obtained. The product was filtered and the filtrate was left for a further week.	The cream solid gave i.r evidence for a Te-O bond. The solution showed absorption due to >C=O in acetic acid.
p-xylene	Fluorescent tube	20 min.	After three days a cream solid was obtained. The product was filtered and the filtrate was left for two weeks more.	The cream solid gave i.r evidence for a Te-O bond. The solution showed absorption due to >C=O in acetic acid

Table 8 (Continued)

Toluene	Fluorescent tube	25 min.	After three days cream solid was obtained. The product was filtered and the filtrate was left for two weeks.	The cream solid gave i.r evidence for a Te-O bond. The solution showed absorption due to >C=O in acetic acid.
Toluene	Visible	20 min.	//	//
Toluene	uv	20 min.	After two days the solution became colourless. This solution was left for one day, brown crystals were obtained.	The brown crystals gave i.r evidence for a Te-O and >C=O bonds. The solution showed absorption due to >C=O in acetic acid.

Table (9) Reaction between diphenylditelluride (Ph_2Te_2) and n-butyraldehyde ($\text{C}_2\text{H}_5\text{CH}_2\text{CHO}$) at room temperature

Solvent	Radiation	Time of Reaction and Product	Infrared Spectra Data
Toluene	Visible	After a week a white precipitate was obtained. m.p = 201-202 °C	The white solid gave i.r evidence for Te-O bond. Also absorption due to $>\text{C}=\text{O}$ bond in n-butyric acid was obtained.
Hexane	uv	After three days a white precipitate was obtained. m.p = 200-201 °C	The white solid gave i.r evidence for Te-O bond. Also absorption due to $>\text{C}=\text{O}$ bond in n-butyric acid was obtained.
Benzene	Fluorescent tube	After five days a white precipitate was obtained. m.p = 198-200 °C	The white solid gave i.r evidence for Te-O bond. Also absorption due to $>\text{C}=\text{O}$ bond in n-butyric acid was obtained.

Table (10) Reaction between diphenylditelluride (Ph_2Te_2) and benzaldehyde (PhCHO) at room temperature.

Solvent	Condition		Time of Reaction and Product	Infrared Spectra Data
	Radiation	Time for which oxygen was bubbled through		
Toluene	uv	20 min	After two hours the black precipitate was filtered and filtrate was left for two weeks. White crystals were obtained. m.p = 103-105°C	The presence of ($\text{C}=\text{O}$) was due to benzoic acid.
Toluene	Visible	30 min	After three days cream solid was filtered and filtrate was left for two weeks. White crystals were obtained. m.p = 103-105°C	The cream solid showed absorption due to the Te-O group. The white crystals were benzoic acid.
Benzene	Visible	30 min	After four days cream solid was filtered and filtrate was left for two weeks. White crystals were obtained. m.p = 103-105°C	The cream solid showed absorption due to the Te-O group. The white crystals were benzoic acid.

Table (11) Reaction between [bis(p-ethoxyphenylditelluride)] (p-EtOC₆H₄)₂Te₂ and benzaldehyde (PhCHO) at room temperature.

Solvent	Condition		Time of Reaction and Product	Infrared Spectra Data
	Radiation	Time for which oxygen was bubbled through		
Hexane	Fluorescent tube	—	After three days white crystals were obtained.	The presence of (C=O) was due to benzoic acid.
Toluene	Fluorescent tube	—	After three days white crystals were obtained.	The presence of (C=O) was due to benzoic acid.
Toluene	Visible	—	After three days white crystals were obtained.	The presence of (C=O) was due to benzoic acid.

Table (12) Reaction between diphenylditelluride (Ph_2Te_2) and [crotonaldehyde(2-butenal)]
 $(\text{CH}_3\text{-CH=CH-CHO})$ at room temperature.

Solvent	Radiation	Time of Reaction and Product	Infrared Spectra Data
Benzene	Fluorescent tube	After three weeks a white solid was obtained. m.p = 180 °C	The white solid gave i.r evidence for Te-O bond.
Toluene	Visible	After two weeks a white solid was obtained. m.p = 195 °C	The white solid gave i.r evidence for Te-O bond.
Toluene	uv	After a week a white solid was obtained. m.p = 198 °C	The white solid gave i.r evidence for Te-O bond.

3.4 Discussion

3.4.1 Reaction of Telluroesters with Copper(I) Chloride and Dichlorobis(benzonitrile)Palladium(II)

Tellurium ligand chemistry still offers a vast area of interesting synthetic organometallic chemistry as well as co-ordination chemistry involving studies of new tellurium-metal linkages and fundamental studies of the ligand properties of tellurium bases.

As mentioned previously, Davies⁵⁹ has studied the ^{125}Te Mössbauer spectra of metal halide complexes of di-(p-ethoxyphenyl)telluride $(\text{p-EtOPh})_2\text{Te}$. This provides one opportunity to extend the work to date on organotellurium chemistry. Instead of using a simple telluride (e.g. R_2Te), the telluroester RCOTeR' was employed. This base was chosen due to the presence of both a 'hard' ($\text{C}=\text{O}$) and a 'soft' (Te) Lewis base centre. Thus the ligand may complex with 'hard' metals such as Cu(II) , Ni(II) etc.

^{125}Te Mössbauer spectroscopy has provided useful information on the properties of tellurium ligands. The ^{125}Te Mössbauer quadrupole splitting, Δ , in diorganotellurides (R_2Te) has been shown⁹⁵ to be greater than in the pyramidal cations (R_3Te^+). It was found¹⁰² that metal complexes of di-(p-ethoxyphenyl)telluride $(\text{p-EtOPh})_2\text{Te}_2$ gave a value of Δ between that of R_2Te and R_3Te^+ .

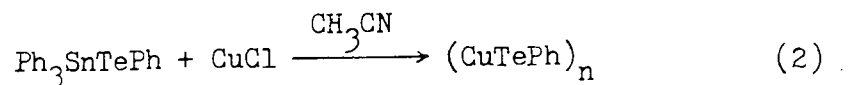
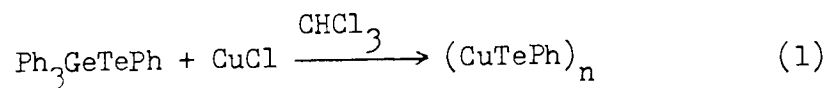
The formation of complexes between organotellurides (R_2Te) and 'soft' metals such as Pd(II) and Cu(I) is relatively easy. It was hoped in this study to utilize initially a 'soft' metal species $(\text{PhCN})_2\text{PdCl}_2$ or CuCl with a telluroester (RCOTeR') to form the desired

complex.

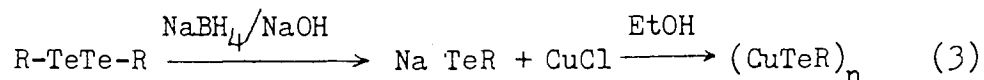
3.4.1.1 With Copper(I) Chloride

A mixture of telluroester ($\text{PhCOTeC}_6\text{H}_4\text{OEt-p}$) and copper(I) chloride (CuCl) was reacted in acetonitrile as solvent according to the method outlined in section (3.2.8 B). The compound formed a dark brown, insoluble solid with melting point around 300°C . An elemental analysis of this compound (table 4) suggested a stoichiometry of CuTeR (R=p-EtOPh). The infrared spectrum for this compound showed no evidence of a carbonyl function. Benzoyl chloride was also isolated as a by-product.

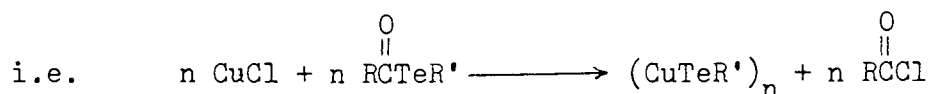
The reaction of Ph_3MTePh ¹⁰³ with cuprous chloride (M=Ge, Sn) gave a red-brown insoluble solid, CuTePh , which is thought to contain bridging Te^- -R ligands in a polymeric structure¹⁰⁴ (equations 1, 2).



Analogous polymeric complexes with organotellurol ligands have been prepared by reaction of NaTeR (generated in situ by borohydride cleavage of R_2Te_2) with CuCl in ethanol (equation 3).



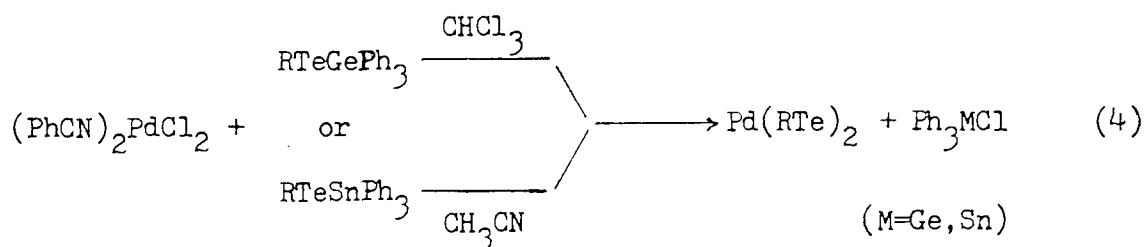
It is evident that the same complex has been formed here using a telluroester (RCOTeR'):



3.4.1.2 With Dichlorobis(benzonitrile)Palladium(II)

Reaction of telluroester (PhCOTeC₆H₄OEt-p) with dichlorobis(benzonitrile)palladium(II) Pd(PhCN)₂Cl₂ gave an extremely insoluble red-brown product. The elemental analysis of this compound (table 4) suggests the following empirical formula : Pd(RTe)₂ (where R=p-EtOPh).

Recent¹⁰⁴ work has shown that RTeMPh₃ (M=Ge,Sn) derivatives are useful reagents for the formation of M(^M-TeR)₂M linkages (equation 4).



Unlike the diaryl^{105,96} or dialkyl^{105,106} tellurides, which easily substitute for the labile benzonitrile ligand in dichlorobis(benzonitrile)palladium(II)

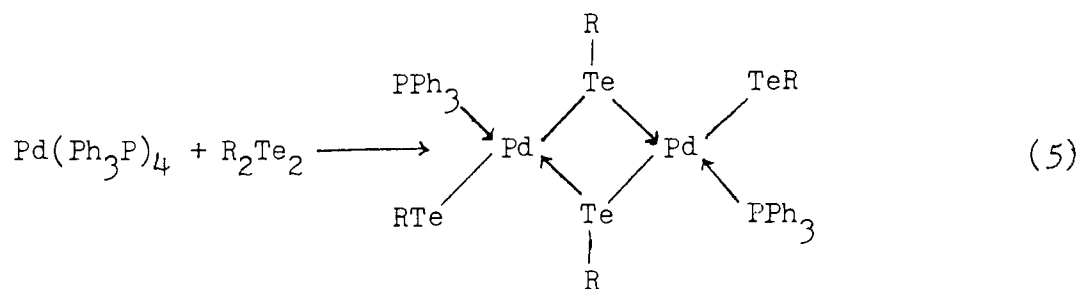
to form four co-ordinate complexes, these unsymmetrical metal-metal bonded tellurides react with a cleavage of the Te-Ge or Te-Sn bond. Reaction is immediate upon mixing of the two starting materials in the solvent, and the products, Pd(RTe)₂, are isolated as dark red-brown, insoluble materials with melting points of 150°C. These materials are likely to be polymeric, although this cannot be verified experimentally because the insolubility of the compounds precluded molecular-weight measurements in solution.

The formation of Pd(RTe)₂ from (PhCN)₂PdCl₂ and a telluroester (RCOTeR'), appears to react in an analogous way to that shown in equation (4). The exact mechanism of this reaction is unknown, but it is likely that an unstable intermediate such as (RTeCOR')₂PdCl₂ which decomposes with the formation of Pd(RTe)₂ and the chloride containing by-products in this case R'COCl.

3.4.2 New Reaction of Ditellurides and Palladium(0) Compounds

3.4.2.1 In Toluene

It was expected that the reaction between [Pd(TeR)₂]_n and PPh₃ would give the complex [(Ph₃P)Pd(TeR)₂]_n. This complex has previously been isolated⁹⁶ from the reaction of (Ph₃P)₄Pd(0) and R₂Te₂ in anhydrous benzene under nitrogen as shown below in equation (5).



The above compound was prepared in the present work by a modification of a literature method⁹⁶, mentioned above, using toluene (for safety), instead of benzene, at room temperature in the presence of normal laboratory light in the presence of air. From the reaction two different products were obtained :

(a) a brown solid : When Ph_2Te_2 was used, the elemental analysis of the brown material suggested an empirical formula $(\text{Ph}_3\text{P})\text{Pd}(\text{TeR})_2$. But when $(p\text{-EtOPh})_2\text{Te}_2$ was used, the product was more complicated, probably a mixture of two complexes $[\text{Pd}(\text{TeR})_2]_n$ and $\text{Pd}(\text{PPh}_3)_2(\text{TeR})_2$ (table 6)

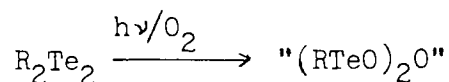
(b) white crystals from the solution : These gave a satisfactory analysis and had a melting point in good agreement with that reported in the literature for benzoic acid. The infrared spectrum showed a strong band at 1680 cm^{-1} attributable to the C=O group in benzoic acid (figure 40). The ^1H NMR spectrum was identical to a standard spectrum of benzoic acid. Fragments due to $\text{C}_6\text{H}_5\text{COOH}^+$, $\text{C}_6\text{H}_5\text{CO}^+$ were observed in the mass spectrum. It is suggested therefore, that benzoic acid must be formed from the solvent, which in this case is toluene.

The formation of benzoic acid from toluene presumably via the mediation of palladium(0) complex and R_2Te_2 in the presence of light and oxygen (from air). The above reaction was repeated under various conditions.

3.4.2.1.1 : From a toluene solution of $(\text{PPh}_3)_4\text{Pd}$ in the presence of visible light and air a white solid was obtained. The analytical data of the solid suggested that it was triphenyl-phosphine oxide (PPh_3O).

The infrared spectrum of the solid showed a strong band at 1195 cm^{-1} due to the P-O group in (PPh_3O) figure (41). The infrared spectrum of the filtrate was identical to that of toluene.

3.4.2.1.2 : From a toluene solution of R_2Te_2 ($\text{R}=\text{Ph}$, $p\text{-EtOPh}$) in presence of visible light and air a white precipitate was formed. Elemental analysis of the white solid suggested an empirical formula " $(\text{RTeO})_2\text{O}$ ". Infrared analysis showed strong bands centred on 550 cm^{-1} which are very characteristic¹⁰⁷ of $\nu(\text{Te-O})$. Thus the product almost certainly contains oxygen.



The infrared spectrum of the solution showed the presence of a C=O group. This suggests that there may have been a little aldehyde or acid formed.

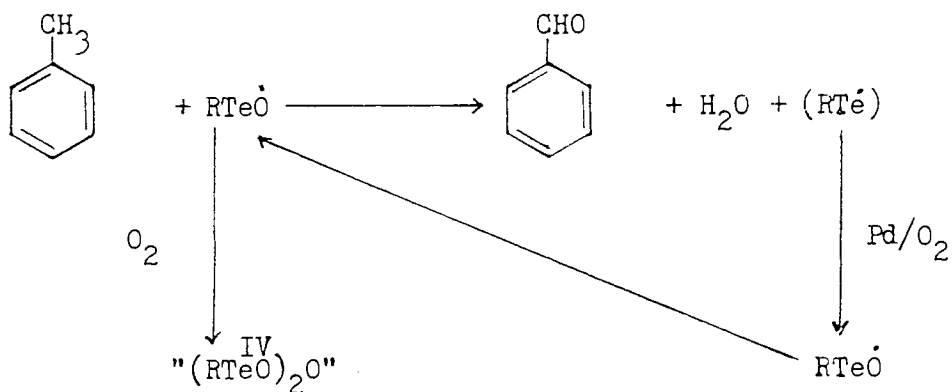
3.4.2.1.3 : From a toluene solution of R_2Te_2 and $(\text{PPh}_3)_4\text{Pd}$ in the presence of visible light and absence of air there was no evidence of the formation of a C=O group.

3.4.2.1.4 : The above experiment was repeated in presence of air and absence of light. The analytical observation was identical to (3.4.2.1.3) above.

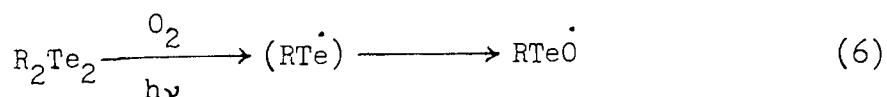
These observations suggest therefore, that aldehyde or acid must be formed from the solvent, but in the presence of four factors, as mentioned below :

- a) $\text{Pd}(\text{PPh}_3)_4$
- b) R_2Te_2
- c) O_2
- d) $h\nu$ (visible light)

A possible mechanism for the reaction may be written as :



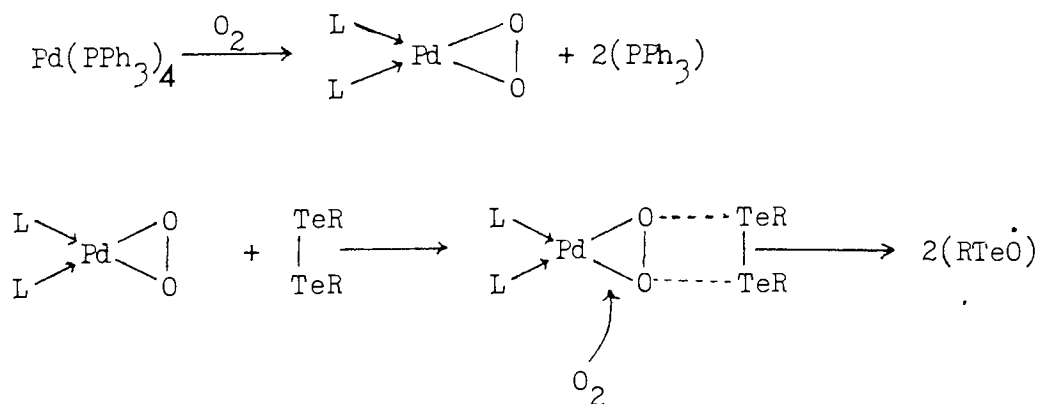
The initiation of the reaction is of some interest. There is evidence that a reaction of ditelluride in solution with oxygen is capable of producing radical intermediates¹⁰⁸, and so it must be accepted that oxygen, when present in the solvent, may play an important role in the reaction of ditellurides. There is also evidence that ditellurides may undergo an ethanol catalysed photochemically initiated reaction with oxygen¹⁰⁹.

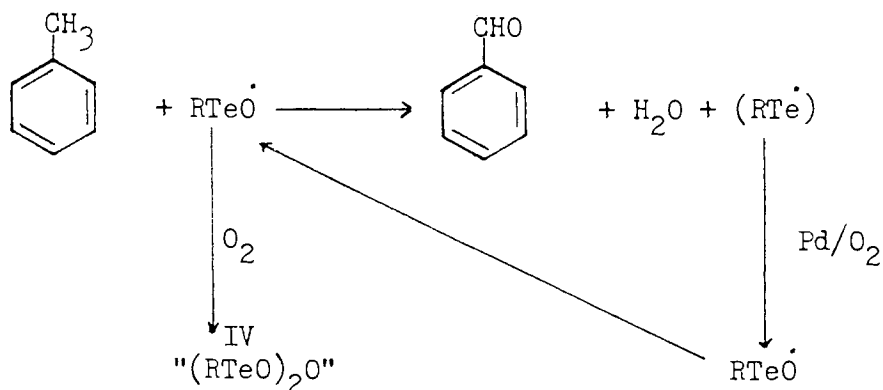


The e.s.r spectrum showed no signal when R_2Te_2 and phenyl-t-butyl-nitrone (PBN) in benzene was photolysed in the presence of t-butyl-bromide and air, but a free radical was detected by e.s.r after the addition of the ethanol and the irradiation of the mixture by visible¹⁰⁸ light. It appears that the addition of ethanol, under certain conditions, may partially dissociate diarylditellurides to radicals. These radicals can react with atmospheric oxygen or with oxygen dissolved in the solvent to form new oxygenated tellurium compounds such as $(R\dot{Te}O)_2O$.

