STUDIES IN ORGANOTELLURIUM CHEMISTRY

By

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Summary

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The initial work carried out in this study was an attempt to introduce bulky groups, namely trimethylsilylmethyl and diphenyl methyl, onto tellurium. The aim of this being to establish the validity of a theory developed by Hoffman showing that groups of high electronegativity, in an axial position, in a molecule of C_{2v} symmetry favour a smaller equatorial bond angle than do groups of low electronegativity. Therefore large equatorial bond angles should favour less electronegative groups, in this case organic groups. This would lead to tetraorganyl tellurium compounds prepared from compounds of the type R_2TeX_2 where R is a bulky group. The attempted synthesis of these R_2TeX_2 compounds failed under the experimental conditions used and a radical decomposition pathway is proposed based on product analysis from various reactions.

An attempt to utilize the oxidative addition of R_2TlX compounds in organotellurium synthesis produced new compounds when the former reacted with $Te(thiourea)_2Cl_2$ or elemental tellurium. The products of these reactions are formulated as $(PhTe)_2TlX$ and on the basis of IR and mass spectral evidence the chloride derivative is believed to be monomeric with three coordinate thallium, a Tl-Cl stretching vibration is assigned. The bromide is believed to be dimeric with bridging bromine atoms.

Tellurium tetrachloride will not directly o-metallate Schiff Bases but undergoes hydrolysis, under the conditions used, producing compounds of the type $(Schiff\ Base\ H)^+TeOCl_3^-$ and $(Schiff\ BaseH)^+$ $TeBr_6^{2-}$. N-(3 methoxybenzilidene)aniline was found to mercurate in the o-position but was only produced in low yields under the conditions used.

New compounds containing a Te-N have been made these being $(p\text{-}EtOC_6H_4)_2TeN(CO)_2(CH_2)_2X$, X = Br and Cl, and $Ph_2TeN(CO)_2(CH_2)_2Cl$ and an attempt made to identify a Te-N stretching vibration in the infra-red. N-Br and N-Cl vibrations have also been assigned in N-Bromosuccinimide and N-Chlorosuccinimide.

Key Words:
Organotellurium
Synthesis
Schiff Base
Succinimide

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TO THE MEMORY OF MY FATHER

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CHAPTER ONE

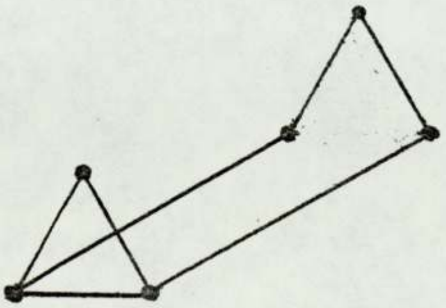
INTRODUCTION

Tellurium was discovered in 1782 by the Austrian Chemist F. J. Mueller von Reichenstein and named by Klaproth sixteen years later [1].

Tellurium is classified in group VIB of the Periodic Table and is located between selenium and polonium. It has the atomic number 52 and an atomic weight of 127.6. The outer shell of tellurium is $5s^2\ 5p^4$ and its inner shell (2.8.18.18) is completely filled. As a member of this group tellurium bears a resemblance to selenium and sulphur in many of its properties. However on descending the group the elements become more metallic in nature as seen by the fact that oxygen and sulphur are insulators, selenium and tellurium semiconductors and polonium a conductor.

The element can exist in a number of oxidation states the most common being II, IV and VI, examples of which are respectively $(thiourea)_2TeCl_2$, $TeCl_4$ and $Te(OH)_6$. By accepting two electrons the telluride ion, Te^{2-}, can be formed, for example dihydrogen telluride, H_2Te. Fractional oxidation states are also known. In 1798 it was reported[2] that elemental tellurium reacted with concentrated sulphuric acid to yield a red solution. Later Bjerrum and Smith [3] studied the reaction of $TeCl_4$ with tellurium in molten $AlCl_3$-NaCl and obtained a purple melt which they concluded contained Te_{2n}^{n+} (possibly Te_4^{2+}).

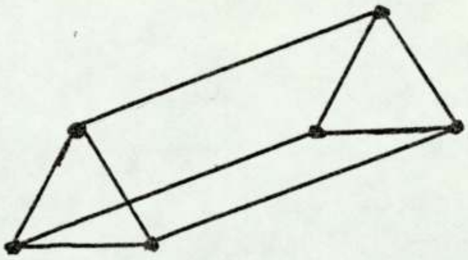
Tellurium also dissolves in fluorosulphuric acid to give a red solution with identical visible and ultra violet spectra as the product in sulphuric acid and molten $AlCl_3$-NaCl [4]. Conductiometric and cryroscopic measurements showed that tellurium was in the ½+ oxidation state and that the ion contains eight or less atoms. Ultra violet, visible and Raman spectra of the solids and their solutions were found to be similar to Se_4^{2+} strongly suggesting that Te_4^{2+} is square planar. This was confirmed by crystallographic studies of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ [5]. Jones [6] has carried out a Mössbauer study to investigate the bonding in Te_4^{2+}. A simple description of the bonding would suggest that each tellurium contributes one 5p electron to each σ bond in the (xy) plane and that each tellurium possesses on average 1.5 electrons in the $5p_z$ orbital directed out of the plane, the p_z orbital participating in π bonding around the ring. The grey solid, empirical formula Te_3AsF_6, has been prepared by Gillespie [7]. The compound is diamagnetic and is therefore probably $Te_6^{2+}(AsF_6^-)_2$. No X-ray data is available for the ion Te_6^{2+} but Jones [6] has postulated the structure as in I.



I

$Te_2Se_4^{2+}$ and $Te_3S_3^{2+}$ have been shown to have a six membered boat shape [8].

Tellurium can also show the oxidation state I, an example of this is provided by the oxidation of tellurium by $S_2O_6F_2$ in fluorosulphuric acid to give the yellow Te_n^{n+}. Solids of empirical formulae $TeSbF_6$, $TeSO_3F$ and $Te_2S_3O_{10}$ have been isolated [8]. The compounds and their concentrated solutions are diamagnetic which rules out Te^+, Te_3^{3+} etc. Cryosopic measurements on Te_n^{n+} in fluorosulphuric acid showed that the cation is not Te_2^{2+} but could not distinguish between Te_4^{4+} , Te_6^{6+} or Te_8^{8+}. Jones has postulated the structure as in II for the ion Te_6^{6+} from Mössbauer results [6].



II

Polyanions are also known for tellurium, for example, $(crypt\text{-}K^+)_2Te_3^{2-}$.en., [4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8.] hexacosane) potassium] tritelluride (2-)-ethylenediamine [9]. This deep red compound has been prepared by the reaction of a solution of K_2Te and the ligand in ethylenediamine with an excess of elemental tellurium. The ion Te_3^{2-} exhibits bond lengths of 2.692 Å and 2.720 Å and an angle of 113.1°.

The slight deviation of Te_3^{2-} from C_{2v} symmetry arises from hydrogen bonding to the ethylenediamine molecule, $d_{Te-N} = 3.46$ Å.

Since its discovery tellurium has found many uses, for example as an additive element it is used to improve the machinability of steel and copper, fuses for explosives, in the rubber industry as a vulcanizing agent, in ceramic and glass as a colouring agent. It has also been used as a catalyst in some chemical reactions e.g. Oxidation of propylene to acrylic acid over cobalt, molybdenum, tellurium and phosphorous oxide catalysts [10].

Recently several Japanese Patents have been published concerning the use of organotellurium compounds in photographic emulsions, for example reference 11 where a nitrogen containing vinyl species and an organotellurium compound are dispersed in a coating medium, which does not dissolve the vinyl or the tellurium compound, to give a photosensitive imaging mixture. This mixture was found to have good sensitivity and shelf life and forms visible images by a single exposure. In a typical experiment the following procedure was used. $(p\text{-}MeOC_6H_4)_2TeCl_2$, 0.1M, N-vinylcarbazoyl, 1M, a paraffin, MP 68-70°C, a second paraffin MP 46-48°C, 0.5grams, and hexamethylenetetramine, 5mg, were mixed in a toluene/chloroform mixture and coated on a polyester film to give a photosensitive film.

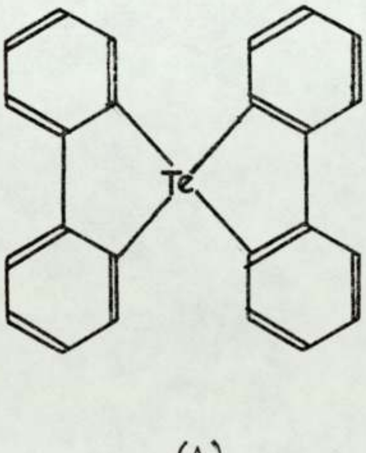
Although in animals tellurium compounds have proved lethal in high dosage and there is one account of fatal results in humans [12] from the accidental ingestion of sodium tellurite, the toxicity of tellurium in industry has not proved as high as that of selenium except for the garlic odour of the breath. It has given rise to a mild syndrome of gastric and nervous disorders and some cases of skin lesions but not the acute dermatitis or 'burns' caused by some selenium compounds [13].

The first organotellurium compound was prepared by Wohler [14] in 1840 and the work carried out from that time until 1971 has been reviewed by Irgolic [15]. Research during the period 1972-77 has also been reviewed by Irgolic.[16,17,18,19] Other reviews published in this field include those of Petragnani and de Moura Campos [20], and Petragnani [21]. "Tellurium" (C. W. Cooper 1971) [1] is a book dealing with all aspects of tellurium chemistry.