It has been demonstrated¹¹⁰, using ^{125}Te NMR spectroscopy that an exchange reaction between ditellurides may occur. It was found that oxygen reacted with these molecules to give new compounds. An interesting feature was the effect of oxygen on the exchange mechanism. The results demonstrated that in the presence of oxygen, reaction shown in equation(6) was in competition with the exchange. However, when oxygen and light are absent the exchange reaction may continue by a slow thermal process.

The above mentioned experiments support the idea that the formation of the various compounds from the reaction mixtures proceed via the free radical $(R\dot{Te}O)$ using $Pd(PPh_3)_4$ as a catalyst, as opposed to ethanol¹⁰⁹. This is illustrated below :



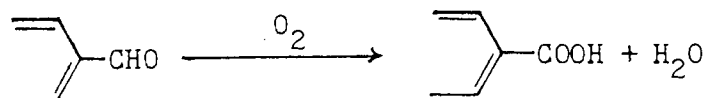


3.4.2.2 In p-xylene

The reaction was carried out using p-xylene, under similar conditions to those described in section (3.4.2.1). In the presence of the four factors mentioned previously ($\text{Pd}(\text{PPh}_3)_4$, R_2Te_2 , O_2 , $h\nu$), a brown precipitate was obtained. The analytical observations of the brown solid were identical to those shown in (a) of section (3.4.2.1) above. A concentration of the filtrate gave a liquid product whose infrared spectrum was identical to a standard spectrum of p-tolualdehyde.

3.4.3 Reaction Between Ditellurides and Range of Aldehydes

It is known that aldehydes are easily oxidized to carboxylic acids :



A range of solutions of aldehydes in the presence of air and light were oxidized to carboxylic acids. Two conditions were selected : (A) in the presence of ditellurides, (B) in the absence of ditellurides. In all cases, when ditellurides were present, a solid was obtained whose infrared spectrum showed an absorption due to a Te-O bond. A concentration of the filtrate gave a liquid or white crystals, depending on the aldehyde, with infrared spectra identical to a standard spectrum of the corresponding acids. In the absence of ditellurides a concentration of the solution gave the same products, identical to the above mentioned. However the formation of acids took longer than when ditellurides were not present. The above reactions demonstrate the use of ditelluride as a catalytic reagent.

3.4.4 Conclusion

It has been shown, using the four factors mentioned previously ($\text{Pd}(\text{PPh}_3)_4$, R_2Te_2 , O_2 , $h\nu$), that a carboxylic acid is formed when the solvent employed is toluene and aldehyde is formed when the solvent is p-xylene. The reaction proceeds via the free radical, $\text{RTe}\dot{\text{O}}$, with $\text{Pd}(\text{PPh}_3)_4$ as a catalyst.

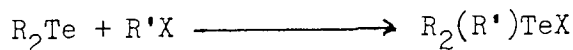
It has also been demonstrated that the oxidation of aldehydes to carboxylic acids is catalysed by ditelluride.

A quantitative study of the above reactions has not been undertaken in this work, but it is thought that further work in this area will be useful and provide a better understanding of the reactions.

3.4.5 Reaction Between $C_2H_5OC_6H_4TeC_6H_5$ and CH_3I

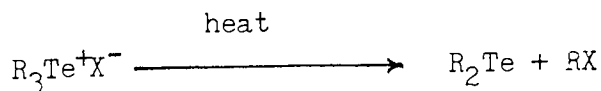
It was originally stated that the ability of telluroesters to complex with hard metals would be investigated. It has also been attempted to utilize initially a 'soft' metal species such as Pd(II) and Cu(I) with a telluroester to form the desired complex. However, evidence was presented for the formation of $Pd(TeR)_2$ from the reaction of dichlorobis(benzonitrile)palladium(II) and the telluroester. The formation of $(RTeCu)_n$ from similar reactions of copper(I) chloride ($CuCl$) and the telluroester ($RCOTeR'$) has also been observed.

Formation of telluronium salts from the reaction between diarylditellurides and alkylhalides is well known^{111,112,113}.

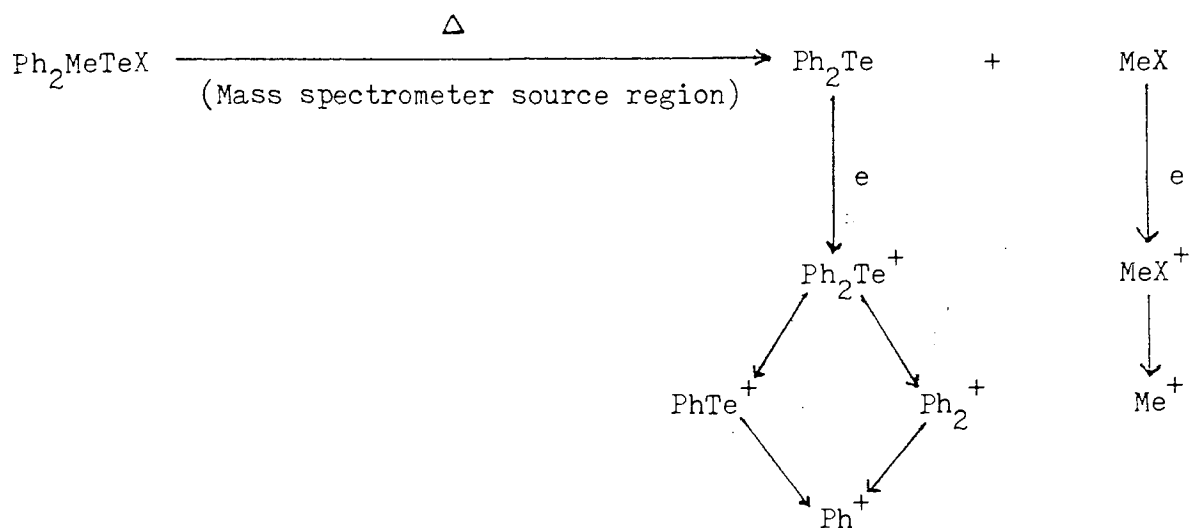


The preparation of telluronium salts from the reaction between telluroester and methyl iodide is of some interest. The compound formed from this reaction appeared as yellow crystals with a melting point of $150^\circ C$. Elemental analysis of this compound (table 4), suggested a stoichiometry of $R(CH_3)_2TeX$ ($R=p-EtOPh$ and $X=I$). The infrared spectrum for this compound showed no evidence of a carbonyl function.

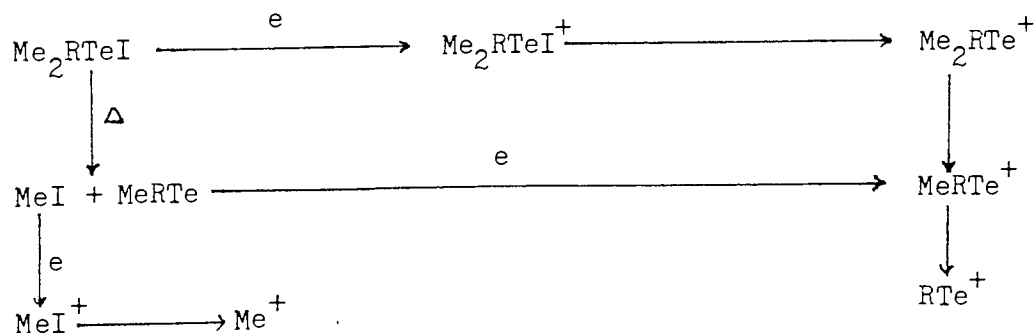
The thermal decomposition of triorganotellurium halides is well known¹¹⁴ and triphenyltelluronium pseudohalides have been shown to decompose in a similar fashion on heating¹¹⁵.



Electron impact mass spectroscopy has previously been used for the characterisation of a series of telluronium salts, $\text{Ph}_2\text{MeTe}^+\text{X}^-$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{NCS}$ and PhCOO)^{116,83,81}. The highest observed mass for this series was diphenyltelluride. In all cases the decomposition involving thermolysis of the telluronium salts to give diphenyltelluride and MeX was observed. The fragmentation patterns are as follows :

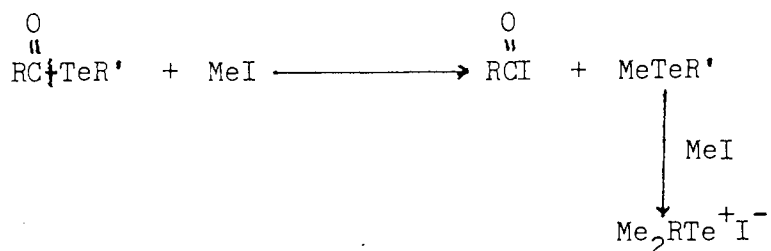


The fragmentation pattern of the compound Me_2RTeI may be represented by following scheme :



As with telluronium salts, the diorganotelluride is present in the highest mass in the spectrum. Other ions visible in the spectrum are listed in table (5). The mass spectrum confirms the formation of Me_2RTeI .

A possible mechanism for the formation of telluronium salts, by using telluroesters, instead of simple tellurides with methyl iodide is :



3.4.6 Conclusion

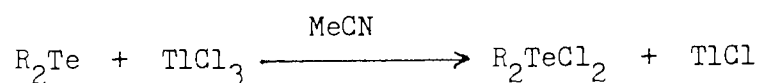
The formation of $[\text{Pd}(\text{TeR})_2]_n$ and $(\text{CuTeR})_n$ from the reaction between telluroesters and Pd(II) or Cu(I) suggested that these organotellurium reagents may be useful precursors of RTe^- ligands in reactions with transition-metal substrates.

Also the formation of telluronium salts $\text{Me}_2\text{RTe}^+\text{I}^-$ from the reaction between telluroesters and methyl iodide, together with the above, confirm the cleavage of $\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--Te}$ bonds rather than $\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--Te}$ bonds.

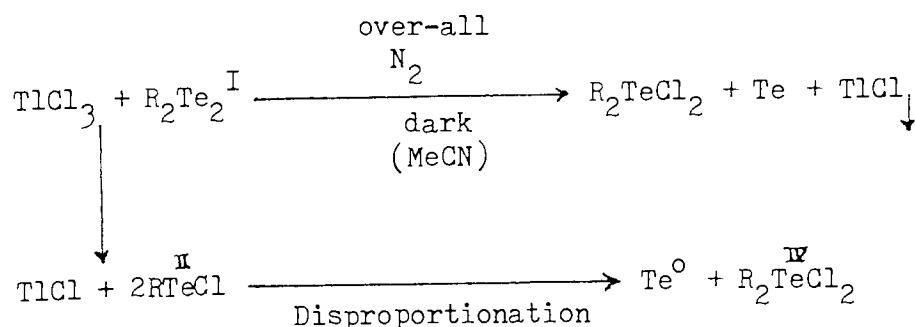
A reaction between $\text{Ph}\overset{\text{O}}{\parallel}{\text{C}}\text{TePh}$ and nickel(II) chloride in ethanol was attempted, but yielded no product and the $\text{Ph}\overset{\text{O}}{\parallel}{\text{C}}\text{TePh}$ was isolated from the reaction mixture.

An attempted reaction of $\text{Ph}\overset{\text{O}}{\parallel}{\text{C}}\text{TePh}$ with thallium(III) chloride

in acetonitrile was unsuccessful, the $TlCl_3$ remaining undissolved. The above reaction was repeated by using a simple telluride instead of the telluroester; $TlCl$ was isolated. From the concentration of filtrate, infrared evidence showed that R_2TeCl_2 had been formed.



The above reaction was repeated by using R_2Te_2 instead of R_2Te . When light was present R_2Te_2 was isolated from the reaction mixture. However, under nitrogen and in the absence of light a mixture of elemental tellurium and $TlCl$ was obtained. The above reaction was repeated under the same conditions. A white precipitate ($TlCl$) was filtered off, the filtrate was left open to light and air (ordinary lab. conditions), the elemental tellurium was deposited slowly.



It may be that the thallium(III) halides could provide a convenient method of oxidising ditellurides to telluronyl halides, since the amount of halogen available for oxidation can be carefully controlled.

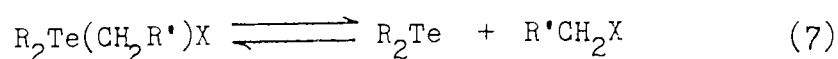
CHAPTER FOUR

FREE RADICALS AND TELLURONIUM SALT FORMATION

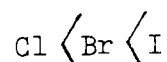
4.1 INTRODUCTION

4.1.1 Solution Studies of Triorganotelluronium Salts

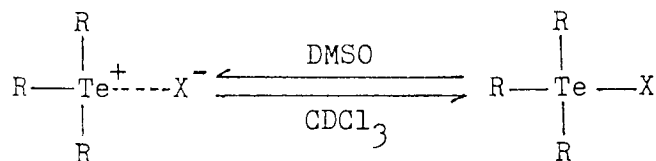
As mentioned previously (chapter one, section 1.2.6) attempts to prepare telluronium ylids from a range of salts $R_2Te(CH_2R')X$ (where R was aryl, R' was Ph or PhCO and X was halogen, generally Br or I) by the salt method, fail due to the rapid dissociation of the telluronium salt into telluride and organic halide^{80,81}, (however, evidence for the synthesis of $Ph_2Te^+-(CH_2COPh)^-$ in solution has been obtained). In several solvents reductive elimination of $R'CH_2X$ occurred more rapidly than removal of HX by base. Extension of the series of salts, e.g. to $R'=H$, revealed that, in solvents such as chloroform, reaction shown in equation (7) was general.



Dance⁸⁰ observed that methylphenyltelluronium salts undergo dissociation in deuteriochloroform solution to diphenyltelluride and methylhalide with a rate which is halogen dependent :

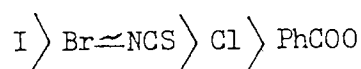


The telluronium salts are covalent in chloroform and more ionic in dimethyl sulphoxide (DMSO) and, to a lesser extent, dimethylformamide (DMF).



Kinetic data⁸¹ show that the reaction of CH_3I with excess Ph_2Te (solvent) affords an equilibrium mixture of ionic and covalent forms of $\text{Ph}_2(\text{CH}_3)\text{TeI}$, the ionic species being formed via the covalent one.

McWhinnie et.al.⁸¹ studied in more detail the solution chemistry of triorganotelluronium salts $\text{Ph}_2(\text{CH}_3)\text{TeX}$ (where $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{PhCOO}, \text{NCS}$). Using ^1H NMR spectroscopy of chloroform solutions, it was shown that the rate of dissociation was in the order :



The values of the molar conductivities of $\text{Ph}_2\text{MeTe}^+\text{X}^-$ (where $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NCS}$ and PhCOO) indicated that most telluronium salts are less than 1:1 electrolytes in dimethyl sulphoxide and dimethylformamide^{81,83}.

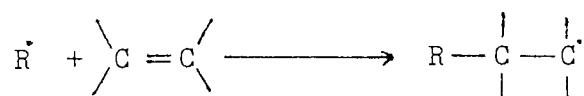
Methyldiphenyltelluronium isothiocyanate⁸³, $\text{MePh}_2\text{Te}(\text{NCS})$ has been synthesised and its behaviour studied in solvents of different polarity. This study showed that reductive elimination of (exclusively) methyl thiocyanate occurred in chloroform solution from a "covalent" form of the "salt". Kinetic data indicated that two pseudo-first order rate processes were involved, the second (faster) of which required the presence of Ph_2Te and this did not become dominant until a reasonable

concentration of telluride built-up. A further suggestion from the study was that, based on circumstantial evidence, a radical mechanism was involved.

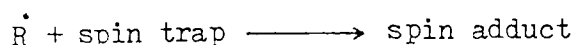
In the present work the oxidative addition of an alkylhalide (RX) to well purified diphenyltelluride (Ph_2Te) and the reductive elimination of alkylhalides from $\text{Ph}_2\text{MeTe}^+\text{X}^-$ have been investigated. Both reactions were studied in pure benzene solutions in the presence of phenyl-N-t-butylnitron ($\text{PhCH}=\text{N}(\text{O})\text{Bu}^t$), a well established spin trap for organic radicals.

4.1.2 Spin Trapping

The addition of a free radical to an unsaturated bond is one of the most important reactions known in free-radical chemistry. Of particular relevance to this study are those free-radical additions which lead to a more "stable" (i.e., longer lived) new radical.

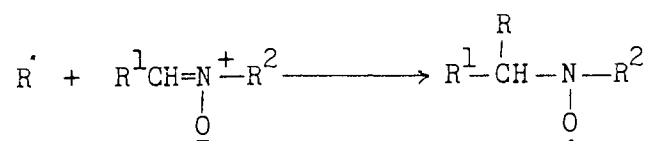
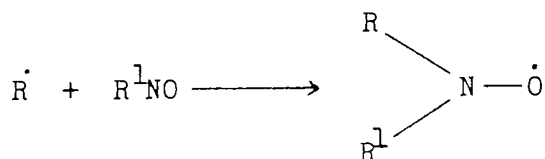


The technique of detecting and identifying short-lived free radicals by addition to an unsaturated function to produce an e.s.r detectable radical has been named ¹¹⁶ spin "trapping". The addition product of the short-lived radical and the spin trap is called a "spin adduct".

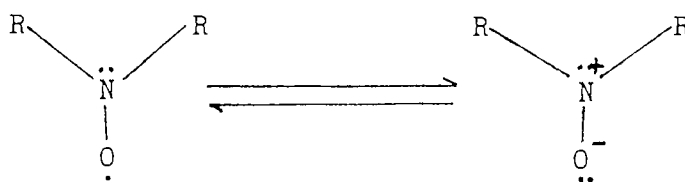


The spin trapping method involves the trapping of a reactive free radical by an addition reaction to produce a more stable radical, detected by e.s.r, whose hyperfine coupling parameters permit identification of the initial radical trapped.

The technique of electron spin resonance spin trapping has recently been developed to detect and identify organic free-radicals in solution^{117,118}. Suitable spin traps are nitroso compounds (e.g. 2-methyl-2-nitrosopropane¹¹⁹ and 2-methyl-2-nitrosobutan-3-one) and nitrones (e.g. phenyl-N-t-butylnitron)¹²⁰. These spin traps have been shown to trap free radicals to give stable nitroxides. The general reactions to give nitroxide adducts from nitroso compounds and nitrones are :

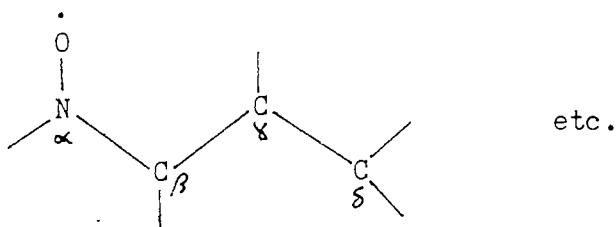


Nitroxide radicals are compounds containing the >N-O group, which has one unpaired electron. The structure of this fragment can be conceived as a superposition of two resonance structures :



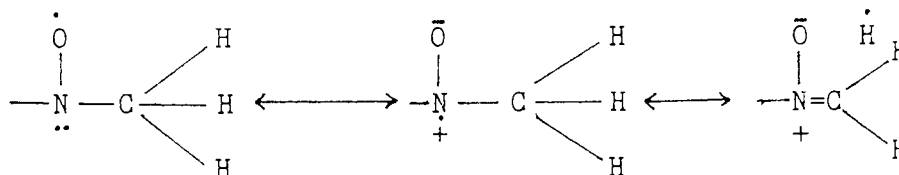
The e.s.r spectrum of the nitroxide function consists of three lines, or groups of three lines, due to the nitrogen hyperfine splitting ($^{14}\text{N}=1$). The nitrogen hyperfine splitting constant (a_{N}) varies substantially with the nature of the substituents attached to nitrogen. Steric or remote powerful electronic effects may cause the a_{N} value to increase or decrease to values outside these limits. Solvent is also important, polar and protic solvents cause an increase in a_{N} probably because of an enhanced contribution of the dipolar resonance from high dielectric or hydrogen bonding solvents¹¹⁶.