The main initial objective of this work was to prepare new tetraorganotellurium compounds and so a brief review of these will be given.

Tetraorganotellurium compounds seem to be the least studied aspect of organotellurium chemistry and only a few examples are known.

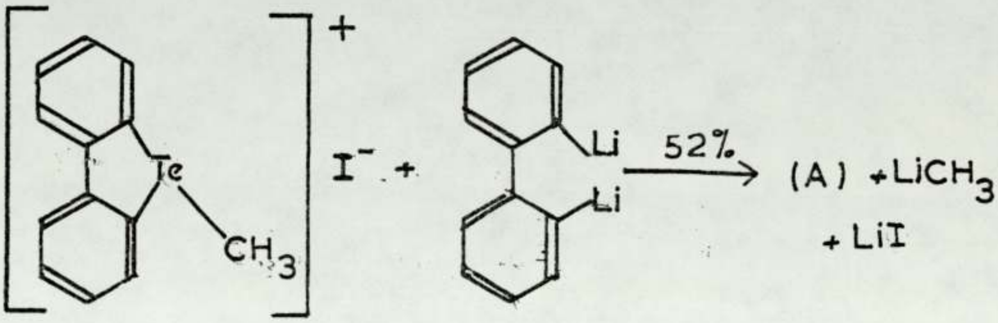
The first reported attempt to prepare a tetraorganotellurium compound was in 1888. Here Marquardt and Michaelis [22] obtained only triethyltelluronium chloride from the reaction between tellurium tetrachloride and diethyl zinc. Wittig and Fritz [23] succeeded in preparing tetraphenyl tellurium in 1952. The compound was synthesised from tellurium tetrachloride and excess phenyl lithium. It can also be prepared from the reaction of triphenyltelluronium chloride or diphenyl tellurium dichloride with excess phenyl lithium. Tetraphenyl tellurium is obtained as yellow crystals melting at 104-6°C with decomposition. The reactions were carried out in anhydrous ether under dry nitrogen. It is also reported that the phenyl lithium used in the reaction must be free of lithium halide. The pentacoordinate species, $[(C_6H_5)_5Te]^-Li^+$, is postulated as an intermediate to explain the fact that an excess of phenyl lithium above the stoichiometrically required amount is used. Hellwinkel and Fahrbach [24] isolated bis(2,2'-biphenylene) tellurium (A) in yields ranging from 40-55 per cent from the reaction of hexamethoxytellurium, tetramethoxytellurium or tellurium tetrachloride with 2,2' biphenylene dilithium.



(A)

This compound, yellow needles melting at 214°C, is more stable than tetraphenyl tellurium. The same authors report the preparation of (A) by the alternative routes (1-4) in later publications.[25,26]

1)



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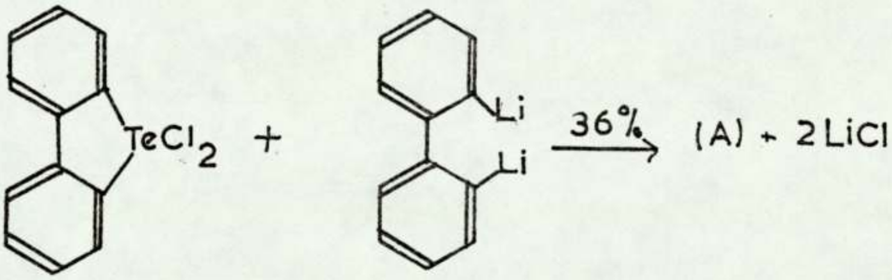

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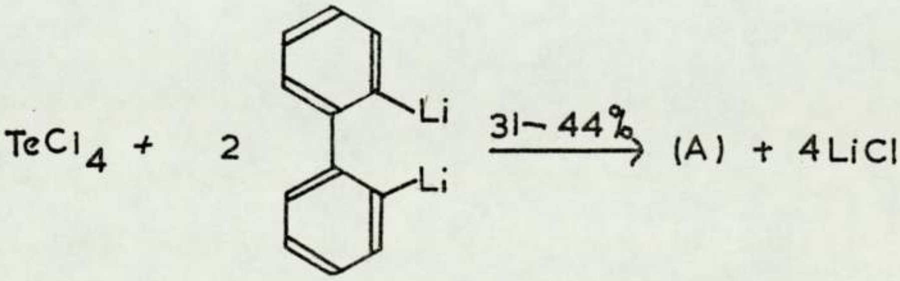

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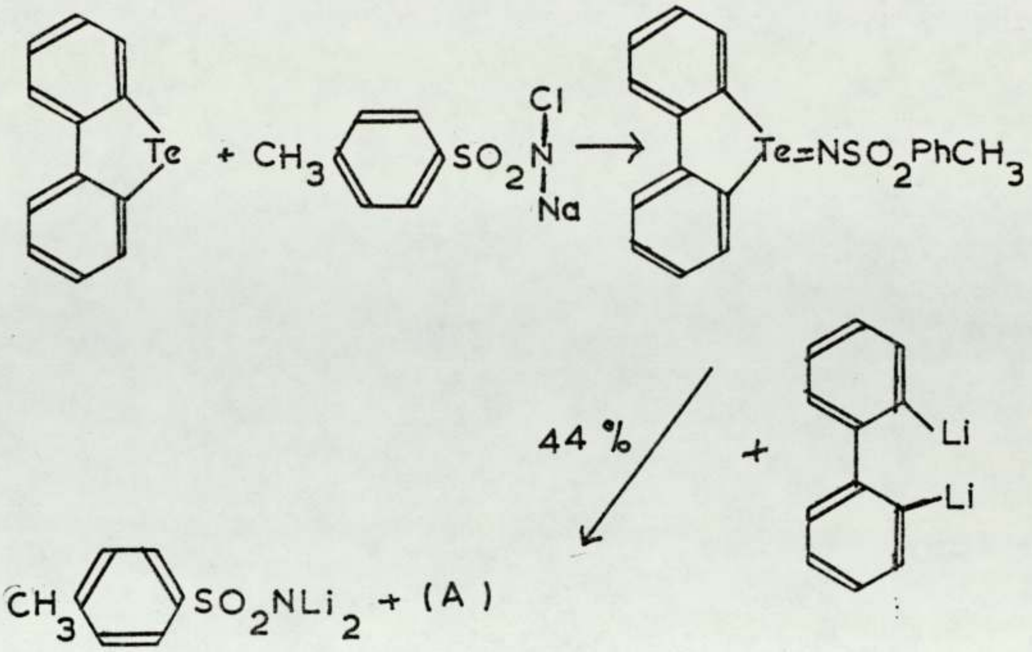
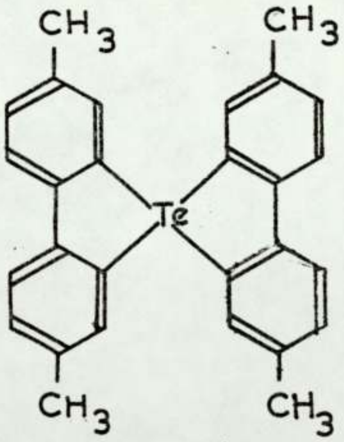


Bis (4,4' dimethyl-2,2' biphenylylene) tellurium, (B), was also prepared by method 2 in 48 per cent yield. This yellow compound decomposes between 204°C and 219°C [26].



(B)

Nefedov [27] and Wheeler [28] obtained ^{125m}Te-tetraphenyl tellurium by β decay of ^{125}Sb in $Sb(C_6H_5)_5$ and $(C_6H_5)_4SbCl$. Tetrakis (pentafluorophenyl)tellurium was the product of the reaction between tellurium tetrachloride and pentafluorophenyl lithium as reported by Cohen et al [29].

Tetraalkyl and dialkyl diaryl tellurium compounds have not yet been isolated. Hellwinkel and Fahrbach [25] have shown, however, that these substances exist in solution. The alkylation of tellurium tetrachloride (5) and trialkyltelluronium iodides (6) with alkyllithium reagents gave tetraalkyl tellurium compounds.

5) $TeCl_4 + 4RLi \longrightarrow R_4Te + 4LiCl$

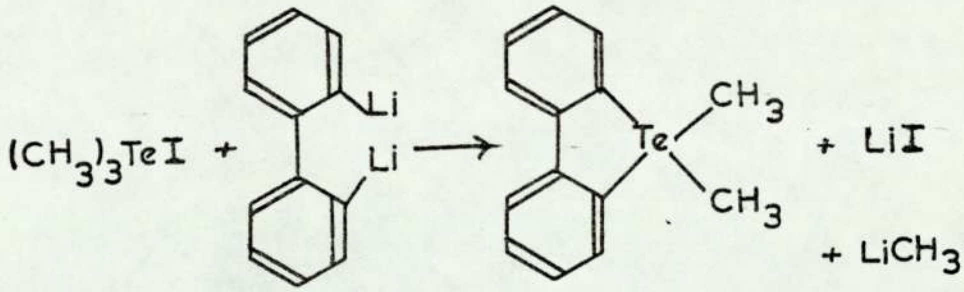
$R = C_4H_9, CH_3$

6) $R_3TeI + RLi \longrightarrow R_4Te + LiI$

$R = C_4H_9, CH_3$

Dimethyl 2,2'biphenylylene tellurium was produced from the reaction between trimethyl telluronium iodide and 2,2' dilithio biphenylylene.

7)



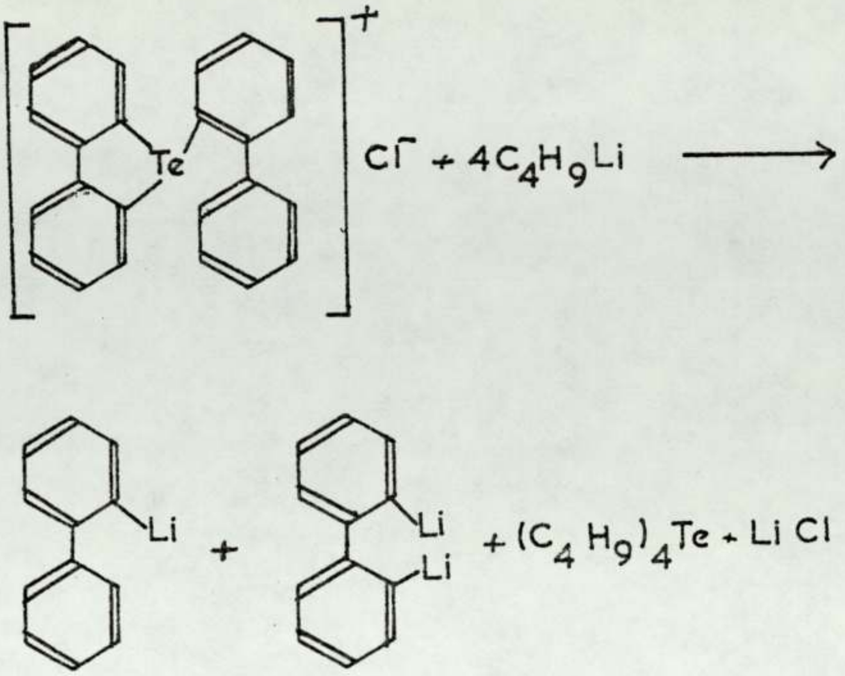
(C)

The formation of this compound requires an exchange of a methyl group which is removed as methyl lithium (7).

With the reaction between triphenyltelluronium bromide (8) or 2,2' biphenylylene 2, biphenyl tellurium chloride (9) and four moles of butyl lithium all the aromatic groups were cleaved from the tellurium as aryl lithium compounds producing tetrabutyl tellurium.

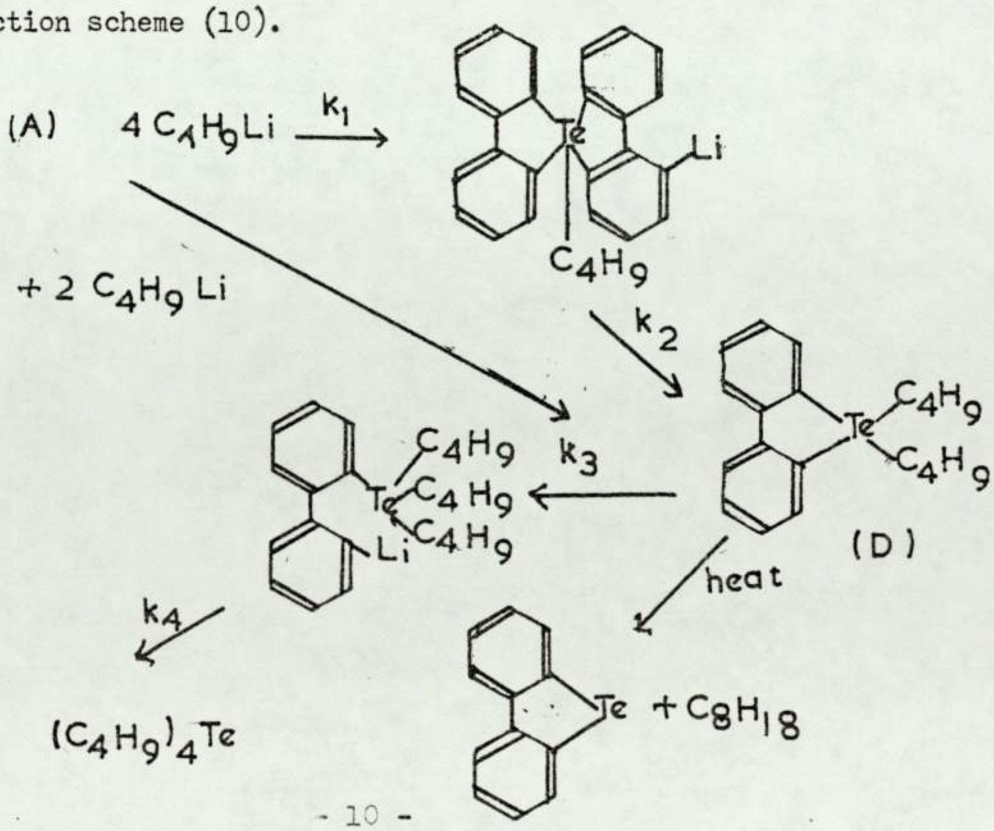
8) $(C_6H_5)_3TeBr + 4C_4H_9Li \longrightarrow (C_4H_9)_4Te + LiBr + 3C_6H_5Li$

9)



Bis(2,2' biphenylylene)tellurium (A) has also been used to prepare a solution of tetrabutyl tellurium by the following reaction scheme (10).

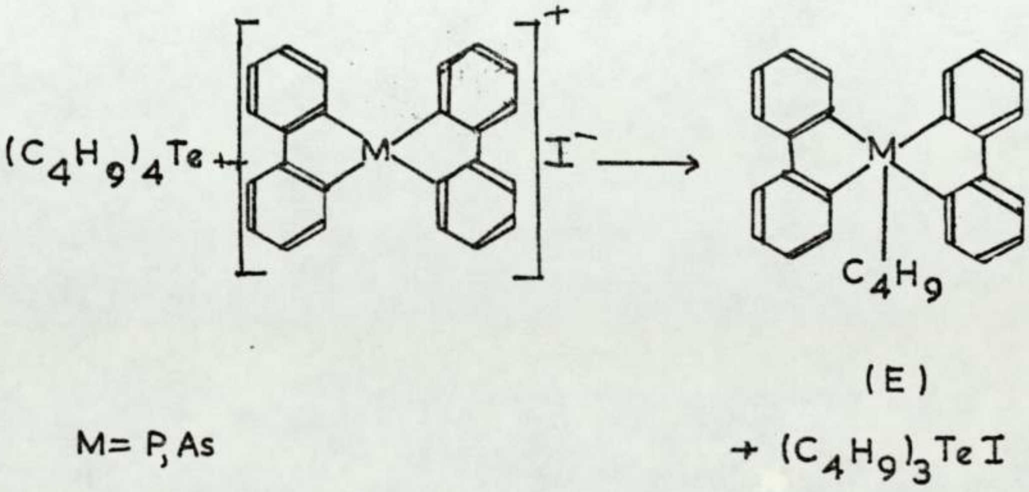
10)



It is suggested [25] that the rate constants for the four steps increase in the order $k_1 > k_3 > k_4 \approx k_2$. These exchange reactions can occur either by an S_{N2} mechanism or via a penta coordinated tellurium intermediate.

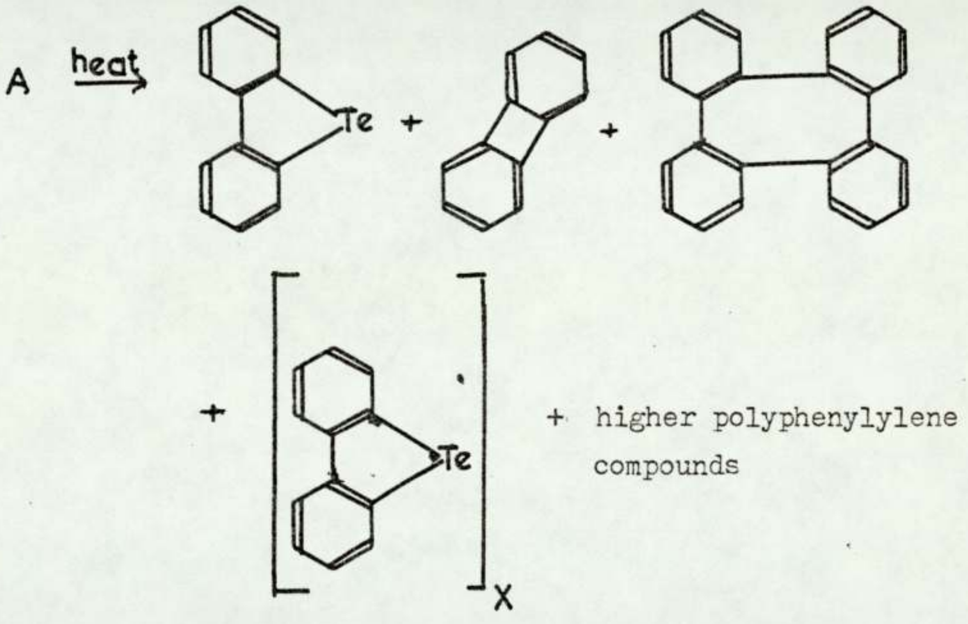
Although tetraalkyl tellurium compounds have not been isolated, the following reactions prove their existence in solution:Hydrolysis of solutions of tetraalkyl tellurium compounds gave trialkyltelluronium hydroxides. Upon distillation of the reaction mixture containing tetrabutyl tellurium decomposition to dialkyl telluride, butane and octane took place [25]. The mixed dialkyl diaryl tellurium compounds (C) and (D) lost the aliphatic group under these conditions and produced 2,2' biphenylylene telluride. The solution containing tetrabutyl tellurium was reacted with bis(2,2'-biphenylylene) arsonium and phosphonium iodide. The transfer of a butyl group from tellurium to either As or P with formation of (E) was taken as further evidence of the existance of tetrabutyl tellurium (11).