Nuclei with spin attached directly to nitrogen or one, two or even three (carbon) atoms removed from the nitroxide function show further hyperfine splitting. From the e.s.r point of view, the following position nomenclature has evolved :



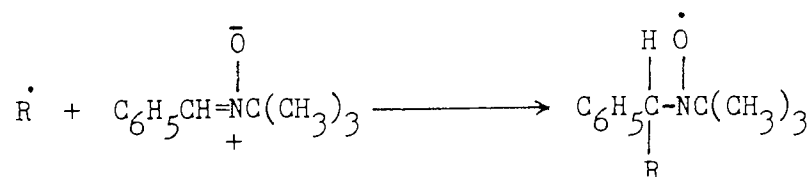
Hydrogen attached directly to nitrogen (α -position) gives

large hyperfine splitting. Hyperfine splitting from hydrogen in the β -position has a strong well understood angular dependence. The mechanism of β -hydrogen hyperfine coupling is most readily ascribed to hyperconjugation, for example in methyl-substituted nitroxides.



The magnitude of this coupling depends both on the spin density on nitrogen and on the dihedral angle between the p-orbital on nitrogen and the C-H bond of the methyl group.

Phenyl-N-tert-butyl nitron (PBN) was employed as a spin trap in the present work, which was initially introduced by Janzen^{121,116}.



In this case identification of the radical trapped is derived from the magnitude of the nitrogen and β -hydrogen hyperfine coupling constant (hfsc). The information necessary to define the structure of the radical trapped lies in the magnitude of the β -hydrogen (β -H)

and nitrogen hyperfine coupling (hfsc). The β -H (hfsc) depends on the dihedral angle which in turn depends on the bulk of R. The magnitude of the β -H (hfsc) decreases with increase in bulk of attached groups¹²². The nitrogen (hfsc) on the other hand is sensitive to the electronegativity of R, inductive electron withdrawal producing a smaller nitrogen (hfsc)¹²³.

4.2 EXPERIMENTAL

4.2.1 Preparation of Diphenyltelluride (Ph₂Te)

McWhinnie³³, has reported the synthesis of diphenyltelluride by a modification of the method of Rheinboldt and Petragani¹²⁴. To an ethereal solution (100 ml) of a Grignard reagent synthesised from bromobenzene (39.3 g) and magnesium (6.1 g) was added benzene (100 ml). The temperature of the solution was lowered to 0°C and vigorous stirring was commenced. Tellurium tetrachloride (13.5 g) in benzene (200 ml) was added slowly to the stirred solution, after which the reaction mixture was heated under reflux for 2 hrs. The cooled solution was treated with saturated ammonium chloride solution (300 ml) and the separated organic layer was washed three times with distilled water and dried. The solvent was removed and the residue was treated with bromine in carbon tetrachloride. The diphenyltellurium dibromide thus formed was reduced employing hydrazine, and pure diphenyltelluride was obtained. No free tellurium was produced by this method, while it has been reported as a side product by Rheinboldt.

Further purification of the product was achieved by distilling under vacuum, the fraction with b.p. 119 - 120°C (0.3 mmHg) being used. The analysis, IR spectrum and mass spectrum indicated purity.

4.2.2 Preparation of a Solution of n-Butyl-Lithium

n-Butyl-lithium (C₄H₉Li) was prepared using a literature method⁸⁴.

4.2.3 Preparation of a Solution of Grignard Reagent (n-Butylmagnesium Bromide)

The Grignard reagent was prepared in anhydrous ether from n-butyl bromide and the stoichiometrically required amount of magnesium⁸⁴.

4.2.4 Preparation of Methyldiphenyltelluronium Iodide; Slight Modification of a Literature Method

Freshly distilled methyl iodide (10-12 ml) and pure diphenyltelluride (5 g) were mixed in a conical flask which was dried and previously flushed with nitrogen. The mixture was left for two hrs (the literature method reported 48 hrs). The yellow crystals were filtered and dried over P_4O_{10} . The solid was placed in a conical flask with some distilled water and heated in a water bath around $60^{\circ}C$. Recrystallization from water gave white crystals of pure methyldiphenyltelluronium iodide which melted at $122-123^{\circ}C$ (lit: $123-124^{\circ}C$).

4.2.5 Preparation of Methyldiphenyltelluronium Thiocyanate
 $Ph_2(CH_3)Te(NCS)$

Methyldiphenyltelluronium thiocyanate ($MePh_2TeNCS$) was prepared by the indicated literature method⁸³. The compound gave satisfactory analysis and had melting point and spectroscopic data (e.g. IR) in good agreement with that reported in the literature.

4.2.6 Phenyl-N-tert-butyl nitone $C_6H_5CH(C_4H_9)N(O)C(CH_3)_2$ (PBN)

Phenyl-N-tert-butyl nitronone was purchased from the Aldrich Chemical Co Ltd, and it was used without further purification.

4.2.7 Solvent

The solvent which was used throughout this work was benzene. It was purified by a literature method⁸⁴.

4.2.8 Sample Preparation for the Study of the Reaction of a Range of Organic Halides (RX)* with Diphenyltelluride in Dry Benzene Under Nitrogen in the Presence of a Spin Trap

A modified e.s.r tube similar to the one shown in figure (42) was constructed.¹²⁵ Aliquots of pure benzene (3 cm^3) and 0.06 M PBN in benzene (3 cm^3) were placed in separate arms of the modified e.s.r tube and the system was flushed with nitrogen. In a separate air free flask fitted with a rubber septum, diphenyltelluride (2 molar portions to ensure no precipitation of the telluronium salt) and the organic halide (1 molar portion) were mixed. Samples of the reaction mixture could be taken after any desired time, added to the benzene solvent arm of the e.s.r tube which was then inverted to bring the reaction mixture into contact with PBN. Initial e.s.r spectra were recorded about one minute after mixing. However, resolution could be much improved by the brief passage of oxygen followed by the further passage of nitrogen through two hypodermic needles extending below the surface of each solution (nitrogen escaped through the open end of the tube). When degassing was complete (15 min.) the exit was closed and the hypodermic needles withdrawn. The solutions were mixed and the resulting mixture forced into

the tube by shaking. The mixture was transferred into an e.s.r tube, which was previously flushed with nitrogen, via a syringe through a rubber septum (figure 42).

* $RX=MeI$, Bu^nBr , $Bu^{sec}Br$, Bu^tBr , $BrCH_2-CH=CH-CH_2Br$ and $Br(CH_2)_4Br$.

Further Observations

- (i) When pure methyl iodide and pure diphenyltelluride were reacted in 1:1 molar ratio, white crystals of $Ph_2(CH_3)TeI$ began to deposit. In the presence of PBN (added as a benzene solution), no solid was seen even after eight days.
- (ii) The reaction of 1,4-dibromobut-2-ene with diphenyltelluride leads to the formation of Ph_2TeBr_2 (quantitative with respect to tellurium)¹¹⁴, however the presence of PBN inhibits the reaction.
- (iii) t-Butylbromide and diphenyltelluride left for over eight weeks produced a solid identified as Ph_2TeO .
- (iv) In one experiment a benzene solution of MeI was mixed with a PBN solution, this gave no evidence for radicals.
- (v) It has been reported¹²⁶ that freshly prepared nitrosobenzene ($PhNO$, spin trap) itself in 1,4-dioxan gave no e.s.r spectrum but after one hour this solution gave rise to a nitroxide radical ($Ph-\overset{\overset{O}{\parallel}}{N}-Ph$). Therefore this was checked in the case of phenyl-N-tert-butylnitron (PBN) in pure benzene. It was found that no free radicals were observed in this solution, even after 24 hrs.
- (vi) Unless deliberately introduced, all solutions were kept oxygen free and no undue exposure to light occurred although it cannot be claimed that the experiments were carried out under light free conditions.

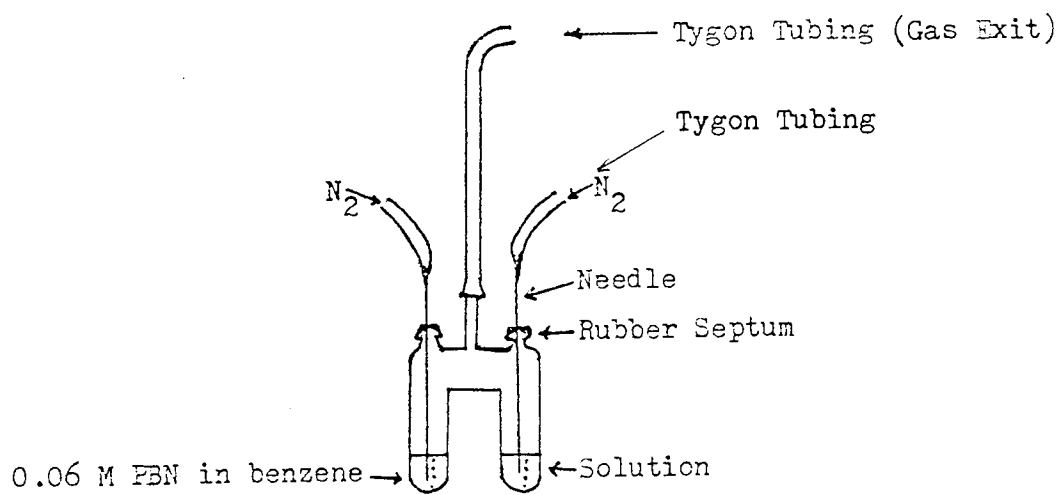


Figure (42) Modified E.S.R tube as
 described by Russell,
 Janzen and Strom¹²⁵.

4.2.9 Sample Preparation for the Decomposition of Methyl-diphenyl-telluronium Thiocyanate $\text{MePh}_2\text{Te}(\text{NCS})$ in Solution in the Presence of a Spin Trap

Pure benzene containing PBN was mixed with a pure benzene solution of $\text{MePh}_2\text{Te}(\text{NCS})$ and the resulting mixture was then examined for radical products using e.s.r spectroscopy. Also, in one experiment a chloroform solution of $\text{MePh}_2\text{Te}(\text{NCS})$ was mixed with a PBN solution and the resulting mixture was then placed in a flat e.s.r tube and examined for radical products by e.s.r spectroscopy. In both cases positive evidence for radicals was found.

4.2.10 Sample Preparation for the Study of Reaction of PBN with Organolithium and Grignard Reagents

The same modified e.s.r tube was used (as described in section 4.2.8) in the reaction of PBN with the organolithium (Bu^nLi) and Grignard reagents (Bu^nMgBr). PBN (0.06 M) in benzene (3 ml) was placed in one arm and 3 ml of benzene in the other. One or two drops of the Bu^nLi or Bu^nMgBr was added to the benzene solution after atmospheric air was flushed out of the modified e.s.r tube with nitrogen. The solutions were mixed and oxygen was bubbled through the solution for two or three minutes. The solution was finally deoxygenated with nitrogen for 15 minutes and investigated. Usually the radical concentration was relatively high and a number of 50:1 dilutions were necessary to obtain good resolution of the e.s.r spectrum. The hyperfine constants obtained are recorded in table (13).

4.2.11 An Attempt to Measure the Molar Conductivity in the Reaction
Between Pure Methyl Iodide and Pure Diphenyltelluride

A simple kinetic investigation of the reaction between methyl iodide and diphenyltelluride was attempted at 35.0°C. The reaction was carried out by addition of MeI to Ph₂Te as solvent over a period of time. Unfortunately the conductivities were so low in the viscous Ph₂Te that it was impossible to make any definitive measurements.

4.3 RESULTS

Spin trapping experiments with phenyl-t-butyl nitron have provided evidence that the oxidative addition of an alkyl halide (RX) to diphenyltelluride to afford a telluronium salt involves free radicals. Also radicals are involved in the reductive elimination of CH_3SCN from $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$.

E.s.r spectra of t-butyl α -substituted benzylnitroxides $\text{C}_6\text{H}_5\text{CHRNC}(\text{CH}_3)_3$ are presented in figures 43-51 and their hyperfine coupling constants are shown in table (13).

The reaction of n-butylbromide and diphenyltelluride over eight weeks produced a solid identified as Ph_2TeO . The infrared spectrum of the product is presented in figure (52).

Table (13) Hyperfine coupling constants of t-butyl α -substituted benzyl nitroxides

Reactants	Radical Trapped	Hyperfine Coupling of Nitroxide	
		a_N (gauss)	a_N/a_H (gauss)
$\text{Ph}_2\text{Te} + \text{CH}_3\text{I}$	$\cdot\text{CH}_3$	14.54	2.06
$\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$	$\cdot\text{CH}_3$	14.49	2.04
$\text{Ph}_2\text{Te} + \text{Br}(\text{CH}_2)_4\text{Br}$	$\cdot\text{CH}_2(\text{CH}_2)_3\text{Br}$	14.48	2.06
$\text{Ph}_2\text{Te} + n\text{-BuBr}$	$\cdot n\text{-Bu}$	14.75	1.92
$n\text{-BuMgBr}$	$\cdot n\text{-Bu}$	14.71	1.99
$\text{Ph}_2\text{Te} + \text{sec-BuBr}$	$\cdot \text{sec-Bu}$	14.63	1.96
$\text{Ph}_2\text{Te} + t\text{-BuBr}$	$\cdot t\text{-Bu}$	14.45	1.92
$\text{Ph}_2\text{Te} + \text{BrCH}_2\text{CH}=\text{CHCH}_2\text{Br}$	$(\text{CH}_2\dot{\text{C}}\text{HCH})\text{CH}_2\text{Br}$	14.45	1.99

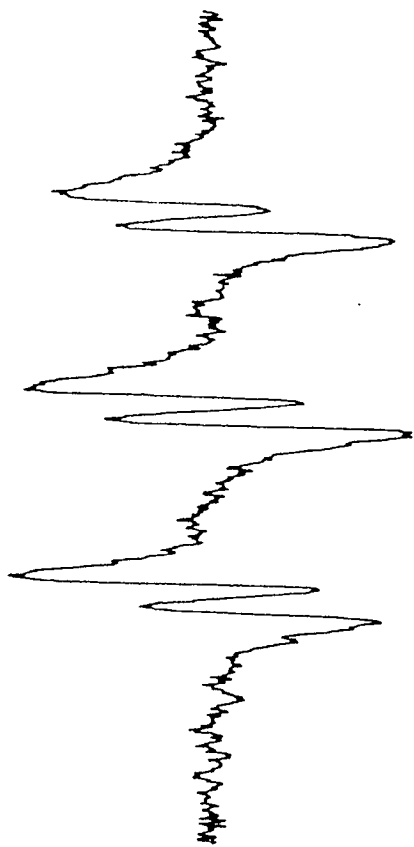


Figure (43) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butylnitronone obtained from the addition of diphenyltelluride to methyl iodide in the presence of phenyl-t-butylnitronone in benzene.

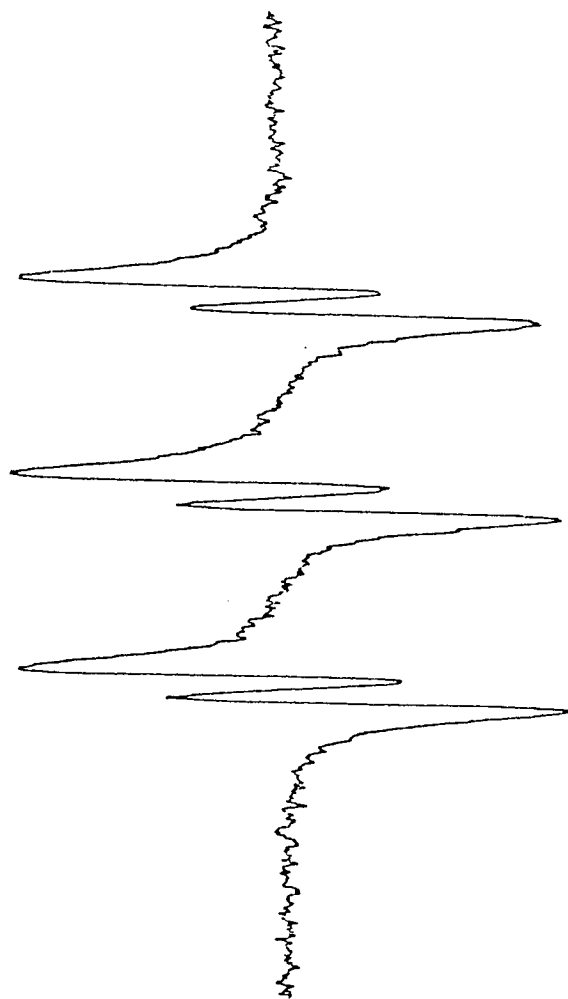


Figure (44) The E.S.R. Spectrum obtained upon Reductive Elimination of
MeSCN from Ph₂(CH₃)Te(NCS) in the presence of Phenyl-*t*-butylnitronone
in benzene.

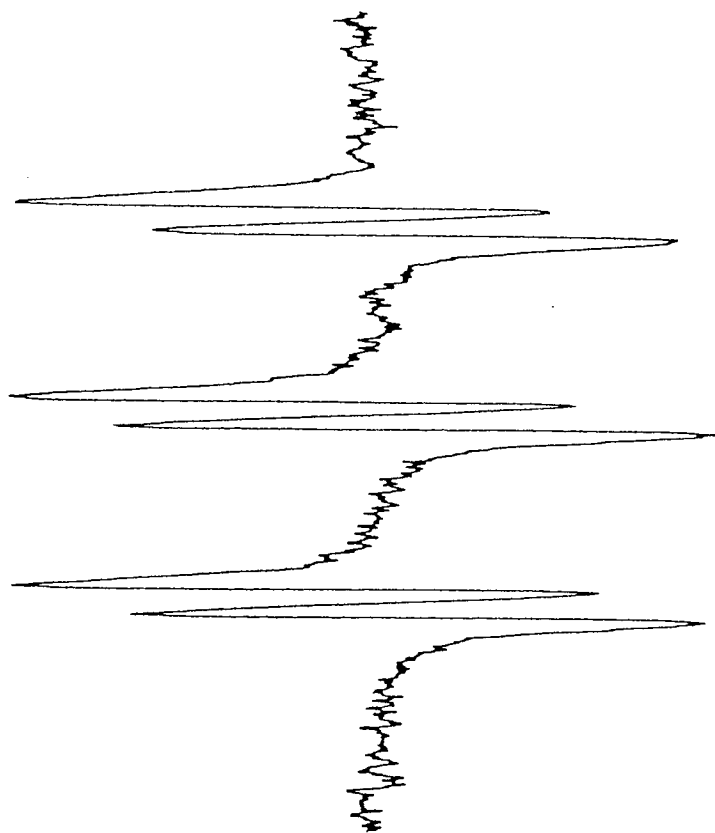


Figure (45) F.S.R spectrum of the n-butyl spin adduct of phenyl-t-butylnitron obtained from the addition of diphenyltelluride to 1,4-dibromobutane in the presence of phenyl-t-butylnitron in benzene.