11)



The thermal stability of the tetraorganyl tellurium compounds increases in the series of alkyl, phenyl, 2,2'biphenylylene. The tetraalkyl derivatives decompose at room temperature while tetraphenyl tellurium is stable to approximately 115°C. Tetrakis(pentafluorophenyl)tellurium [28] produced the telluride and bis(pentafluorophenyl) when heated in a sealed tube at 200-220°C. Bis(2,2'biphenylylene)tellurium remains largely unchanged when heated to 210°C. At 260°C, in vacuum, decomposition takes place according to equation 12 [26].

12)



The corresponding 4-methylsubstituted derivative behaves similarly [26].

The mechanism of the thermal decomposition of tetraorganyltellurium compounds has been investigated by Barton [30]. Tetraphenyl tellurium decomposed at 140°C in vacuo in a sealed tube to $(C_6H_5)_2Te$, biphenyl and benzene. Similar decomposition experiments, under a nitrogen atmosphere, but at $80^{o}C$ in the presence of toluene, triethylsilane, furan or styrene gave similar results indicating little radical trapping. Only traces of polymer were found during the decomposition of tetraphenyl tellurium in styrene, when decomposition of dibenzoyl peroxide under similar conditions produced polystyrene in 77 per cent yield.

Tetrakis(4-methylphenyl)tellurium gave similar results.

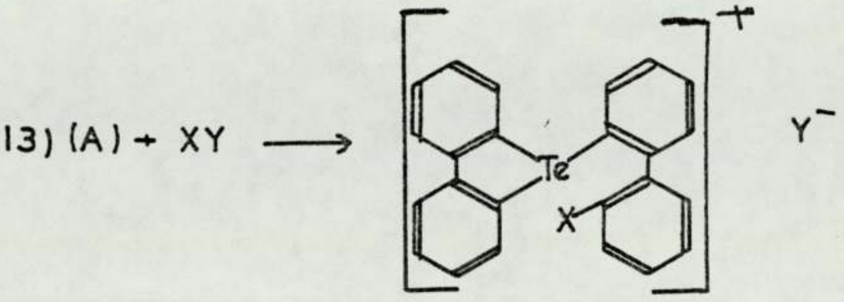
These results indicate that radicals, which can be trapped, are not found during the decomposition reaction. Decomposition of mixtures of $(C_6H_5)_4Te/(4\text{-}CH_3C_6H_4)_4Te$ and $(C_6H_5)_4Te/(C_6D_5)_4Te$ gave large quantities of mixed biaryls and unsymmetrical diorganyl tellurides.

Barton and his coworkers [30] concluded that " Tetraorganyltellurium compounds exchange ligands by a fast non-radical process prior to decomposition to diaryl telluride and biaryls. The decomposition process itself is concerted, does not involve radicals and represents an interesting procedure for the formation of C-C bonds".

It may be that a system such as $R_3Te^+ - R_5Te^-$ is important as is seen in the reaction of $B(Ph)_3$ with $TePh_4$ [25] (15).

Most of the chemical reactions of tetraorganyl tellurium compounds that have been studied involve the cleavage of at least one Te-C bond. The 2,2' biphenylylene derivatives seem to be more stable than tetraphenyl tellurium, e.g. tetraphenyltellurium is easily hydrolysed by water whereas bis(2,2' biphenylylene) tellurium (A) is relatively stable under these conditions [26].

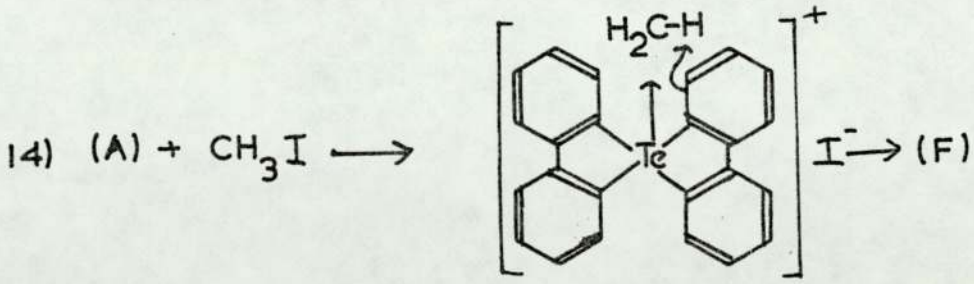
Hydrogen chloride in ethanol or bromine and iodine in carbon tetrachloride convert (A) into the corresponding telluronium compounds [26] (13).



(F)

X, Y = H, OH; H, Cl; Br, Br; I, I.

Compound (F), X = CH_3, Y = I, is also formed when (A) is treated with excess methyl iodide at room temperature. A pentavalent tellurium intermediate has been proposed [25] for this reaction as shown in equation 14.

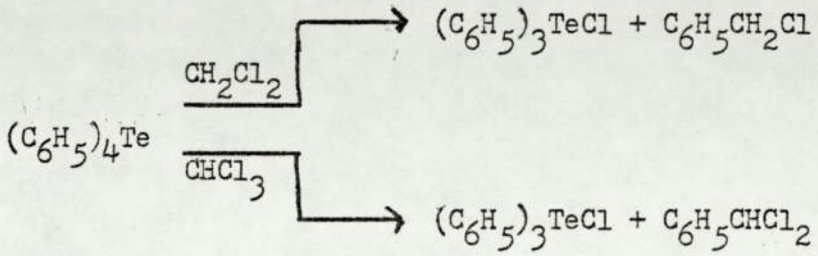


X = CH_3, Y = I

The ease with which one phenyl group is cleaved in tetraphenyl tellurium is demonstrated by the formation of triphenyltelluronium tetraphenyl borate from triphenyl boron and tetraphenyl tellurium in ethereal solution [25] (15).

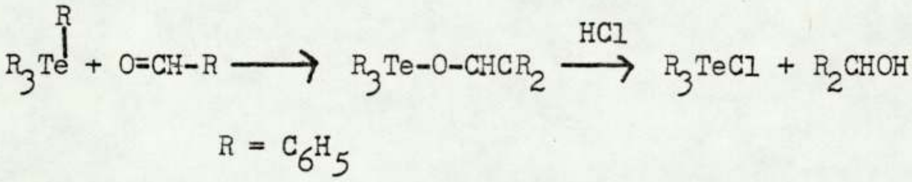
15) $B(C_6H_5)_3 + (C_6H_5)_4Te \longrightarrow (C_6H_5)_3Te^+B(C_6H_5)_4^-$

Tetraphenyl tellurium has a similar reactivity to other organometallic reagents in its reaction with methylene chloride, chloroform (16) and benzaldehyde (17).

16)


$$(C_6H_5)_4Te \xrightarrow{CH_2Cl_2} (C_6H_5)_3TeCl + C_6H_5CH_2Cl$$

$$(C_6H_5)_4Te \xrightarrow{CHCl_3} (C_6H_5)_3TeCl + C_6H_5CHCl_2$$

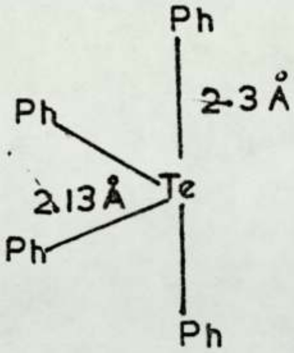
17)


$$R_3\overset{R}{Te} + O{=}CH{-}R \longrightarrow R_3Te{-}O{-}CHCR_2 \xrightarrow{HCl} R_3TeCl + R_2CHOH$$

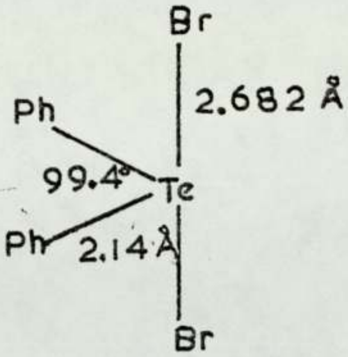
$$R = C_6H_5$$

Reaction (17) carried out in ether, under nitrogen, gave a 47.3 per cent yield of diphenyl methanol [23].

Very little structural data is available for tetraorganyltellurium compounds, the only example being the X-ray crystallographic study of $(C_6H_5)_4Te.C_6H_6$ [31]. Ziolo found a trigonalbipyramidal arrangement of the four phenyl groups as shown in III



III



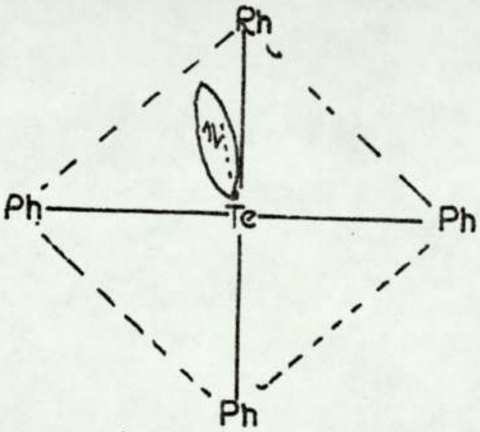
IV

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 diorganyl tellurium dihalides, for example $(C_6H_5)_2TeBr_2$ [32] (IV).

Work carried out by Hellwinkel has not shown conclusively that the compound bis(4,4' dimethyl 2,2' biphenylylene) tellurium (B) [26] is trigonal bipyramidal. If the lone pair is to occupy an equatorial position then the bidentate ligands 4,4' dimethyl 2,2'biphenylylene must each occupy one equatorial and one axial position. The ^{1}H NMR of compound (B) was studied [26] and showed only one peak due to the methyl hydrogen atom in the temperature range -55°C to room temperature. This result is inconsistent with the trigonal bipyramidal structure. The author postulates the rapid interconversion of the trigonal bipyramid to the other trigonal bipyramid as an explanation of the equivalence of the methyl groups. This situation is found in the species 2-biphenyl-bis(4,4' dimethyl 2,2' biphenylyl) antimony [33] where separate methyl resonances were observed when the temperature was reduced to -66°C.