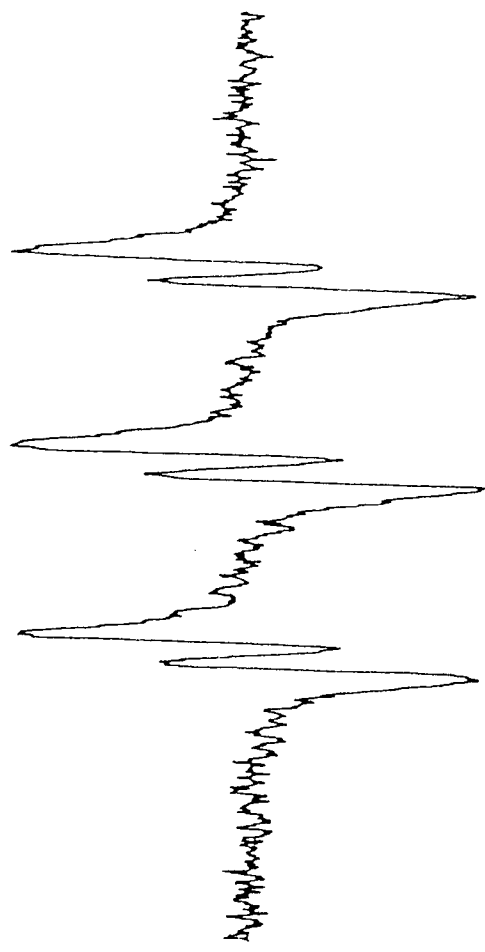


Figure (46) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butylnitronone obtained from the addition of the diphenyltelluride to n-butyl bromide in the presence of phenyl-t-butylnitronone in benzene

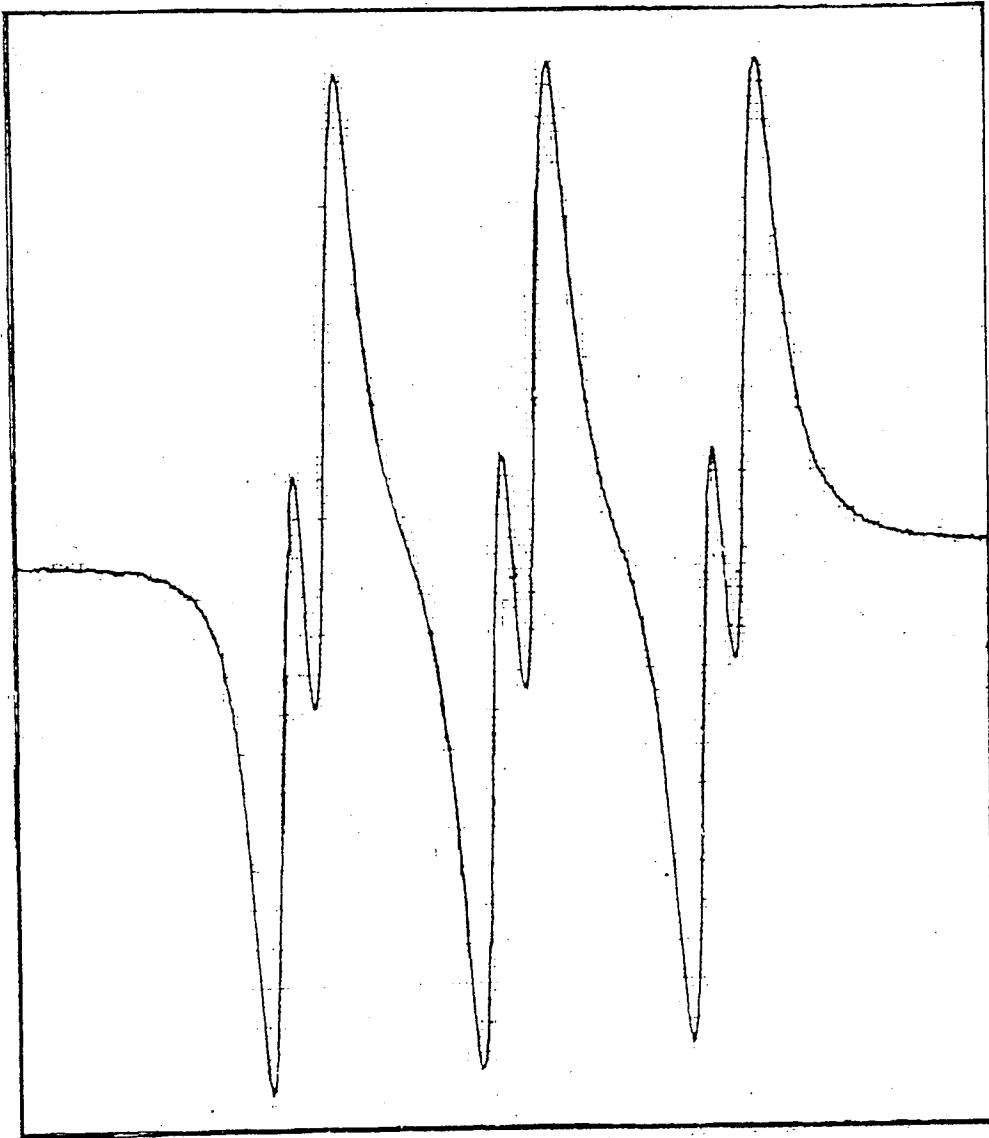


Figure (47) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butyl nitronone produced by the addition of the Grignard reagent(n-BuMgBr) to phenyl-t-butyl nitronone in benzene.

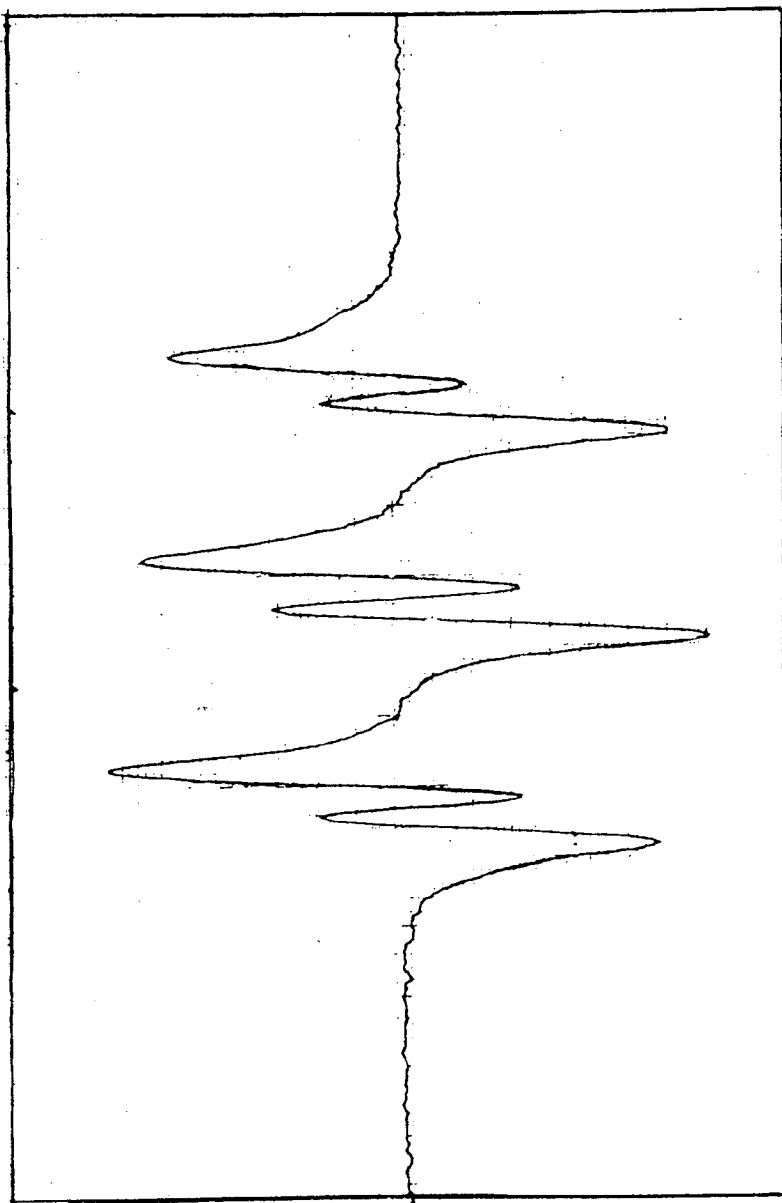


Figure (48) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butyl
nitronone produced by the addition of the n-butylolithium
to phenyl-t-butyl nitronone in benzene.

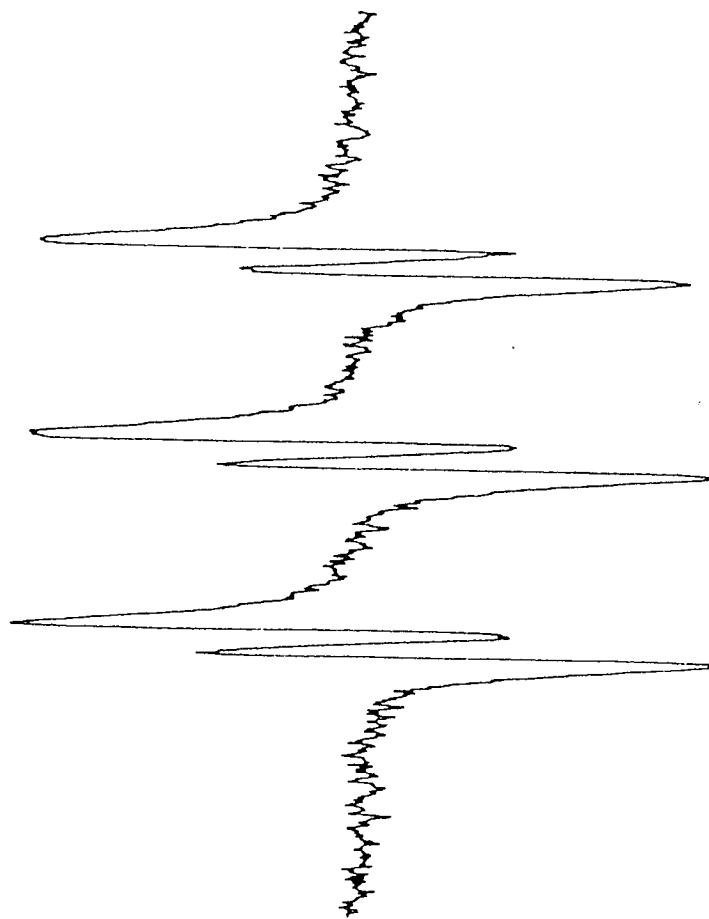


Figure (49) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butyl nitron obtained from the addition of diphenyltelluride to sec-butyl bromide in the presence of phenyl-t-butyl nitron in benzene

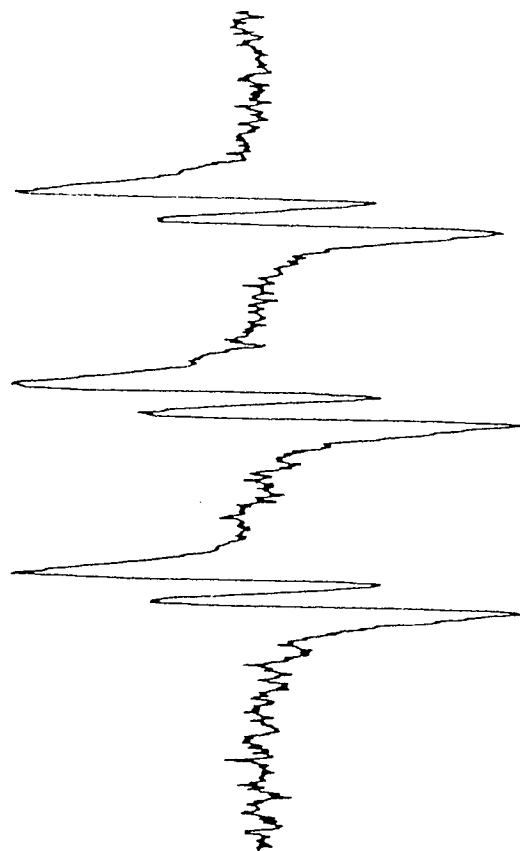


Figure (50) E.S.R spectrum of the t-butyl spin adduct of phenyl-t-butyl nitronne obtained from the addition of diphenyltelluride to tert-butyl bromide in the presence of phenyl-t-butyl nitronne in benzene.

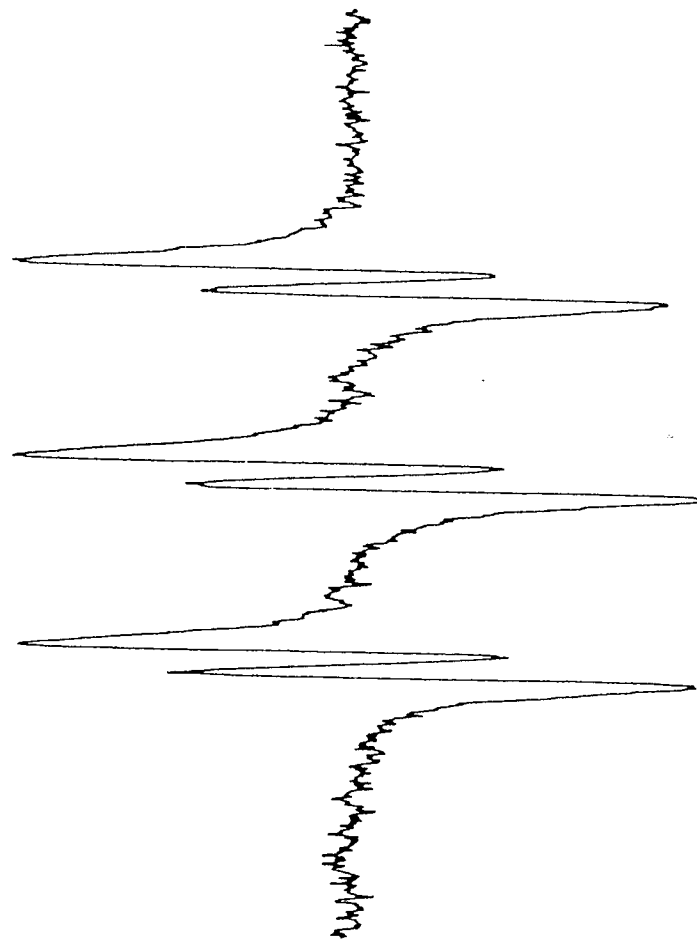


Figure (51) E.S.R spectrum of the n-butyl spin adduct of phenyl-t-butylnitronone obtained from the addition of the diphenylyltelluride to 1,4-dibromo-2-butene in the presence of phenyl-t-butylnitronone in benzene.

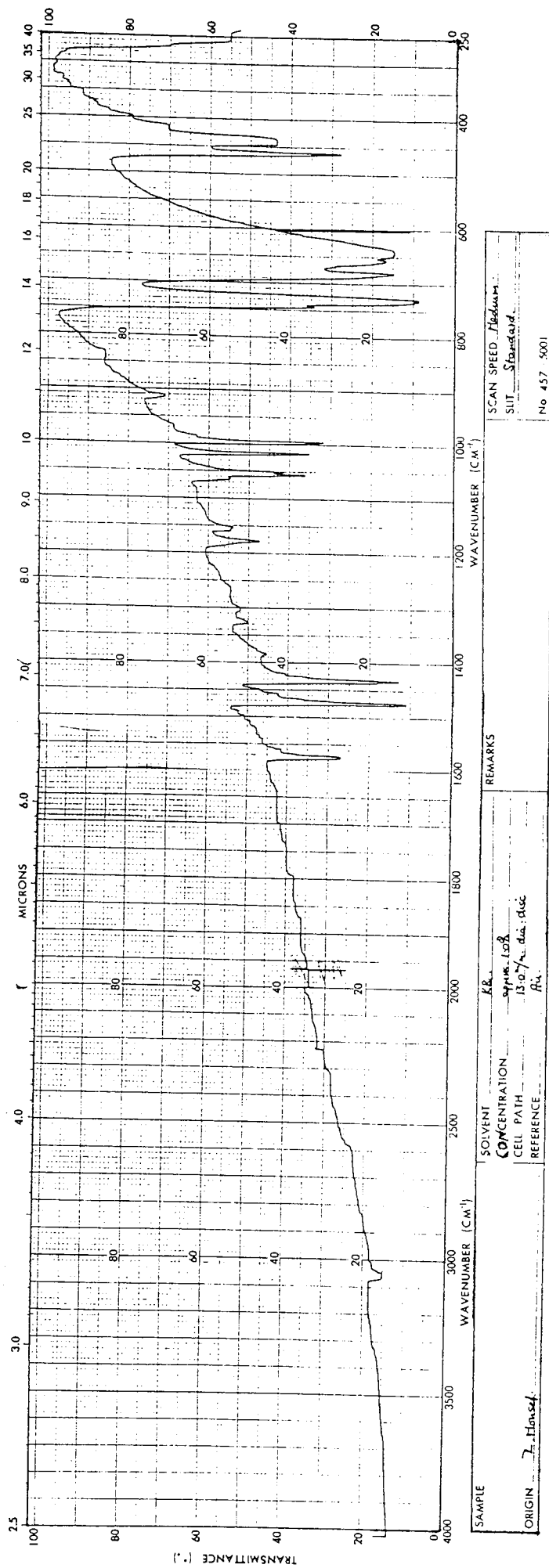


Figure (52) Infra-red spectrum of the reaction between diphenyltelluride and tertiary butyl bromide(after eight weeks).

4.4 DISCUSSION

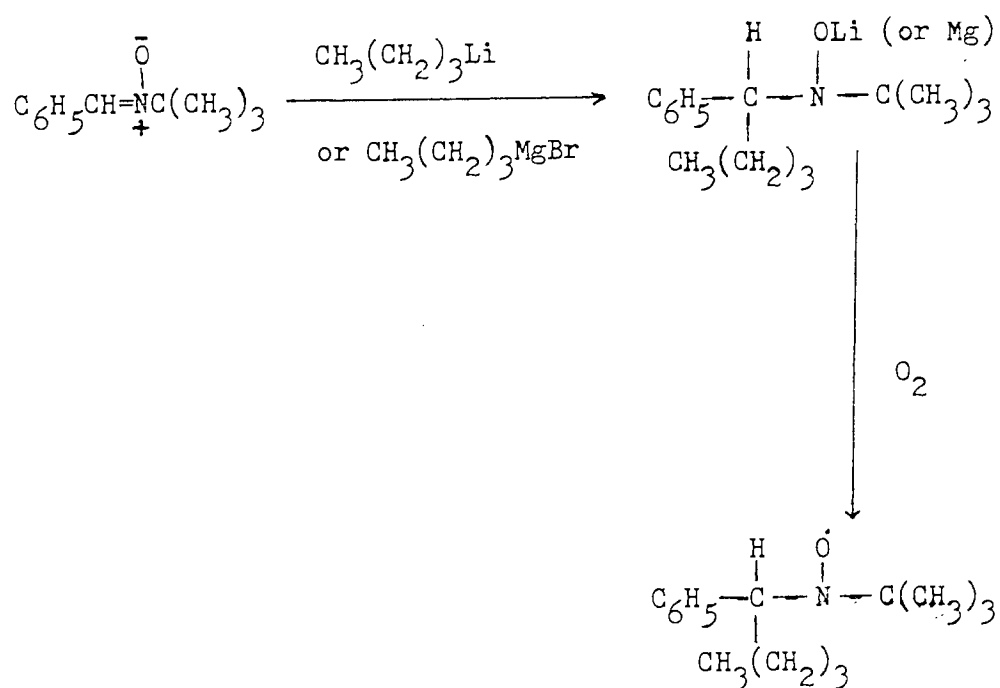
The addition of PBN to a mixture of Ph_2Te and (RX) in benzene at room temperature gave immediate evidence for free radicals (figures 43 - 51). A signal of three doublets due to a nitroxide (spin adduct) was obtained.

Although the detection of a spin adduct by e.s.r appears to provide proof of the presence of a short-lived reactive free radical in solution, more information is required before identification of the structure of the free radical trapped can be made. The identification of the radicals (spin adduct) must depend on the measurement of the hyperfine coupling constants a_N (~ 14 Hz) and $a_{\beta H}$ ($\sim 2-3$ Hz). The three large splittings are due to the nuclear hyperfine splitting of ^{14}N . The smaller hyperfine splittings are due to the presence of a hydrogen atom (βH). The bulk and group electronegativity of the radical trapped determines the magnitude of the nitrogen and β -hydrogen coupling constants. However the magnitudes of these coupling constants are not necessarily known for a given spin adduct since relatively few nitroxides with these structures have been previously reported. Since solvent effects change the nitrogen coupling constant (increases to larger values in protic solvents) and in turn the β -H coupling, it is advantageous to have spectra of nitroxides of "known" structure available for comparison in the same solvent.

Janzen and Blackburn¹²⁰ have verified the structure of certain nitroxide radicals by addition of organolithium or Grignard compounds to PBN (Grignard reagents are known to add to aldonitrones in a 1,3 fashion)¹²¹ followed by oxygen oxidation to the nitroxide. From the reaction between phenyl-lithium and PBN in benzene the usual

set of three doublets was obtained. The spectrum was identified as being due to the presence of benzhydryl t-butyl nitroxide.

In the present work attempts were made to generate authentic specimens of the suspected free radicals by reaction of Grignard or organolithium reagents with PBN, followed by oxidation with oxygen¹²⁰, in this way we could "calibrate" our own spectra. Spin adducts were made by both n-butyllithium and n-butylmagnesium bromide addition to PBN.



This method works extremely well for all primary carbanions. The final yield of nitroxide radical was obtained immediately and in very high yield. Extensive dilution of such solutions has been

necessary for good resolution due to "concentration" broadening. The values for the nitrogen and β -hydrogen (β -H) hyperfine coupling (hfc) are shown in table (13). Oxidative addition of diphenyltelluride with n-butyl-bromide in benzene containing PBN gave a strong e.s.r signal consisting of three doublets, $a_N = 14.75$, $a_{\beta H} = 1.92$ gauss, and a complex set of lines due to the n-butyl spin adduct of phenyl-t-butyl-nitron $\left[C_6H_5CH(C_4H_9)N(\dot{O})C(CH_3)_3 \right]$ radical.

Lappert and coworkers have used successfully spin trapping techniques¹²⁷ in their study of addition to tin(II) compounds. The presence of Ph_2Te in our solutions produced considerable broadening of the e.s.r spectra, again (as mentioned previously in the experimental section) a function of increased viscosity, in this instance slowing molecular tumbling in solution. One consequence of this is that the uncertainty in the measurement of the smaller hyperfine parameter ($a_{\beta H}$) is large (table 13).

Our values do not agree particularly well with those reported by Janzen for given radicals. We found generally that the spectra were fairly broad placing a good deal of uncertainty on $a_{\beta H}$. Each experiment was repeated several times. We are satisfied that the internal consistency of our data is good and that radicals have been correctly identified. Information obtained from the spin trapping experiments is gathered into table (13).

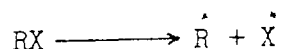
As mentioned previously it has been shown⁸³ that reductive elimination of (exclusively) methyl thiocyanate occurred in chloroform solution from a "covalent" form of the "salt". Kinetic data indicated that two pseudo-first order rate processes were involved, the second (faster) of which required the presence of Ph_2Te and this did not become dominant until a reasonable concentration of telluride built-up.

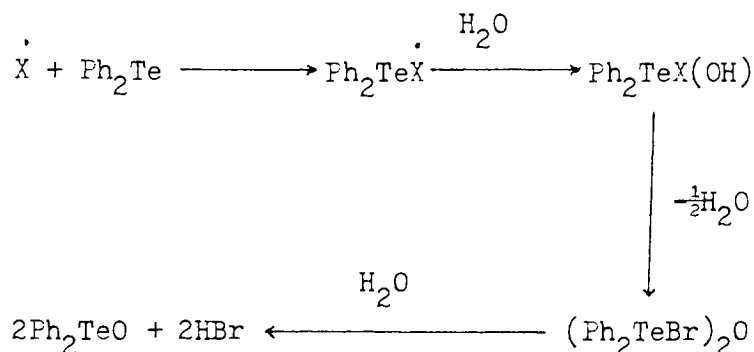
A further suggestion from the study was that, based on circumstantial evidence, a radical mechanism was involved.

We now have positive evidence for radical path ways in both oxidative addition to Ph_2Te and for reductive elimination from $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$. The experiments were carried out under strictly anaerobic conditions, however if oxygen was then deliberately introduced the concentration of the (same) trapped radical increased. This was experimentally useful in that it gave us a better spectrum to work with, but there is a clear indication that the spin trap not only reacts with the equilibrium concentration of radicals, but also reacts with another species which, on oxidation affords further radicals. We have not attempted in any one case to prepare that trapped radical species in 100% yield so perhaps we should acknowledge that other pathways may also be involved, although none of our data suggest this to be likely.

The nature of the products depends on the organic halide (the stability of $\dot{\text{R}}$). It has been shown¹²⁸ that the reaction of n-butylbromide and diphenyltelluride produced diphenyltellurium oxide (Ph_2TeO) and sometimes a phenyltellurium oxy-bromide $(\text{Ph}_2\text{TeBr})_2\text{O}$, over a long period, when petroleum ether was used as a solvent. However diphenyltellurium oxide was the major product. When no solvent was used, no reaction was observed with primary butyl bromide, whereas tertiary butyl bromide and diphenyltelluride produced diphenyltellurium oxide and $(\text{Ph}_2\text{TeBr})_2\text{O}$ after eight weeks (figure 52).

The formation of Ph_2TeO in the reaction mixture is due to the presence of water in the system. A possible reaction is :

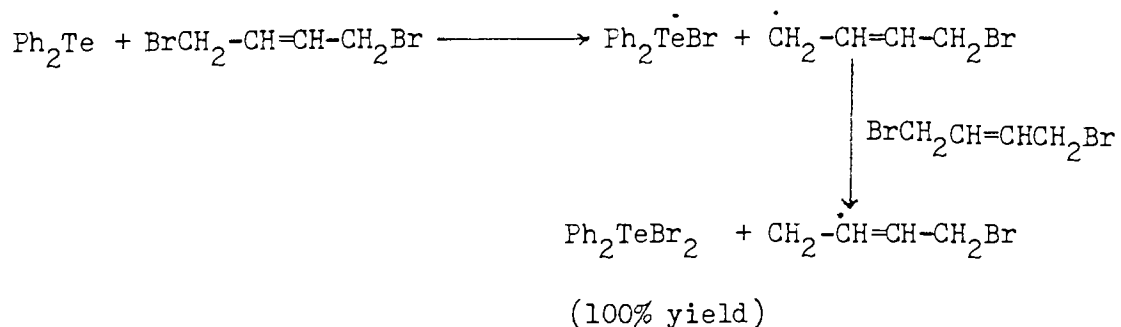


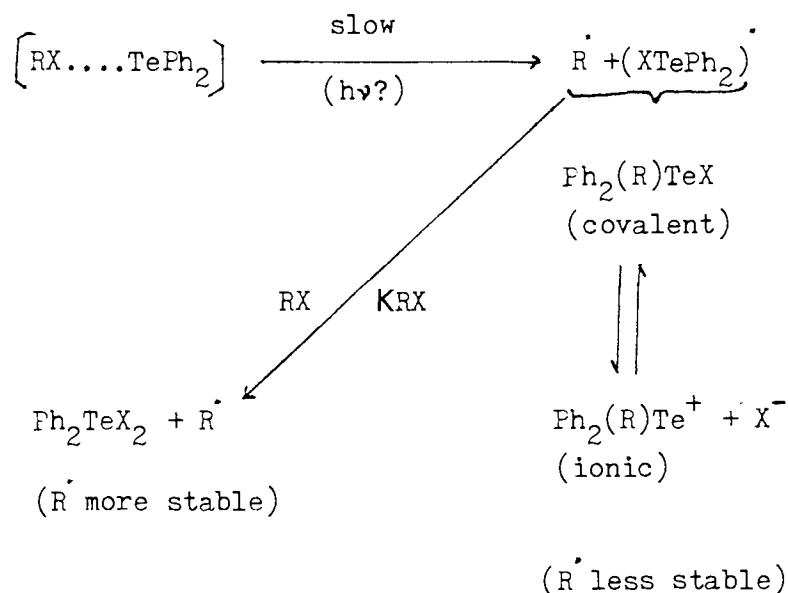


The butyl bromide can form two radicals, with the bromine radical reacting with diphenyltelluride. This radical then reacts with water producing an hydroxide, which then loses water to form the anhydride. The anhydride in the presence of extra water may hydrolyse to oxide.

The fact that only the tertiary butyl bromide forms the product (from the direct combination), suggests that a radical process occurs, as the tertiary butyl radical would be expected to be more stable than that of the primary butyl radical. So it could be expected that the tertiary butyl radical exists, and is long enough lived for a reaction to occur between diphenyltelluride, bromine radical and water.

Thus, the reaction of 1,4-dibromobut-2-ene with Ph_2Te , which produces an allylic radical, affords a 100% yield of Ph_2TeBr_2 .

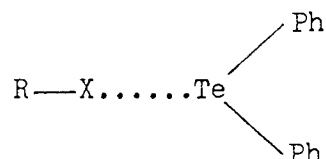




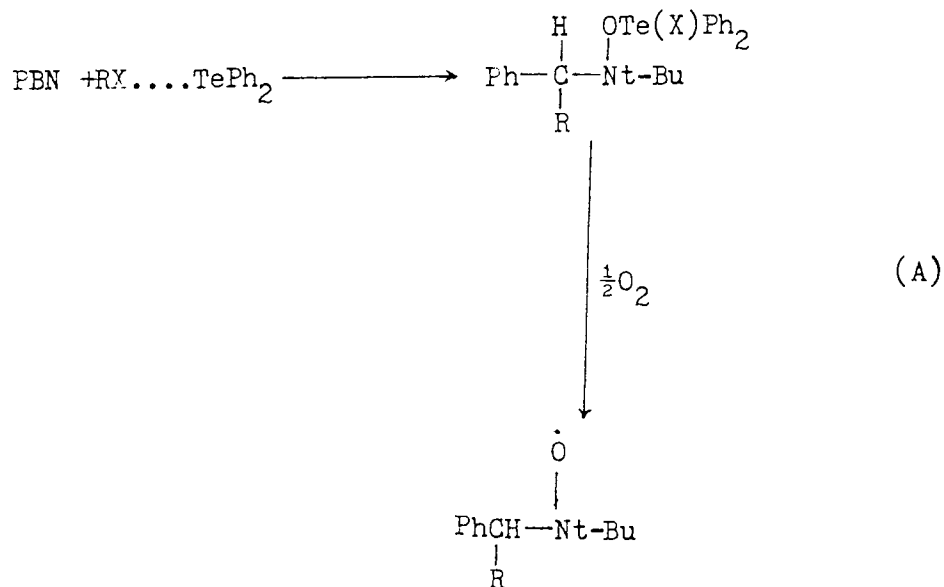
The initiation of the reaction is a matter of interest. Often preparation of Ph_2Te may be contaminated with Ph_2Te_2 and there is evidence that ditellurides may undergo an ethanol¹⁰⁹ catalysed photochemically initiated reaction with oxygen. No signal has been detected¹⁰⁸ when $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2$ and (PBN) in benzene was photolysed in the presence of *t*-butylbromide and air, but a free radical was detected by e.s.r after the addition of the ethanol and irradiation of the mixture by visible light. However, under our experimental conditions we were unable to trap radicals in benzene solutions of diphenylditelluride whether irradiated or not.

It may be, as Lappert proposes for oxidative addition of an alkyl or aryl halide (RX) to tin(II) compounds¹²⁹, that an interaction between RX and Ph_2Te gives a radical ion pair, $[\text{Ph}_2\text{Te}]^{\cdot+} [\text{RX}]^-$. We

are not attracted to this proposal which attributes reducing characteristics to Ph_2Te . We suggested that a charge transfer complex is initially formed:



Which is similar to some proposed in selenium chemistry. Since we have not excluded light from the reaction we would favour photochemical activation of the complex. The postulation of the complex also enables us to suggest an explanation for the observation that the concentration of PBN trapped radicals increases on the passage of oxygen. The addition of PBN to charge transfer to produce $\text{Ph}\overset{\text{O}}{\underset{\text{R}}{\text{C}}}-\text{Nt}-\text{Bu}$ now seems very plausible, we have reaction (A) :



4.5 CONCLUSION

From the spin trapping experiments it has been suggested that radicals are involved in both the oxidative addition and reductive elimination of alkyl halides and pseudohalides.

The experiments were carried out under strictly anaerobic conditions. The nature of the products depends on the stability of the organic radical (R).

The conductivity measurement of the reaction between methyl iodide and diphenyltelluride failed because the high viscosity of Ph_2Te made it impossible to make any definitive measurements.

The initiation of the reaction is suggested to be via a charge transfer complex. Therefore oxidative addition of methyl halides to Ph_2Te proceeds along a radical pathway via the initial formation of a charge transfer complex, and that the initial product of the oxidative addition is a covalent molecule from which, depending on the solvent, ionisation may occur.

An SN_2 mechanism is not favoured in this case. It may be that the mechanism proposed by Lappert¹²⁹ for his tin(II) systems is the one best able to account for the observations in this work.

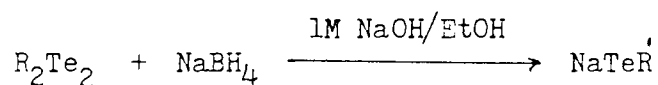
CHAPTER FIVE

SYNTHESIS OF ORGANOTELLURIUM COMPOUNDS

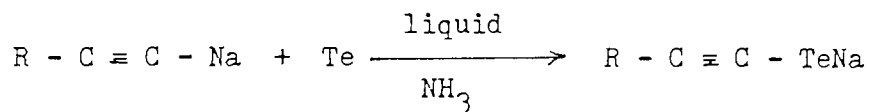
DERIVED FROM TERMINAL DIHALOALKANES

5.1 INTRODUCTION

A number of aromatic ditellurides have been reduced to aryl sodium telluride (NaTeR) by aqueous alkaline sodium borohydride in an ethanol/benzene solvent.

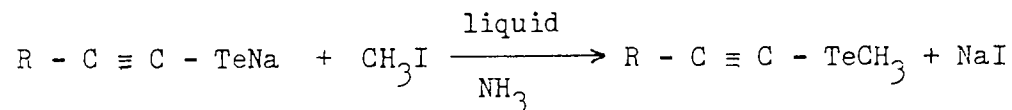


Acetylenic hydrocarbons with a hydrogen atom at one of the triply bonded carbon atoms form sodium acetylides upon treatment with sodium or sodium amide in liquid ammonia. The compounds $R - C \equiv C - Te - Na$ have been prepared by the addition of elemental tellurium to sodium acetylide in liquid ammonia. Tellurium inserts into the C-Na bond¹³⁰.



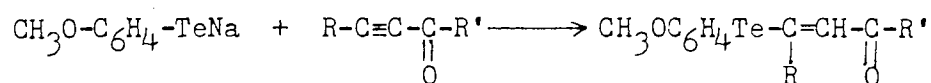
The alkyl sodium tellurides have never been isolated, but may be reacted with alkyl halides to give alkynyl alkyl tellurides e.g. alkylthioethynylmethyltellurides^{131,132} and ethynyl methyl telluride¹³³. These are isolable when methyl iodide is added to the

ethynyl sodium telluride in liquid ammonia.

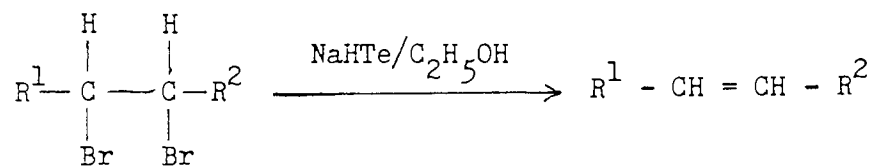


where : R = R₃S, C₃H₇S and H

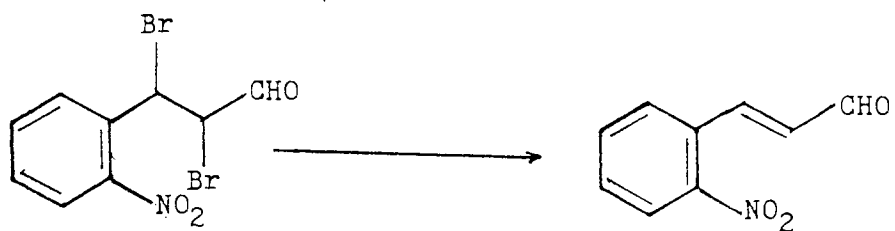
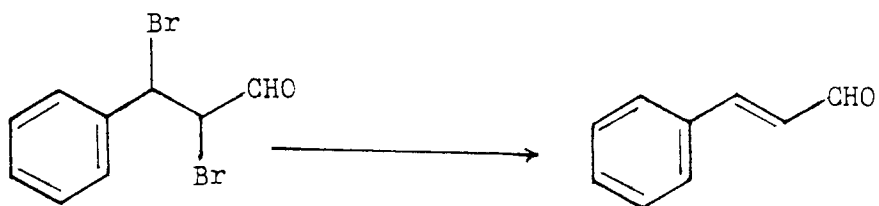
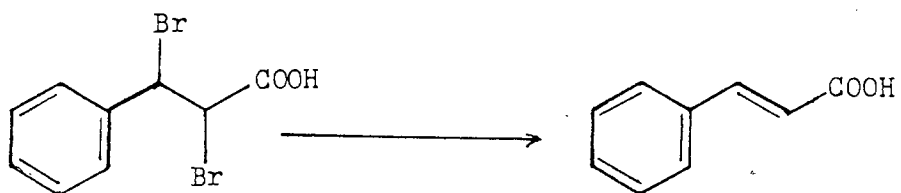
Sadekov¹³⁴ prepared diaryl tellurides, R-Te-R', (R, R' = C₆H₅, C₆H₅; C₆H₅, 4-CH₃C₆H₅; C₆H₅, 4-ClC₆H₅; 4-CH₃OC₆H₅, 4-CH₃C₆H₅) by reacting RTeNa with the appropriate diazonium tetrafluoroborates, R'⁺N₂BF₄⁻. It has been suggested¹³⁵ that the RTe⁻ anion adds across the triple bond of acetylene oxo compounds producing aryl-1-phenyl-3-oxo-1-alkenes.