An alternative structure proposed by Hellwinkel [26] was that of a tetrahedron with a stereochemically inactive lone pair.

In spite of the X-ray crystallographic structure of $(C_6H_5)_4Te.C_6H_6$ [31] which shows that the $(C_6H_5)_4Te$ unit is trigonal bipyramidal it may be that if the structure of $(C_6H_5)_4Te$ alone is determined a different structure may be found namely a square based pyramid with the lone pair in the apexial position (V).



V

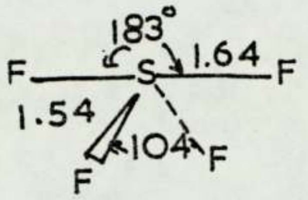
This phenomenon is known in organoantimony chemistry. Pentaorganoantimony compounds normally exist as a trigonal bipyramid, for example, pentamethylantimony is known to be trigonal bipyramidal from infra red spectroscopy [35]. However two examples are known for which the pentaorganoantimony species is square pyramidal, pentacyclopropylantimony was assigned a square pyramidal structure from its vibrational spectra [36]. Also pentaphenylantimony is known to be square pyramidal in the solid state from X-ray diffraction [37,38] and the same structure is maintained in CH_2Cl_2 and CH_2Br_2 solution from vibrational spectra [40] and NMR [39], however it is reported [35] that the pentaphenylantimony molecule in the crystal $(C_6H_5)_5Sb. \frac{1}{2} C_6H_{12}$ has a trigonal bipyramidal strcture with virtually no distortion.

It is obvious that a lot more work needs to be carried out concerning the structure of tetraorganyltellurium compounds and it was one of the aims of this project to undertake some of this work.

The only other physical data available for tetraphenyl tellurium is a list of absorption frequencies in the infra red from 4000 cm^{-1} to 400 cm^{-1} by Fritz [41]. No assignments were attempted.

Due to the relative instabilty of tetraorganyltellurium compounds a method was sought which would enable one to prepare more stable compounds. Hoffman [42] has made a theoretical study of sulphuranes concerned with bonding, substitutional site preferences and geometrical distortion and it was thought that his conclusions would be applicable to tellurium compounds. A brief review of this paper will be appropriate at this stage.

The prototype SR_4, sulphurane, structure was that of SF_4. As shown in VI, the molecule has C_{2v} symmetry.



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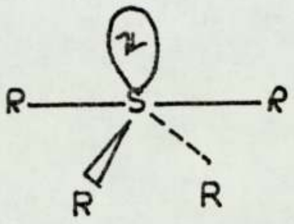
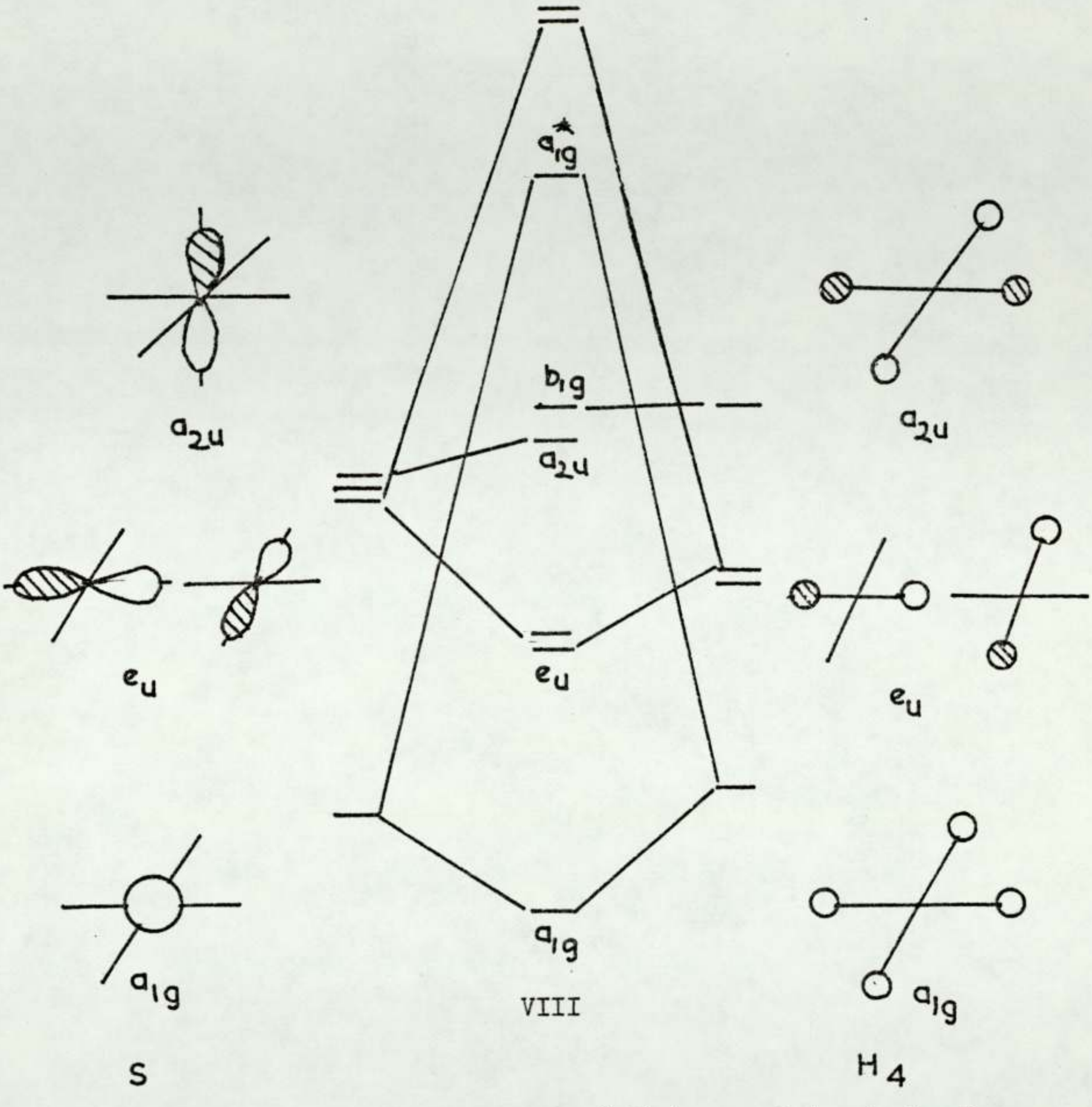


VII

Other SR_4 and related Se and Te compounds show similar geometrical features, e.g. $Cl_2S(C_6H_4Cl)_2$ [43a], $Br_2Se(C_6H_5)_2$ [43b], $Br_2Te(C_6H_5)_2$[32]. The sulphurane structures are best described as close to a trigonal bipyramidal geometry with an equatorial lone pair and distinguishable axial and equatorial sites.

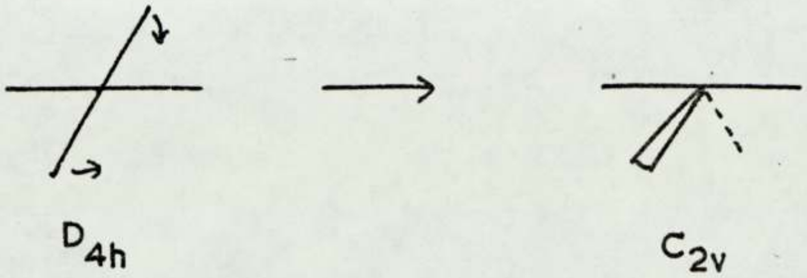
It has been pointed out by Muertterties and Schunn [44] that electronegative substituents prefer the axial sites and that these axial bonds are weak. Evidence for bond weakening comes from the solid state bond lengths, which can exceed the sum of the covalent radii by as much as 0.25 Å.

Hoffman considers the effects on the molecular orbitals of SH_4 when the molecule is distorted from D_{4h} symmetry to C_{2v}. (VIII) shows how the orbitals of a square planar (D_{4h}) SH_4 are formed from the 3s and 3p orbitals of S and the symmetry-adapted H 1s combination. In SH_4 all orbitals through the b_{1g} are occupied by the ten valence electrons. There is some uncertainty about the ordering of the two higher occupied orbitals, a_{2u} and b_{1g}. The former is entirely on the central atom, the latter entirely on the ligands. The ordering of the two M.O.s could depend on the nature of the R groups in SR_4.