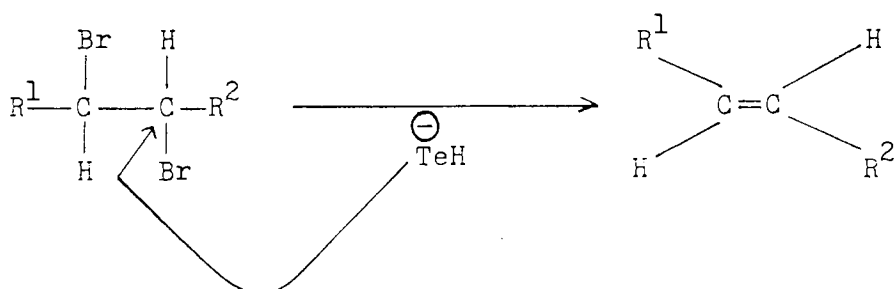
The debromination of vic-dibromoalkanes to alkenes effected by sodium hydrogen telluride (NaHTe) in ethanol solution in the presence of sodium borohydride has been reported by Ramasamy et.al¹³⁶.



The dibromides prepared from the trans-compounds gave the trans-alkenes as shown below :



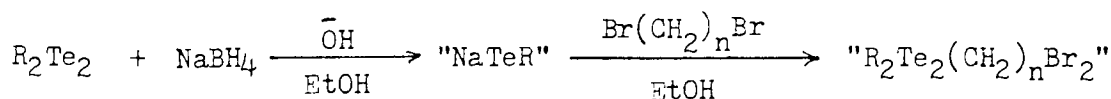
This leads to the assumption that the debromination occurs by an E-type β -elimination¹³⁷ as illustrated below.



Diorganylditellurides, R_2Te_2 often undergo tellurium-tellurium bond cleavage when reacted with transition metal compounds to afford materials in which RTe groups bridge metal centres, but a few elements have been reported to give simple complexes with diorganyl ditellurides e.g. $[(Ph_2Te_2)HgCl_2]$ and $[(p-MeO.C_6H_4)_2Te_2.HgI_2]$ ¹⁰².

Tellurol derivatives have been prepared from the reaction of triphenyltin hydride and the appropriate ditelluride⁸⁰. Treatment of a solution of copper(I) chloride in acetonitrile with an ethereal solution of Ph_3SnTeR affords a brown precipitate of $CuTeR$.

As mentioned previously Davies⁷⁴ suggested that the reaction between various diorganylditellurides and the compounds $Br(CH_2)_nBr$ ($n=1,3,4$) in the presence of an alkaline alcoholic solution of sodium borohydride forms a new class of organotellurium compounds.



These compounds have been assigned an empirical formula $(R\text{Te})_2(\text{CH}_2)_n\text{Br}_2$ on the basis of analytical data⁷⁴; conductivity measurements in acetonitrile were claimed to show a 1:2 species for the methylene compound, and a 1:1 species for the other compounds.

Mössbauer data have shown that the methylene compound is different from the others. The results obtained are more consistent with tellurium(II) species when compared with values obtained for other tellurium compounds. The other compounds were more similar to a telluronium species. Davies has concluded that the methylene species may be considered to be of the form shown in figure (30b) in chapter one i.e. more charge transfer, hence greater 'telluride' character leading to a larger splitting factor; and the others more of the form shown in figure (30a) in chapter one i.e. more of a 'telluronium' character, consistent with lower values of the splitting factor.

An attempt to produce $(R\text{Te})_2(\text{CH}_2)_n\text{Br}_2$ using the method described by Davies⁷⁴ together with other methods of preparation is described in this work. One method involved the use of phase-transfer catalysis.

5.2 EXPERIMENTAL

5.2.1 A Modification of the Method of Davies⁷⁴

R_2Te_2 (R=Ph and p-EtOPh) (1 mmol) was dissolved in ethanol (50 ml). An excess of sodium borohydride (10 mmol) in 2M sodium hydroxide solution (10 ml) was added to the above solution in a dropwise fashion. The reaction mixture was vigorously stirred for two hours, during which time the solution changed from red to colourless. At this point 1,4-dibromobutane $Br(CH_2)_4Br$ (1 mmol) was added. The resulting mixture was stirred for 24 hours at room temperature. On standing for a further two hours a fibrous white precipitate was obtained. This was filtered, washed with ethanol and ether and vacuum dried.

5.2.2 The Method of Mixed Organic Solvents

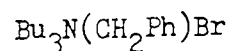
A solution of R_2Te_2 (R=Ph and p-EtOPh) (6.2 mmol) in 2.5 ml of benzene and 7.5 ml of ethanol was heated to reflux. To this solution sodium borohydride (10 mmol) in 8.5 ml of 1M sodium hydroxide was added in a dropwise fashion. The reaction mixture evolved hydrogen during the addition and became colourless at the end of the addition. At this point 1,4-dibromobutane $Br(CH_2)_4Br$ (1 mmol) in benzene (5 ml) was then added, and the warm mixture was stirred for 30 minutes. A fibrous white precipitate was obtained. This was filtered, washed with ether and vacuum dried.

5.2.3 In the Presence of Tetraphenylarsonium Chloride (Ph_4AsCl)

R_2Te_2 (1 mmol) (R=Ph and p-EtOPh) was dissolved in benzene

(50 ml). Sodium borohydride (10 mmol) in water (10 ml), 2M sodium hydroxide solution (10 ml) and tetraphenylarsonium chloride (1.5 mmol) in water (30 ml) was added to the above solution. The solution was vigorously stirred for two hours at room temperature, during which time the solution changed from red to colourless. At this point 1,4-dibromobutane $\text{Br}(\text{CH}_2)_4\text{Br}$ (1 mmol) was added to the mixture. The resulting mixture was stirred for five hours at room temperature a fibrous white precipitate was obtained. This was filtered, washed with ether and vacuum dried.

5.2.4 In the Presence of Benzyltri-n-butylammonium Bromide



R_2Te_2 (1 mmol) (R=Ph and p-EtOPh) was dissolved in benzene (50 ml). Sodium borohydride (10 mmol) in water (10 ml), 2 M sodium hydroxide solution (10 ml) and $\text{Bu}_3\text{N}(\text{CH}_2\text{Ph})\text{Br}$ (2 mmol) in water (30 ml) was added to the above solution. The solution was vigorously stirred for two hours at room temperature, during which time the solution changed from red to colourless. At this point 1,4-dibromobutane $\text{Br}(\text{CH}_2)_4\text{Br}$ (1 mmol) was added. The resulting mixture was stirred for four hours at room temperature. On standing for a further two hours a fibrous white precipitate was obtained. This was filtered, washed with ether and vacuum dried.

Note :

- (1) The compounds obtained using methods (5.2.1, 5.2.2, 5.2.3 and 5.2.4) were found to be identical.
- (2) The other derivatives were prepared separately by using,

in each case methods (5.2.1, 5.2.2, 5.2.3 and 5.2.4).

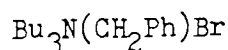
(3) The alkylhalides used were of the formula $X(\text{CH}_2)_nX$ where $n=1,2,3$ or 4 and $X=\text{Br}, \text{Cl}$ or I .

(4) When $n=2$ above, R_2Te_2 was isolated, and ethene was formed.

(5) The compounds (where $n=4$ and $X=\text{Cl}, \text{Br}$) were recrystallized from acetonitrile or nitromethane, as was necessary.

(6) Details of the compounds obtained are given in table (15).

5.2.5 Preparation of Benzyltri-n-butylammonium Bromide



Benzyl bromide (12 ml) was added to tri-n-butylamine (24 ml). The mixture was stirred at room temperature for two hours. A white solid which was benzyltri-n-butylammonium bromide (Q^+Br^-) was formed.

5.2.6 Preparation of Diarylditellurides

The diarylditellurides were prepared as mentioned previously (chapter three sections 3.2.1 and 3.2.2).

5.3 RESULTS

The analytical data for the compounds formed from the reaction between RTeNa and organic dihalides are given in table (14).

The molar conductivity of compounds $p\text{-EtOC}_6\text{H}_4\text{Te}(\text{CH}_2)_4\text{X}$ (where X=Cl, Br) in water is shown in table (15). Conductivities of various concentrations in water were also measured (figures 53 and 54).

The infrared spectra of $p\text{-EtOC}_6\text{H}_4\text{Te}(\text{CH}_2)_4\text{X}$ (where X=Cl, Br) in the range $4000\text{-}250\text{ cm}^{-1}$ as a KBr disc were recorded and presented in figures (55 and 56).

The Mössbauer parameters are given in table (16).

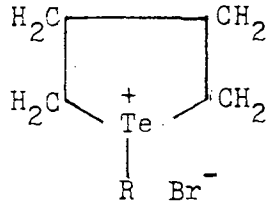
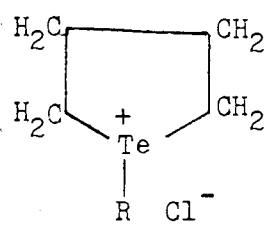
The mass spectra for the compounds are tabulated in tables (17-20).

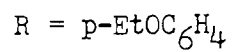
Table (14) Analytical data (along with melting points and colour for new organotellurium compounds)

Complex	Found%		Required%		°C m.p	Colour
	C	H	C	H		
$(p\text{-EtOC}_6\text{H}_4)_4\text{Te}(\text{CH}_2)_4\text{Br}$	37.2	4.40	37.4	4.40	258-260	white
$\text{PhTe}(\text{CH}_2)_4\text{Br}$	37.9	3.60	35.1	3.80	280	white
$(p\text{-EtOC}_6\text{H}_4)_4\text{Te}(\text{CH}_2)_4\text{Cl}$	41.9	5.10	42.3	4.90	228-230	white
$\text{PhTe}(\text{CH}_2)_4\text{Cl}$	39.9	4.10	40.4	4.37	240	white
$(p\text{-EtOC}_6\text{H}_4)_3\text{Te}(\text{CH}_2)_3\text{Br}$	36.0	3.80	35.5	4.00	260-262	pale yellow
$[(p\text{-EtOC}_6\text{H}_4)_4\text{Te}]_2\text{CH}_2 \cdot \text{CH}_2\text{Br}_2$ ⁽¹⁴¹⁾	30.0	3.11	31.5	3.21	152-154	cream
$[(p\text{-EtOC}_6\text{H}_4)_4\text{Te}]_2\text{CH}_2 \cdot \text{CH}_2\text{I}_2$ ⁽¹⁴¹⁾	27.2	2.90	27.8	2.80	118	deep yellow

Table (15) Conductivity measurements of cyclictelluronium
salt (1-telluracyclopentane derivative)

in water

Compounds	Solvent/Molar Conductivity (ohm ⁻¹ cm ² mol ⁻¹)
	176
	185



Solutions were 10⁻³M

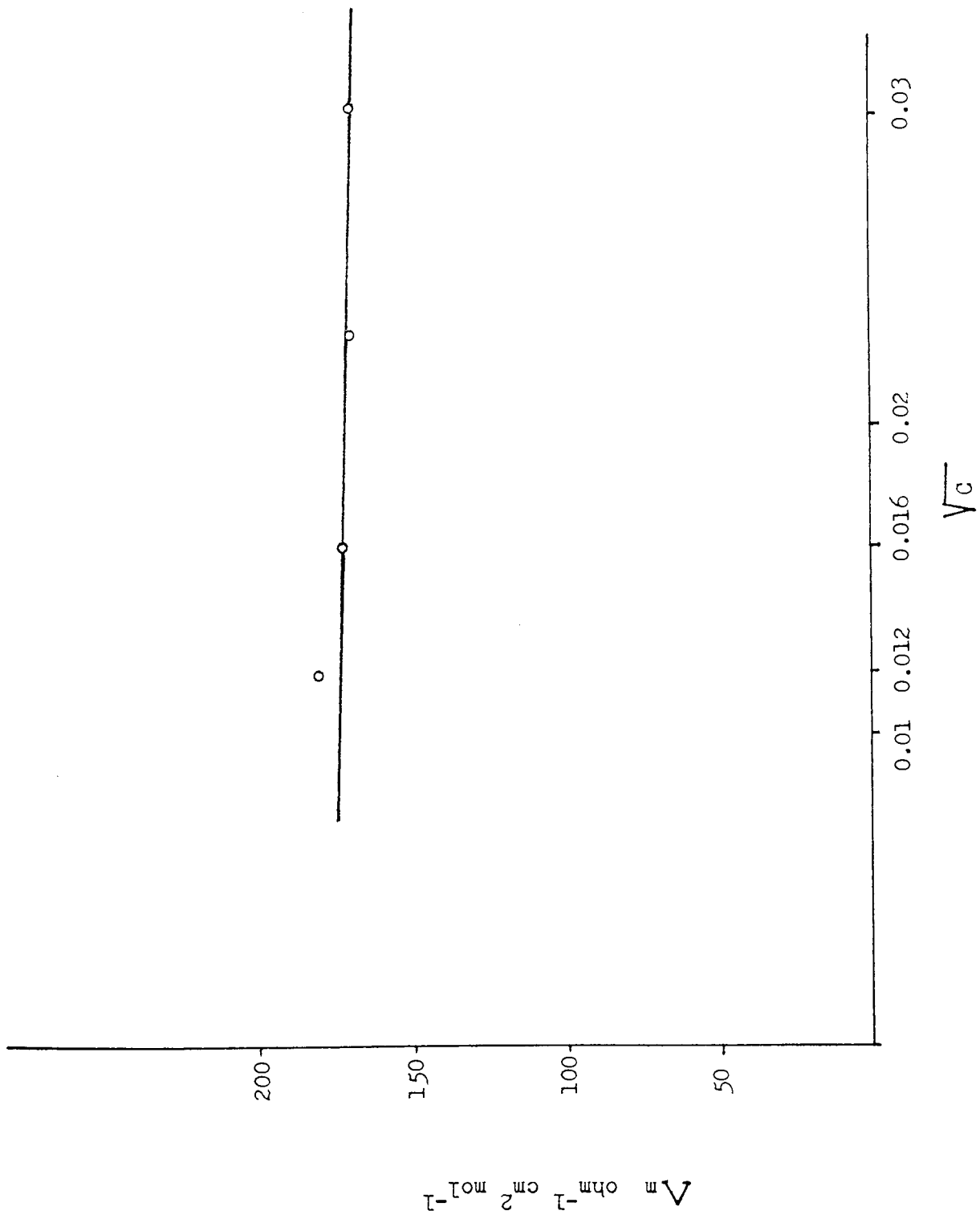


Figure (53) Conductivity of (p-EtOC₆H₄)Te(CH₂)₄Br in water.

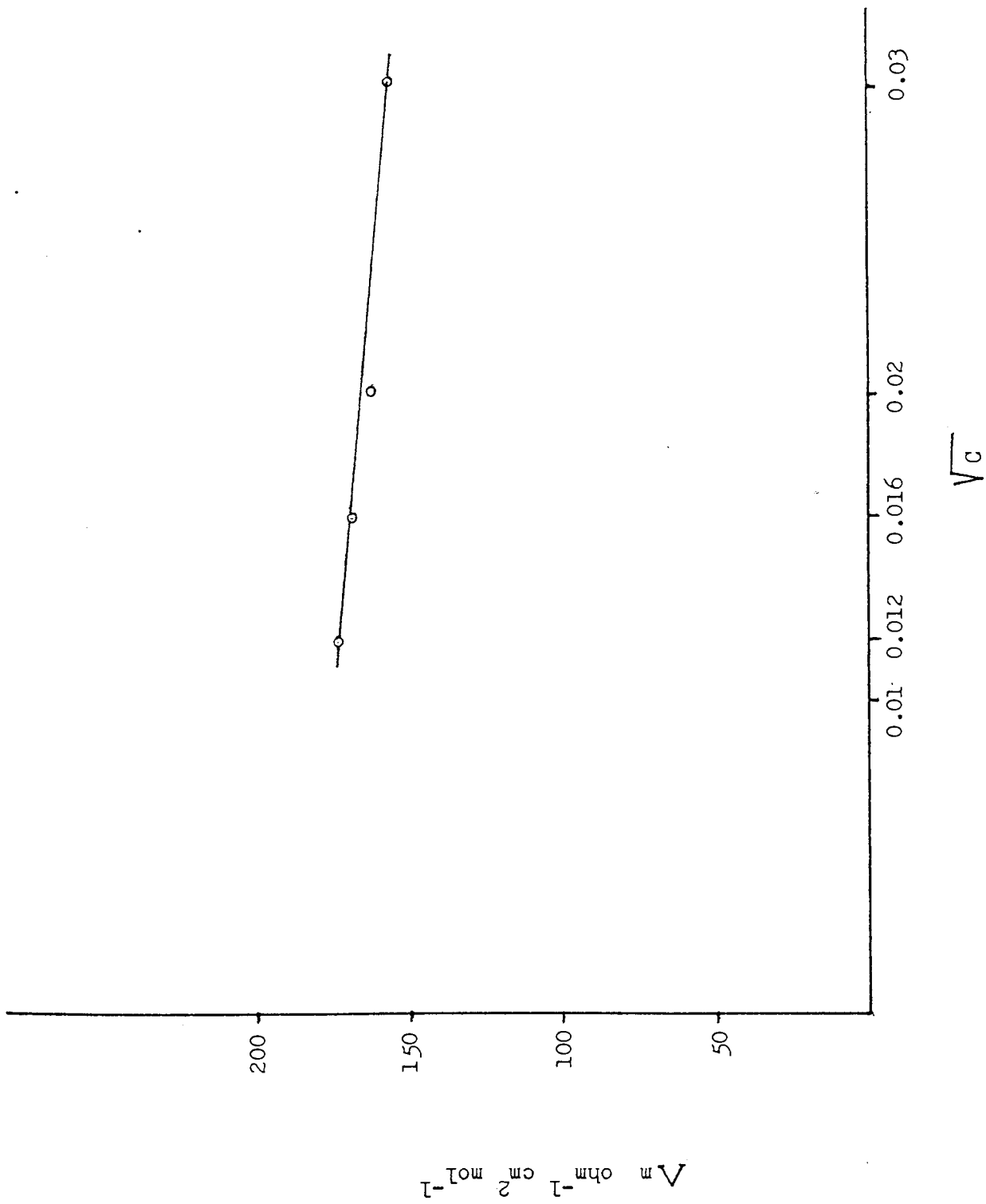


Figure (54) Conductivity of (p-EtOC₆H₄)Te(CH₂)₄Cl in water.

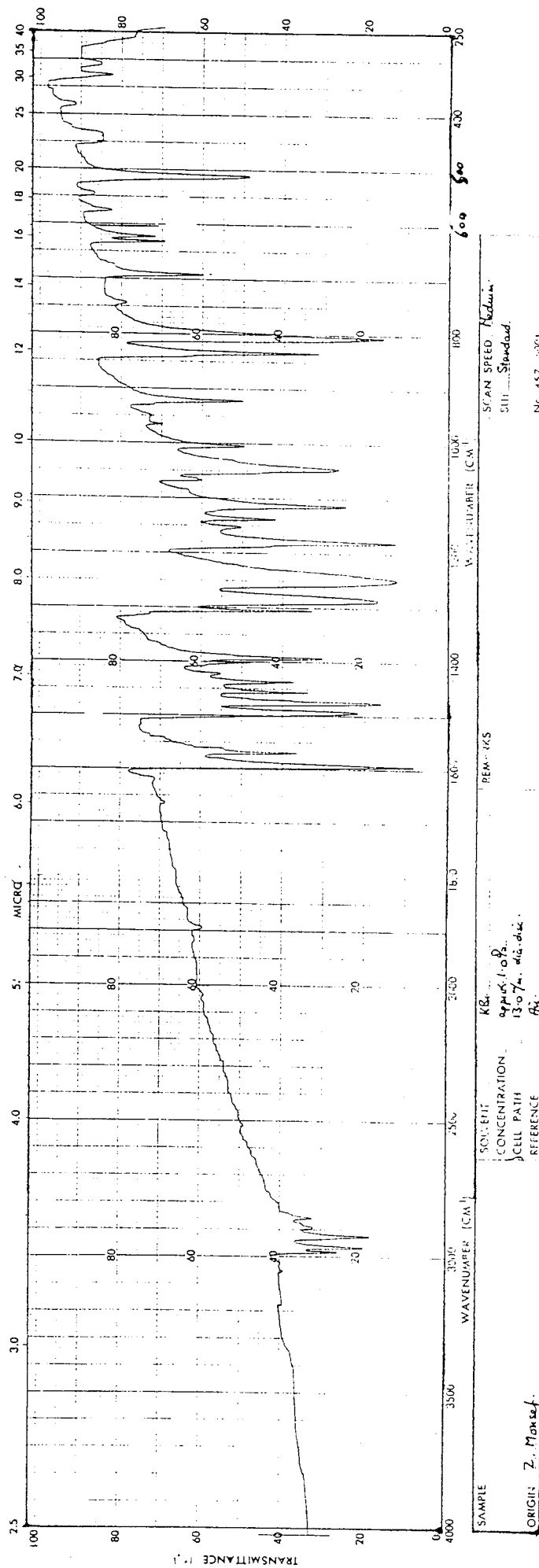


Figure (55) Infra-red spectrum of (p-EtOC₆H₄)Te(CH₂)₄Br

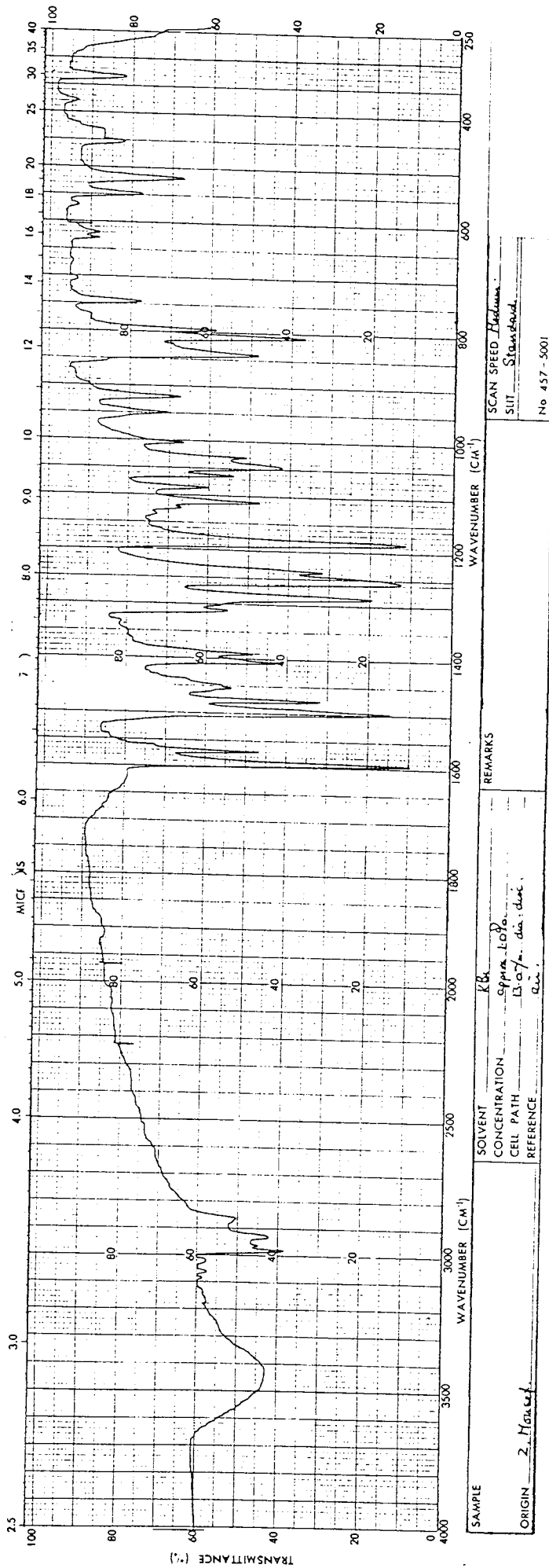


Figure (56) Infra-red spectrum of $(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)_4\text{Cl}$

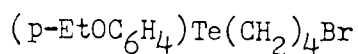
Table (16) ^{125}Te Mössbauer data for reaction products
of $\text{NaTe}(\text{C}_6\text{H}_4\text{OEt-p})$ with dibromo alkenes.

Compound	δ^a mm sec $^{-1}$	Δ^b mm sec $^{-1}$	$\Gamma_{\frac{1}{2}}$ mm sec $^{-1}$
$[(\text{p-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)\cdot\text{CH}_2\text{Br}_2$	0.53	7.58	6.33
$(\text{p-EtOC}_6\text{H}_4)\overline{\text{Te}}(\text{CH}_2)_3\cdot\text{Br}$	0.36	5.58	5.68
$(\text{p-EtOC}_6\text{H}_4)\overline{\text{Te}}(\text{CH}_2)_4\cdot\text{Br}$	0.38	5.50	5.43

a ± 0.08 mm sec $^{-1}$, vs. $^{125}\text{Sb}/\text{Cu}$

b ± 0.1 mm sec $^{-1}$.

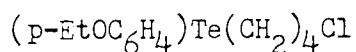
Table (17) Mass spectroscopic data for



m/e	Species	Relative Intensity
502	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{Te}^+$	weak
474	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{TeTeC}_6\text{H}_4\text{OH}^+$	weak
388	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)\text{Te}(\text{CH}_2)_4\text{Br}^+$	98
372	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{Te}^+$	35.7
307	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)\text{Te}(\text{CH}_2)_4^+$	99.0
251	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)\text{Te}^+$	95.4
242	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)_2^+$	98.0
223	$(\text{HOC}_6\text{H}_4)\text{Te}^+$	98.1
137	$(\text{CH}_2)_4\text{Br}^+$	99.0
186	$(\text{CH}_2)_4\text{Te}^+$	100
122	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_5^+$	99.0
78	C_6H_6^+	67.8
55	C_4H_7^+	73.3

(A Relative to ^1H ^{12}C ^{130}Te ^{81}Br ^{16}O)

Table (18) Mass spectroscopic data for



m/e	Species	Relative Intensity
446	$\text{Te}_2(\text{C}_6\text{H}_4\text{OH})_2$	41.2
372	$(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{Te}^+$	37.4
344	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}(\text{CH}_2)_4\text{Cl}^+$	weak
307	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}(\text{CH}_2)_4^+$	100
251	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{Te}^+$	100
223	$\text{Te}(\text{C}_6\text{H}_4\text{OH})^+$	100
186	$(\text{CH}_2)_4\text{Te}^+$	71.9
181	CH_2TeCl^+	100
122	$\text{C}_2\text{H}_5\text{OC}_6\text{H}_5^+$	98.1
92	OC_6H_5^+	99.0
93	$(\text{CH}_2)_4\text{Cl}^+$	100
78	C_6H_6^+	80.3
55	C_4H_7^+	100

(A Relative to ^1H ^{12}C ^{130}Te ^{37}Cl ^{16}O)

Table (19) Mass spectroscopic data for $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)\cdot\text{CH}_2\text{I}_2^{(14)}$

m/e	Species	Relative Intensity
516	$(p\text{-EtOC}_6\text{H}_4)\text{Te}_2(\text{CH}_2)^+$	30.5
502	$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}_2^+$	6.1
372	$(p\text{-EtOC}_6\text{H}_4)_2\text{Te}^+$	100
268	CH_2I_2^+	29.0
265	$(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)^+$	90.7
251	$(p\text{-EtOC}_6\text{H}_4)\text{Te}^+$	100
242	$(p\text{-EtOC}_6\text{H}_4)_2^+$	98.1
223	$(p\text{-HOC}_6\text{H}_4)\text{Te}^+$	100
93	OC_6H_5^+	100
78	C_6H_6	100
45	OC_2H_5	95.3

(A Relative to ^1H ^{12}C ^{130}Te ^{127}I ^{16}O)

Table (20) Mass spectroscopic data for $(\text{PhTe})_2(\text{CH}_2)\cdot\text{CH}_2\text{I}_2$

m/e	Species	Relative Intensity
428	$(\text{PhTe})_2(\text{CH}_2)^+$	22.4
414	Ph_2Te_2^+	weak
348	$\text{Ph}(\text{CH}_2)\text{TeI}^+$	51.0
284	Ph_2Te^+	100
268	CH_2I_2^+	100
221	PhTeCH_2^+	99.0
207	PhTe^+	100
154	Ph_2^+	95.3
141	CH_2I^+	99.0
77	Ph^+	100

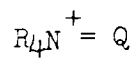
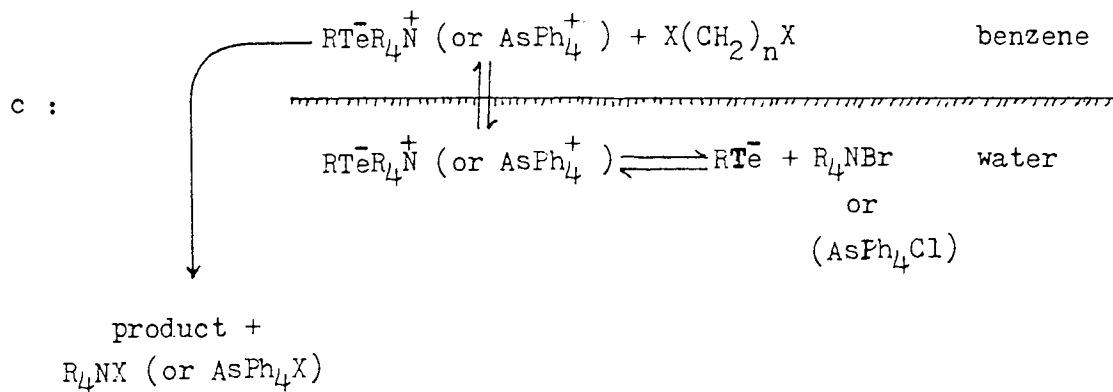
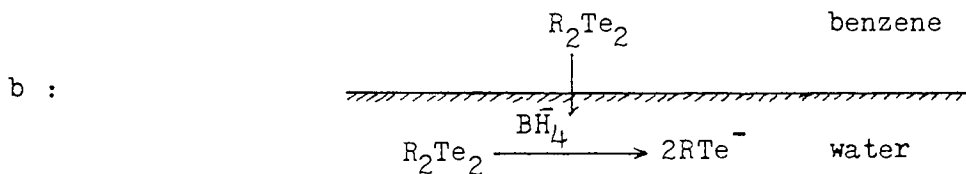
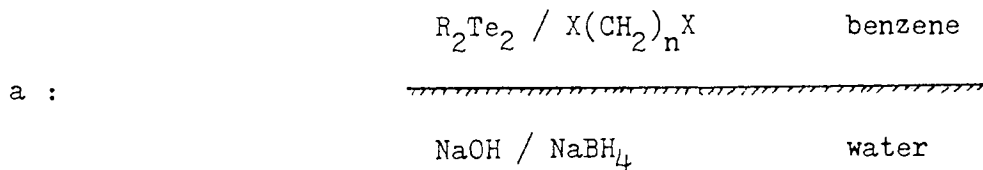
(A Relative to ^1H ^{12}C ^{130}Te ^{127}I ^{16}O)

5.4 DISCUSSION

It was proposed to synthesise a range of new organotellurium compounds, $R_2Te_2(CH_2)_nX_2$ (where $R=Ph$, $p-EtOC_6H_4$, $X=Cl, Br, I$ and $n=1, 3, 4$). Attempts were made to produce the above mentioned compounds by using the method described by Davies⁷⁴. However, analytical data of $R_2Te_2(CH_2)_nX_2$, which Davies claimed had been prepared, did not support this formulation.

In the present work conductivity measurements were performed at first, using acetonitrile, as Davies reported had been done. However because of the difficulty experienced with dissolving the compound in cold acetonitrile, conductivity measurements could not be performed. The solubility of the compound in hot acetonitrile was found to be high and this solvent was found to be suitable for recrystallization. Similarly, nitromethane was found to be a poor solvent for conductivity measurements, although suitable for recrystallization.

The above work was repeated with attempts to modify the preparation by adding either tetraphenylarsonium chloride (Ph_4AsCl) or benzyltri-n-butylammonium bromide $Bu_3N(CH_2Ph)Br$. There are two immiscible phases. One of these phases (aqueous) contains a reservoir of the salt expected to function as an ion. The second phase is organic and contains the substrate which is expected to react with the salt. A phase transfer catalyst is present in the mixture which contains a lipophilic cation. The lipophilic cation enjoys solubility in both aqueous and organic media. The process can be represented schematically as shown below :



Experiments were carried out by using a solution of diorgano-ditelluride R_2Te_2 (where $R=Ph$, $p-EtOC_6H_4$) in one portion of benzene and three portions of ethanol. The reaction between the above solution and aqueous alkaline sodium borohydride affords a solution with the chemical properties of $NaTeR$. Addition of $X(CH_2)_n$ (where $X=Cl, Br, I$ and $n=1, 3, 4$) to $NaTeR$ solution gave compounds similar to those obtained by using the other methods.

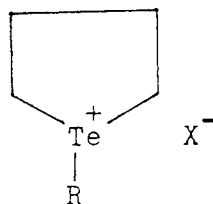
The compounds produced are white when $n=4$ and $X=Cl$ or Br , pale yellow when $n=3$ and $X=Br$, and cream when $n=1$ and $X=Br$, and deep yellow when $n=1$ and $X=I$. From the analytical data the empirical formula of $RTe(CH_2)_nX$ ($n=3, 4, X=Cl, Br$ and $R=Ph, p-EtOC_6H_4$) and $(RTe)_2CH_2 \cdot CH_2X_2$ (where $R=p-EtOC_6H_4, Ph$ and $X=Br$ or I) are obtained (analytical data are given in table 14). Conductivity measurements for compounds $RTe(CH_2)_nX$ (where $n=4$ and $X=Cl, Br$) were made in water. The results are presented in table (15). The values of the molar conductivity indicate that the compounds $RTe(CH_2)_nX$ (where $n=4$ and $X=Br$ and Cl) are 1:1 electrolytes in water. Conductivities are also measured as a function of concentration in water. Plots of molar conductance against $(concentration)^{\frac{1}{2}}$ are typical of strong electrolytes (figures 53 and 54). For all the compounds, bands seen in the infrared spectra can be assigned to the organic groups attached to tellurium in cyclic telluronium salts (figures 55 and 56).

One route by which these compounds are prepared involves the use of an alcoholic medium and therefore uptake of some oxygen containing species is plausible. However, inspection of the infrared spectra shows the complete absence of any $\bar{O}H$ or $Te-O$ absorptions. This, together with the fact that oxygen was not found in the physical

analysis, leads to the conclusion that the only groups present are those postulated above.

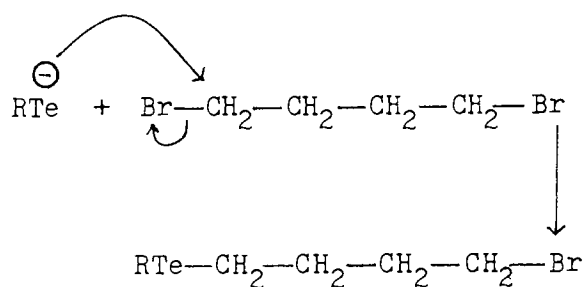
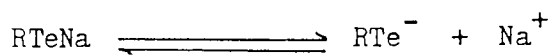
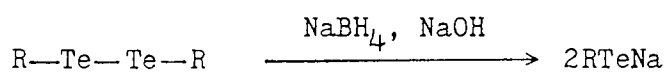
The use of conventional phase transfer catalysis was of no obvious advantage in reactions of 1,4-dichloro or 1,4-dibromobutane with sodium organotellurates (NaTeR). However, it has been shown that when the catalyst is supported on an expandable clay good yield of product may be obtained in a short time¹³⁹.

¹²⁵Te Mössbauer data for (p-EtOC₆H₄)Te(CH₂)₄Br are typical of a tellurium(IV) compound. The tellurium(IV) is supposed⁹⁵ to be present as a telluronium species which should lead to a small quadrupole splitting of the order of 5-6 mm s⁻¹. The tellurium(II) species however, has a much greater p orbital imbalance and splittings of the order of 10-12 mm s⁻¹ can be confidently predicted. The isomer shifts of tellurium(IV) species are more positive than those of the tellurium(II) compounds. For the compound (p-EtOC₆H₄)Te(CH₂)₄Br, the value of Δ is in the expected range for a telluronium salt (table 16). Therefore it must be concluded that the most acceptable formulation of the product is as a telluronium salt derived from 1-telluracyclopentane as illustrated below.