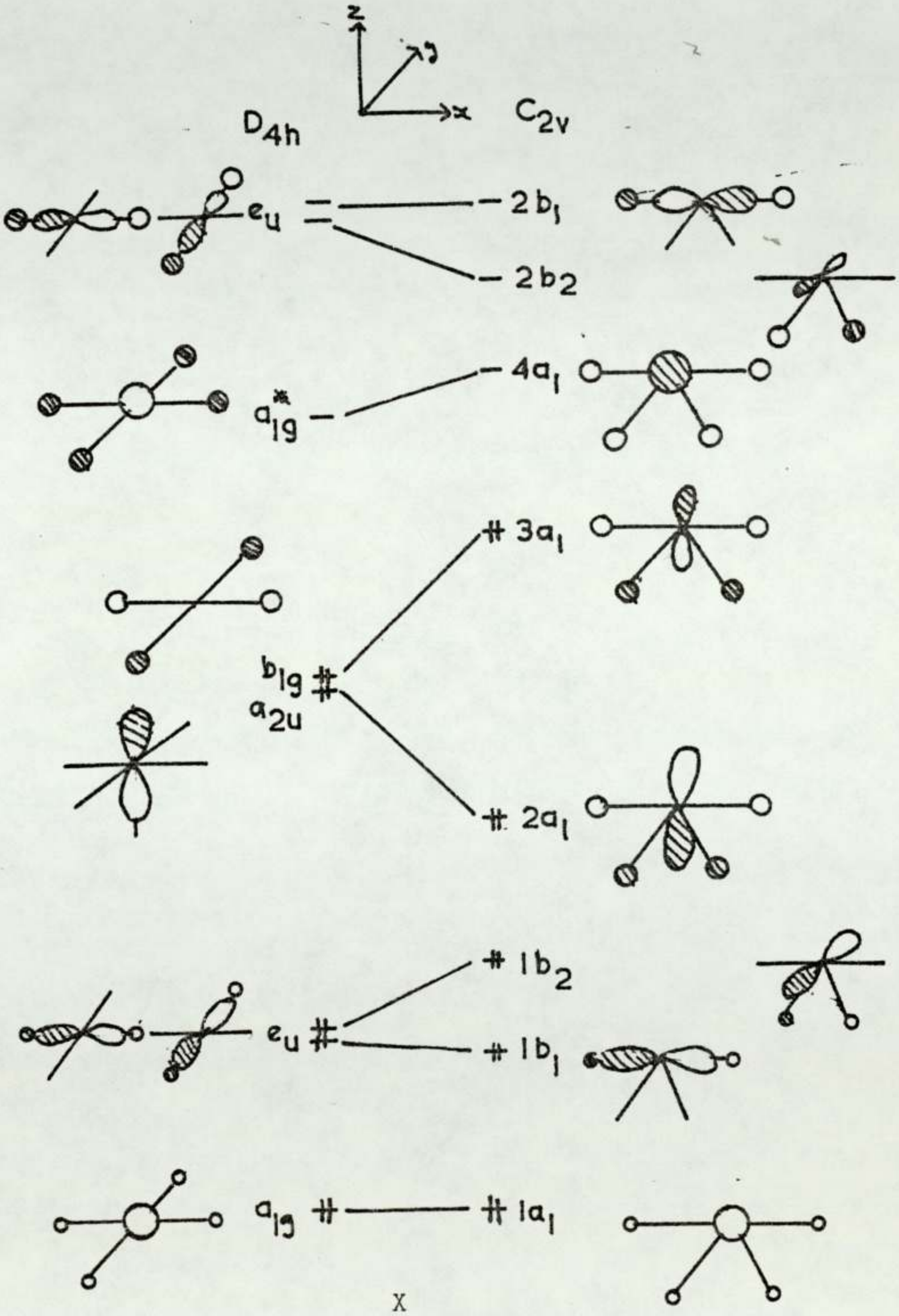


VIII

If the distortion indicated in (IX) is carried out, bending two trans hydrogens down until they make an angle of 120° the resultant energy changes are shown in (X).


D4h
C2v

IX


z
y
x
D4h
C2v
eu
2b1
2b2
a1g*
4a1
3a1
b1g
a2u
2a1
1b2
eu
1b1
a1g
1a1

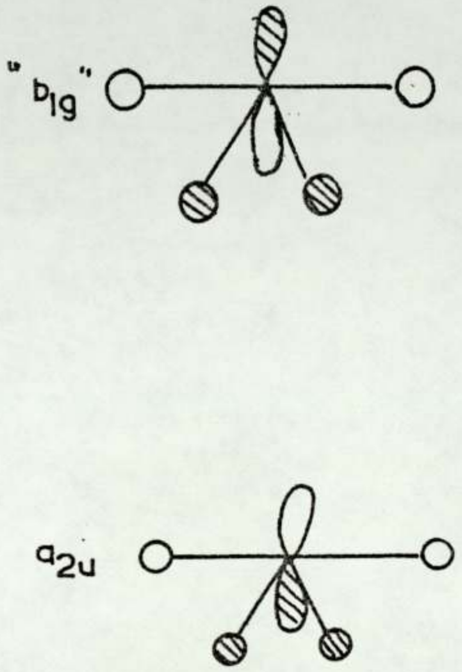
X

The effect on the bonding is as follows. One member of the e_u set, the one along the axial direction, is unaffected by the distortion. The other e_u component, the one in the equatorial plane, loses bonding overlap between S 3p and H 1s and turns on an antibonding interaction between the equatorial hydrogens. For both these reasons that e_u component, b_2 in C_{2v}, is destabalized.

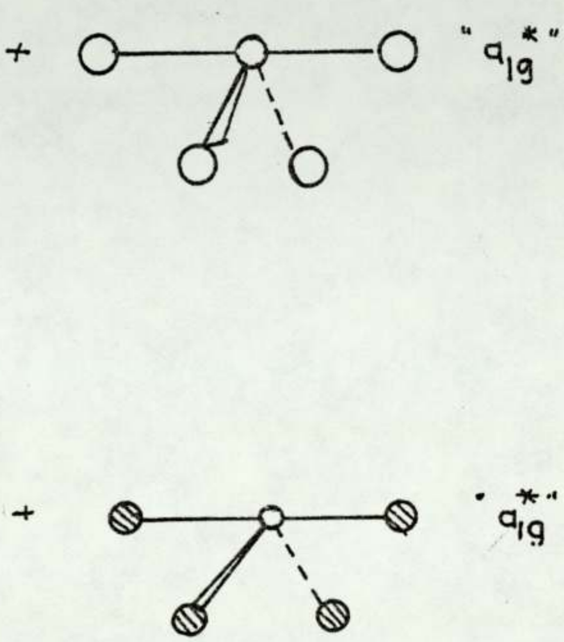
In the lower symmetry of the C_{2v} geometry of SH_4 all levels which were of a_{1g}, a_{2u} and b_{1g} symmetry in D_{4h} are reduced to a_1 and hence may interact. In considering the changes in the two highest occupied orbitals, a_{2u} and b_{1g}, it is only necessary to introduce mixing with the unoccupied a_{1g}^{*} level.

Starting with the a_{2u}, pure $3p_z$, the distortion of two trans hydrogens, downwards in the yz plane, is considered. As the D_{4h} symmetry is lost, what was the b_{1g} level begins to mix into $3p_z$ in a bonding manner. (The b_{1g} is assumed to be at a higher energy in the absence of any distortion) The bonding relationship is here set by the $3p_z$ pushing it up in energy. The resulting orbitals are represented schematically in (XI).

So far the mixing of the two filled levels causes neither differential acculumation of charge on the axial or equatorial hydrogens, nor a modification of the two bond types. These can come about only through the secondary mixing with the empty a_{1g}^{*}, Because that a_{1g}^{*} is above the occupied levels it will mix into them in a bonding way, i.e. bonding to the p_z



XI



XII

in each since the overlap between the components of the wave function located on the hydrogens is zero. (XII) represents the contribution from the secondary mixing with the correct phase relative to (XI). Summing (XI) and (XII) will give the orbitals displayed in (X).

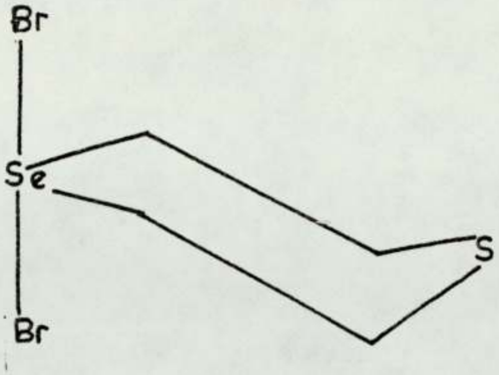
The more one bends the equatorial hydrogens down, the more will the a_{1g}^{*} orbital mix in. Considering the HOMO made up by a superposition of the two contributions in the top row of (XI) and (XII). The greater the mixing in of a_{1g}^{*}, that is the greater the bending, the more concentrated is the HOMO wave function in the axial ligands. Also the more a_{1g}^{*} mixes in the more weakened are the axial bonds. Stating the same fact in a different way, the smaller the equatorial angle the more accumulation of electron density in the axial position thus favouring more electronegative substituents. Also the axial bonds will become longer, i.e. weaker, the smaller the equatorial angle.

The main conclusions Hoffmann draws are:

i) The difference in axial and equatorial bond strengths should lessen with increasing equatorial angle, i.e. in a molecule with a large equatorial angle the axial bond lengths should approach those for the equatorial bonds.

ii) Conversly if the axial bonds are stretched the equatorial angle should decrease.

An interesting example is the structure of 1-thia-4-selenacyclohexane 4,4 dibromide (G).



(G)

Here one may expect approximatly equal angles at S and Se. This conclusion is based on the fact that the angle at Se in 1,4 - diselenacyclohexane [45], 98°, is similar to that found in 1,4 - dithiocyclohexane [46], 99°. While the angle at the two coordinate sulphur in the 1 - thia - 4 - selenacyclohexane is normal, 97°, the equatorial angle at the four coordinate selenium opens up to 108°.

(iii) Substitution in the axial position by more electronegative ligands should favour a smaller angle between the equatorial ligands.

The reasoning here is as follows: decreasing the equatorial angle increases the electron density at the axial position, Electronegative axial substituents take advantage of that accumalation of electron density, and so they will encourage a dimunation of the equatorial angle. Some experimental support for this is to be found in Table 1.1.

Compound	Equatorial angle	Reference
$(OR)_2S(Ph)_2$	104.4	47a
$Cl_2S(C_6H_4Cl)_2$	108.6	43a
$Cl_2Se(C_6H_4CH_3)_2$	106.5	47b
$Br_2Se(C_6H_4CH_3)_2$	108.0	47b
$Br_2Te(C_6H_5)_2$	94.4	32
$I_2Te(C_6H_4Cl)_2$	101.1	47c

Table 1.1

It is considered worthwhile at this stage to examine the structure of $Te(C_6H_4)_4$ as determined by Ziolo [31], (III), and compare it with that of $(C_6H_5)_2TeBr_2$ (IV).

It can be seen that the $Te\text{-}C_{axial}$ bond length is shorter than the the Te-Br bond length and is only slightly longer than the $Te\text{-}C_{equatorial}$ bond length in both cases. It would be expected, if Hoffmann's first conclusion is to be believed, that the C-Te-C bond angle in $(C_6H_5)_4Te$ would be greater than that found in $(C_6H_5)_2TeBr_2$. The same conclusion can be arrived at by using Hoffmann's third conclusion, i.e. that substitution in axial positions by more electronegative ligands should favour a smaller angle between the equatorial bonds. In this case bromine is more electronegative than phenyl and so one would expect a smaller equatorial angle in $(C_6H_5)_2TeBr_2$ than in $(C_6H_5)_4Te$.

It seems that, in the light of the limited data available for $(C_6H_5)_4Te$, that Hoffmann's conclusions are valid and may prove useful in the study of tetraorganyl tellurium chemistry.

In the present study it was hoped to make use of the third conclusion and try to synthesise tellurium compounds with large equatorial bond angles and subsequently try and introduce less electronegative groups, organic as opposed to halide, into the axial position.

The majority of synthesis carried out in this project have involved the use of organometallic reagents for the introduction of tellurium into an organic molecule and so a brief review of the use of these compounds in organotellurium synthesis will be given.

The first reported use of an organometallic reagent for the synthesis of an organotellurium compound was that of Marquardt and Michaelis [22] who reacted diethyl zinc with tellurium tetrachloride to produce triethyl telluronium chloride. When heated with excess diethyl zinc at 100 - 110°C butane and diethyltelluride were produced. It seems possible that this reaction produces tetraethyl tellurium which then undergoes thermal decomposition to give the observed products. This type of thermal decomposition is known for other tetraorganyl tellurium species. [24-26,30]

Since this time many different types of organometallic reagents have been used in the synthesis of organotellurium compounds.

Organolithium reagents have found use either as the simple reagent, RLi, or as the organyl lithium telluride, RTeLi.

The simple organolithium reagent can be prepared by reaction of the appropriate alkyl or aryl halide with lithium metal in either dry ether or dry tetrahydrofuran. The reactions are normally carried out under an atmosphere of dry nitrogen or argon. If the direct reaction between the halide and lithium metal is not feasible then the organic halide is reacted with n-butyl lithium under the same conditions. The resulting solution can be estimated by taking a suitable aliquot, hydrolysing and titrating with a standard acid solution.

The standardised solution of the organolithium reagent is then reacted with either tellurium tetrachloride or a substituted tellurium halide, e.g. the preparation of tetraphenyl tellurium from the reaction of phenyl lithium with either tellurium tetrachloride or diphenyl tellurium dichloride.[23]

Reaction of perfluorophenyl lithium, C_6F_5Li, with tellurium tetrachloride in a 2:1 molar ratio produced triperfluorophenyl telluronium chloride instead of the expected product diperfluorophenyl tellurium dichloride.[48]

Aryl lithium compounds react with tellurium metal to produce aryl lithium tellurides. This reaction is carried out in THF by adding tellurium metal to a solution of the appropriate aryl lithium reagent. The mixture is then refluxed for a time to allow the reaction to proceed to completion.[49]

The aryl lithium telluride can also be prepared by the reaction of a ditelluride, R_2Te_2, with lithium metal, again in THF.[50]

It has also been reported that tellurium will react with butyl lithium to give butyl lithium telluride[51] and that lithium will cleave diethyl telluride to give ethyl lithium telluride.[52]

Once the aryl lithium telluride has been formed it can be reacted with various alkyl, or aryl, halides to give mixed tellurides e.g. Irgolic[53] reacted PhTeLi, generated from diphenyl ditelluride and lithium, with alkyl halides to produce alkyl phenyl tellurides which were isolated as light sensitive yellow oils.

Phenyl lithium telluride has also been used to form tellurium-transition metal bonds, e.g. reaction with $(\pi\text{-}C_5H_5)_2NbCl_2$ gave the green complex $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$.[54]

Hydrolysis of solutions containing PhTeLi using 6M HCl produces the ditelluride.[55]

Tellurium metal will react with organic lithium reagents containing a metal - lithium bond producing compounds such as $(C_6H_5)_3MTeLi$, M = Ge[56a] Sn,[56b] or Pb.[56c] These are unstable products and are further reacted with triphenyl metal chlorides to produce compounds of the type $[(C_6H_5)_3M]_2Te$.

The starting organo lithium reagent is prepared from the corresponding triphenyl metal chloride and lithium metal in THF. The tellurium is then added and the reaction mixture refluxed for two hours giving a grey solution containing $(C_6H_5)_3MTeLi$.

The above method can also be used to prepare mixed tellurides

$$R_3MTeLi + Cl\text{-}M'\text{-}R_3 \longrightarrow R_3M\text{-}Te\text{-}M'R_3 + LiCl$$

$R = C_6H_5$; $M, M' = Ge, Sn, Pb$.

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. Tellurium added to such a reaction mixture inserts into the carbon-sodium bond.[57]

e.g. $C_6H_5\text{-}C{\equiv}C\text{-}Na + Te \longrightarrow R\text{-}C{\equiv}C\text{-}Te\text{-}Na$

The alkynyl sodium tellurides were never isolated, but were reacted with alkyl halides to give alkynyl alkyl tellurides e.g. alkylthioethynyl methyl tellurides[58a,b] and ethynyl methyl telluride[58c] were isolated when methyl iodide was added to the ethynyl sodium telluride in liquid ammonia.

$$R\text{-}C{\equiv}C\text{-}TeNa + CH_3I \xrightarrow{NH_3(l)} R\text{-}C{\equiv}C\text{-}TeCH_3 + NaI$$

$R = CH_3S$, C_3H_7S and H.

For organic compounds not possessing an acetylenic group the aryl sodium telluride can be produced by reduction of diaryl ditellurides. The reduction is carried out by dissolving the ditellurides in an ethanol / benzene mixture and adding a sodium hydroxide solution of sodium borohydride.

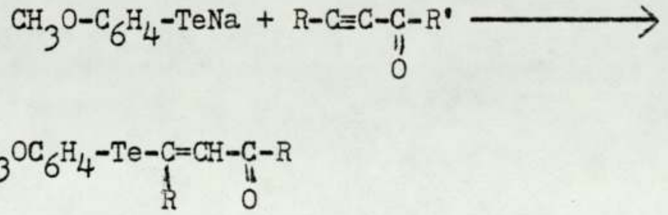
The aryl sodium telluride is not isolated but can be reacted with a variety of compounds, e.g. Sadekov[59] prepared diaryl tellurides, R-Te-R', ($R, R' = C_6H_5, C_6H_5$; C_6H_5, $4\text{-}CH_3C_6H_5$;

C_6H_5, 4-ClC_6H_5; 4-$CH_3OC_6H_5$, 4-$CH_3C_6H_5$) by reacting RTeNa with the appropriate diazonium tetrafluoroborates, $R'N_2^+\ BF_4^-$.

Piette [60] reacted RTeNa with 3-chloropropionic acids yielding aryl-2-carboxy tellurides.

It is suggested by Sadekov [61] that the RTe anion adds across the triple bond of acetylene oxo compounds producing aryl-1-phenyl-3-oxo-1-alkenes,

e.g.



$$CH_3O\text{-}C_6H_4\text{-}TeNa + R\text{-}C{\equiv}C\text{-}\underset{\underset{O}{\|}}{C}\text{-}R' \longrightarrow$$

$$CH_3OC_6H_4\text{-}Te\text{-}\underset{\underset{R}{|}}{C}{=}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$$

Organomercury compounds have found use in the synthesis of organyltellurium trihalides and diorganyl tellurium dihalides, either symmetric or unsymmetric. Diorganomercury, R_2Hg, and organyl mercury halides have been used.

A number of workers have reacted diarylmercury with elemental tellurium to produce diaryl tellurides. The organomercury compound transfers the organic groups to tellurium upon heating the reactants under an inert atmosphere in a sealed tube to 230°C for several hours.

e.g. $Ph_2Hg + Te \longrightarrow Ph_2Te + Hg$ – ref 29.