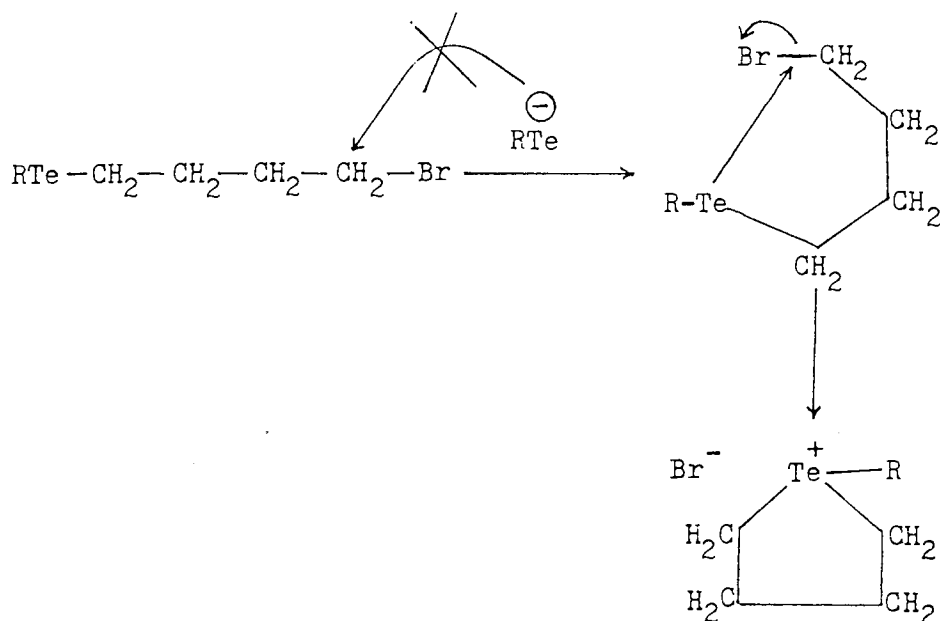


The possible mechanism for this reaction may be written as follows :

(i) nucleophilic substitution of one of the bromine atoms by RTe^- ,

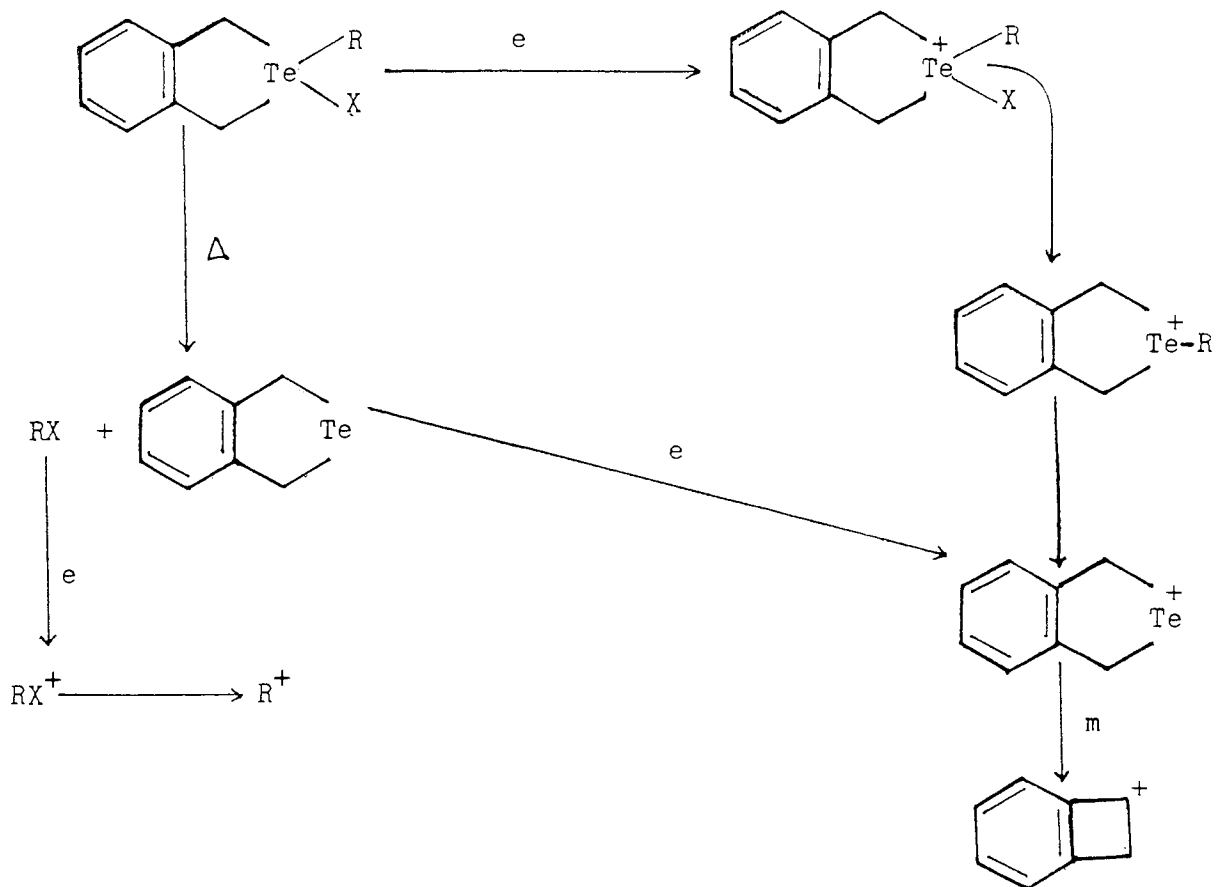


(ii) the rapid cyclisation to form the cyclic telluronium salt.



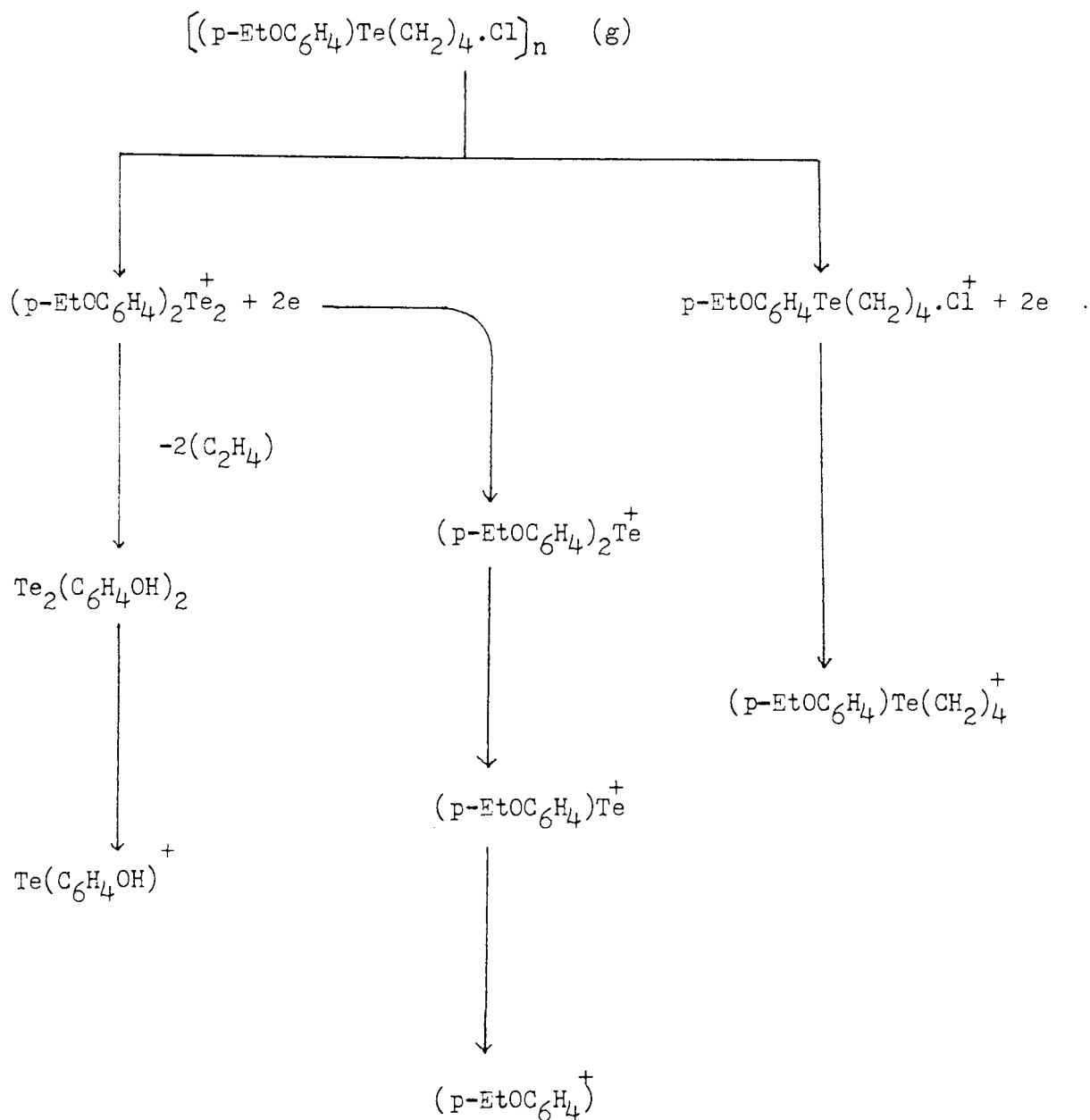
Step (ii) takes place immediately after step (i), and before a further attack at the second C-X bond by $R\text{Te}^-$. (It seems likely that the telluronium salt may function as a phase transfer catalyst once small quantities have been formed thus helping to explain why no advantage occurs from the use of either tetraphenylarsonium chloride or benzyltri-n-butylammonium bromide).

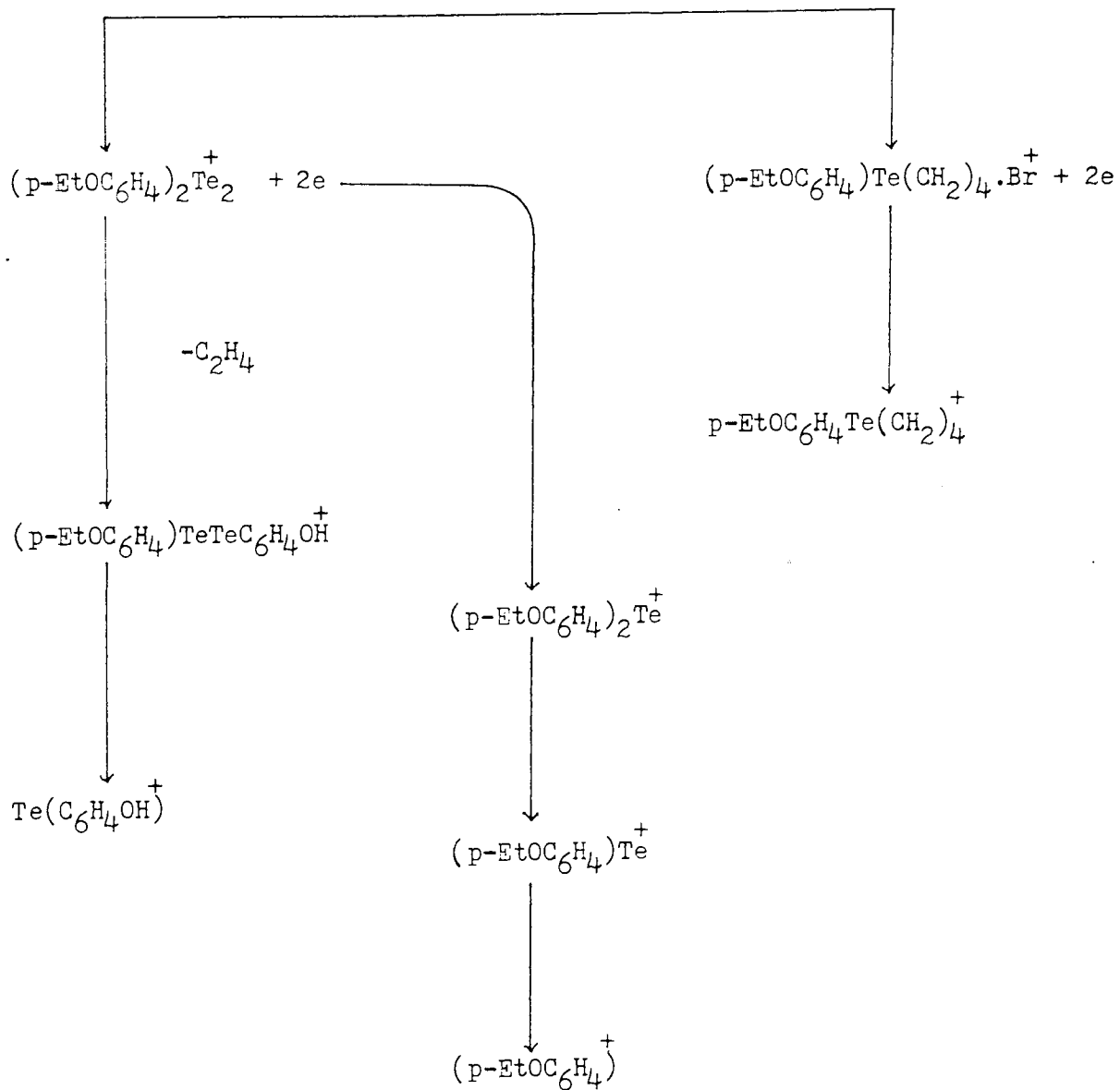
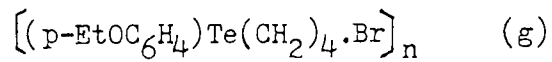
As mentioned previously (section 3.4.5) mass spectroscopy has been used for the characterisation of several telluronium salts. Mass spectroscopy studies of $\text{Ph}_2\text{MeTeX}^+$ ($X=\text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{NCS}$ and PhCOO) have shown the decomposition involving thermolysis of the telluronium salts to give diphenyltelluride and MeX . It has been shown¹⁰⁸ that the mass spectra of a range of salts based on 3,4-benzo-1-telluracyclopentane in general closely resemble those of diphenylmethyltelluronium salts. The fragmentation patterns are represented as follows :



It was shown¹⁰⁸ that the most important features of the mass spectra of cyclic telluronium salts are that there are also unexpected organo- and organotellurium ions which implies that there are several possible routes for the fragmentation of cyclic telluronium salts. The mass spectra of $C_8H_8RTe^+X^-$ (where R=allyl and phenacyl; X=Br) showed ions appearing at higher mass charge ratios than that corresponding to the monomer telluronium salt ion. Thus the spectra of these two cyclic telluronium salts clearly indicate that the telluronium salts are associated and the original molecule must be at least a dimer. From the molecular weight data, it has been shown that some cyclic telluronium salts exist as dimers in chloroform solution.

The mass spectra of $RTe(CH_2)_4X$ (X=Br, Cl) support the formulation of a 1-telluracyclopentane derivative (table 17, 18). The mass spectra of these cyclic telluronium salts, in general, closely resemble those of the above range of salts based on 3,4-benzo-1-telluracyclopentane. In principle, the fragmentations in the spectra of $RTe(CH_2)_4X$ should follow those expected of cyclic telluronium salts. The observation of fragments containing two tellurium atoms may reflect a degree of association in the solid state which is quite normal for this variety of compound. The broad features of the spectra may be represented by following schemes :



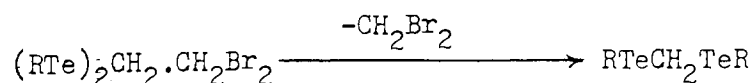


The above schemes are completely consistent with the proposed formulation of $\text{RTe}(\text{CH}_2)_4\text{X}$ as telluronium salts derived from 1-telluracyclopentane. When $\text{R} = \text{EtO.C}_6\text{H}_4^-$, it is quite normal for ethene to be lost in some fragmentation steps e.g.



Mössbauer data have shown that the product of the reaction of NaTeR with $\text{X}(\text{CH}_2)_n\text{X}$ (where $n=3$, $\text{R}=\text{p-EtOC}_6\text{H}_4$ and $\text{X}=\text{Br}$) is similar to a telluronium salt (table 16). It seems unlikely that it should be formulated as a derivative of 1-telluracyclobutane because of the instability of four membered rings. Thus a polymeric formulation appears more plausible, with the mass spectra of such compounds being very complex and having many fragments of significantly higher m/e than $(\text{RTe}(\text{CH}_2)_3\text{X})^+$.

The products of the reaction of NaTeR with dibromo- or diiodomethane (CH_2X_2) are different from the others. The analytical data gave an empirical formula of $[(\text{RTe})_2\text{CH}_2.\text{CH}_2\text{X}_2]$ ($\text{X}=\text{Br}, \text{I}$). The product from the reaction with CH_2Br_2 sometimes showed variable carbon figures but this correlates with partial loss of dibromomethane (CH_2Br_2 will be more volatile than CH_2I_2) as shown below.



It seems likely, therefore, that substitution of both halogen atoms proceeds but the products are isolated as pale yellow (CH_2Br_2) or deep yellow (CH_2I_2) solids containing one mole of dihalomethane. The mass spectra tables (19, 20) are in accord with this formulation.

From the Mössbauer data (table 16) it is seen that the methylene compounds (where $\text{R}=\text{p-EtOC}_6\text{H}_4$, $\text{X}=\text{Br}$, I) are different from the others. The results obtained are more consistent with a tellurium(II) species when compared with values obtained for other tellurium compounds⁹⁵. The chemical isomer shift is, within the errors, more positive than is δ for the other two compounds which implies a greater s electron density at tellurium in this compound. This may imply that some mechanism is operative which leads to withdrawal of $5p$ electron density thus deshielding the $5s$ pair. This hypothesis gains more positive support from the value of Δ which is significantly lower than that expected (10 mm sec^{-1}) for a telluronium salt. Thus the methylene species are considered to be of two possible formulations, illustrated in figures (57a and 57b).

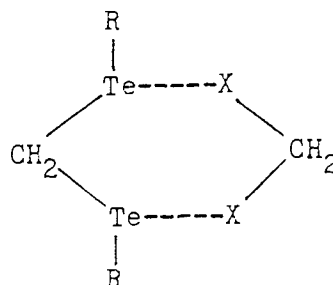


Figure (57a)

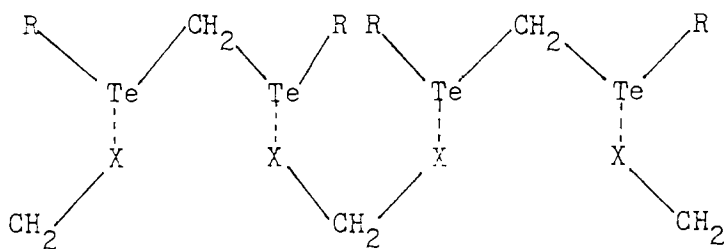


Figure (57b)

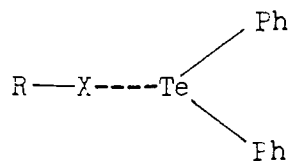
A charge transfer interaction between a bistelluride and the dihalomethane is proposed. If tellurium (as donor) loses spare-pair p-electron density to dihalomethane (acceptor), removal of such electron density will decrease the p-orbital imbalance (and hence Δ), also the s-electrons will be deshielded and δ should be more positive. The formulation therefore offers a self consistent interpretation of the Mössbauer data. Similar effects have been noted for organotellurium complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the implication is that charge transfer is considerable¹⁴⁰.

Work has also been done by using electron spin resonance spectroscopy¹⁴¹. A broad e.s.r signal was obtained from

(p-EtOC₆H₄)Te₂(CH₂).CH₂CH₂I₂ in the solid state centred on $g = 2.18$.

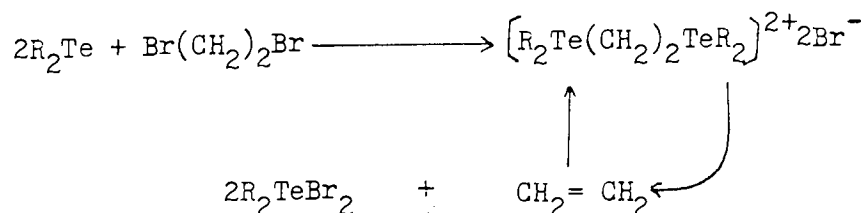
It was suggested in chapter four that a charge transfer

interaction may be the first step in the oxidative addition of methyl iodide to diphenyltelluride.

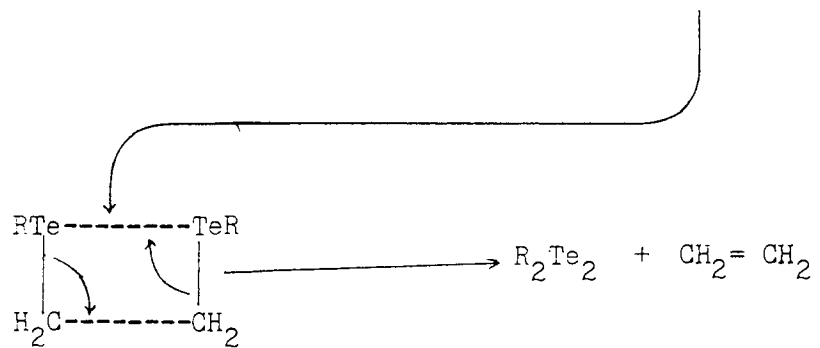
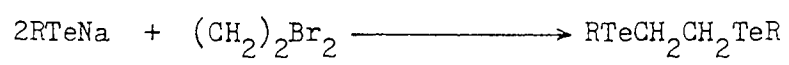


These data support that hypothesis.

It has been reported¹⁴² from the reaction between tellurides and vic-dibromides that telluronium species were formed. Upon reflux with the vic-dibromide, the products ethene and diorganyl tellurium dibromide were obtained.



Addition of these dibromides to the colourless solution of NaTeR produced effervescence and the formation of the ditelluride. The effervescence was due to the evolution of ethene. Thus it is possible that the nucleophilic substitution proceeds and that ditelluride then eliminates in a concerted process :



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