Organyl tellurium trihalides when heated with diaryl mercury compounds (2 : 1) in dioxan for several hours produce diorganyl tellurium dihalides. [63] This method can be used to prepare unsymmetrical dihalides and hence tellurides by reduction,

$$2\ RTeCl_3 + R'_2Hg \longrightarrow RR'TeCl_2$$

Petragnani and coworkers [64] obtained diorganyl tellurium dihalides by refluxing a dioxan solution of tellurium tetrachloride and the appropriate organyl mercuric chloride (1:2),

$$TeCl_4 + 4\text{-}RC_6H_4HgCl \longrightarrow (4\text{-}RC_6H_4)_2TeCl_2 + HgCl_2$$

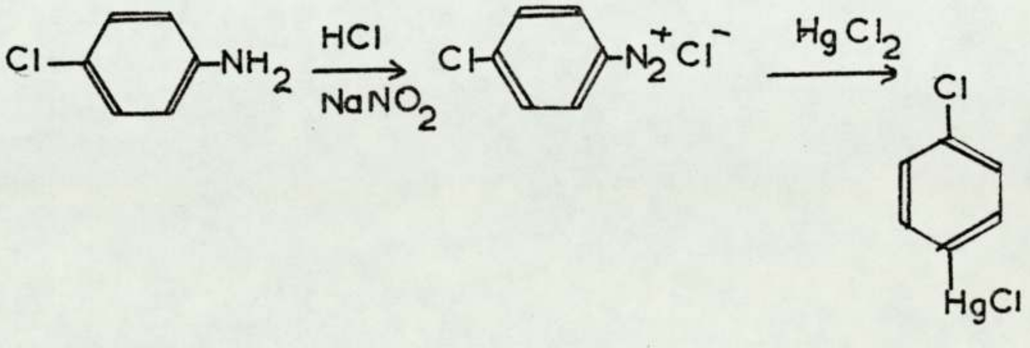
where R = H, CH_3.

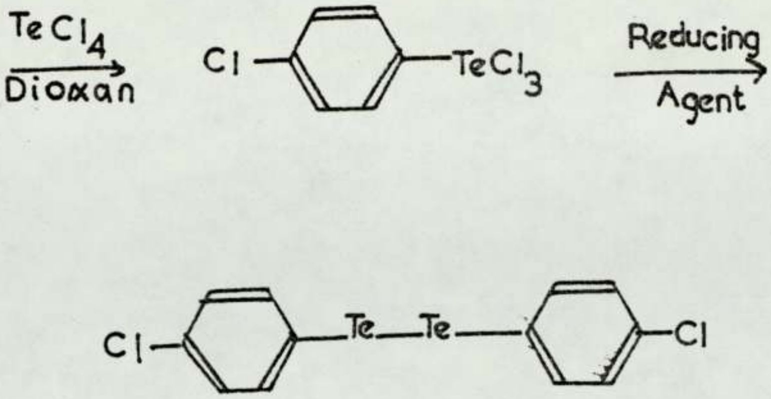
Yields were greater than 90 per cent.

Sadekov has also prepared unsymmetrical diorganyl tellurium dichlorides by boiling equimolar amounts of aryl tellurium trihalides and aryl mercury chlorides in dioxan.[65]

One of the most important uses of organomercury compounds in organotellurium synthesis has been the reaction of aryl mercury halides and tellurium tetrachloride in dioxan. The resulting organyl tellurium trichlorides can then be reduced to the corresponding ditelluride. The use of dioxan as solvent is favoured because of the formation of the mercuric chloride-dioxan complex which crystallises as the solution is allowed to cool.

If the starting organomercury halides are not commercially available then they can be made either by direct mercuration or via the diazonium compounds. An example of a typical reaction scheme would be as follows,





One of the more extensively used organometallic reagents in organotellurium synthesis are the Grignard reagents. These have been used in the preparation of tellurides, ditellurides and triorganyl telluronium chlorides.

The Grignard reagent is prepared from the appropriate alkyl or aryl bromide and magnesium metal in dry diethyl ether. The product of the reaction will react with elemental tellurium, tellurium tetrachloride, organyl tellurenyl halides, diorganyl ditellurides or diorganyl tellurium dihalides.

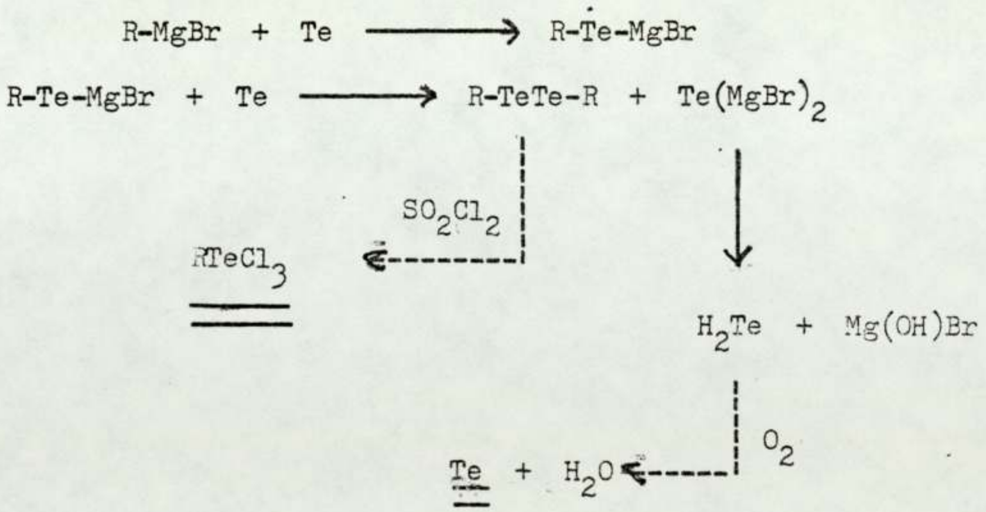
Elemental tellurium will insert into the carbon-magnesium bond of the Grignard reagent producing a compound of the type RTeMgX.

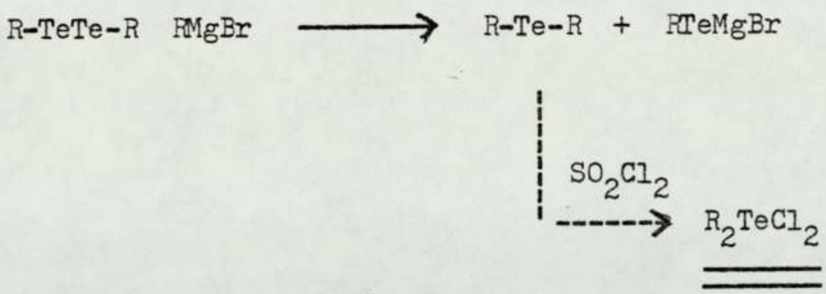
$$\text{R-MgX} + \text{Te} \longrightarrow \text{RTeMgX}$$

The product of this reaction is unstable and is not isolated. Reaction of the organyl bromomagnesium telluride with the appropriate alkyl or aryl halide will produce an unsymmetric telluride,

$$C_6H_5Te\text{-}MgBr + RI \longrightarrow C_6H_5\text{-}Te\text{-}R + MgBrI$$

The reactions are, however, not as simple as indicated in the previous two equations. Petragnani and de Moura Campos[49] reported the isolation of phenyl tellurium trichloride, diphenyl tellurium dichloride and elemental tellurium after treating the reaction mixture, which originally contained tellurium and phenyl magnesium bromide with SO_2Cl_2. They did not obtain an unsymmetric telluride upon addition of ethyl iodide to the reaction mixture, while Bowdon and Braude[67] successfully synthesised ethyl phenyl telluride under similar conditions. Petragnani and de Moura Campos[66] proposed a radical mechanism and the reaction sequence given below which both explain the results of their investigation.





------- secondary reaction

═══════ isolated products $R = C_6H_5$

The detailed mechanism of this reaction must still be considered unsolved and a lot more work still needs to be done.

It has been shown [68] that tellurium and a number of aromatic Grignard reagents in tetrahydrofuran produce, in the presence of oxygen, diaryl tellurides in high yields, as much as 80 %. Aliphatic Grignard reagents did not react. Reaction of 2 - biphenyl magnesium iodide with tellurium in tetrahydrofuran followed by oxidation of the reaction mixture with air, gave for the first time, bis (2-biphenyl)ditelluride [68a].

A recent American patent has claimed that if an organylhalo magnesium telluride is contacted with a ceramic support the resulting material, when air is blown, catalyses the polymerisation of alkyl vinyl ethers [69]

The reaction of tellurium tetrachloride with an excess of a Grignard reagent in ether or an ether - benzene mixture is complex. It is not possible to prepare, for example, a diorganyl tellurium dichloride in good yield by adding two moles of Grignard reagent to one mole of tellurium tetrachloride as in the following equation,

$$2RMgX + TeCl_4 \xrightarrow{\qquad} R_2TeCl_2 + 2MgXCl$$

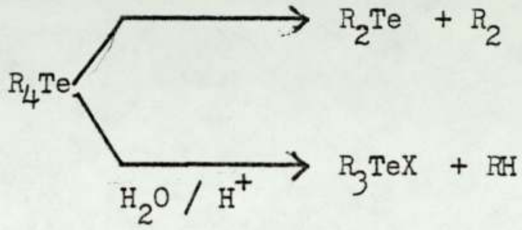
Elemental tellurium, diorganyl tellurium dichlorides, diorganyl tellurides and triorganyl telluronium chlorides have been observed as products of such reactions. Rheinboldt and Petragnani [70] observed that the formation of elemental tellurium by reduction of tellurium tetrachloride is largely prevented when the etherial Grignard solution, diluted with twice the volume of benzene is added to an ice cold suspension of the tetrachloride in ether. Refluxing such a mixture gave diorganyl tellurides in yields of more than 80 %. McWhinnie [71] noted that no tellurium was produced when C_6H_5MgBr or C_6F_5MgBr reacted with tellurium tetrachloride at 0°C in an ether / benzene mixture. The reaction was carried out with a 5 : 1 molar ratio of Grignard reagent to tellurium tetrachloride.

Since it is known [15] that diorganyl tellurium dichlorides are reduced by Grignard reagents to diorganyl tellurides, according to the equation below, it is likely that the diorganyl dihalides are intermediates in the direct preparation of the tellurides from tellurium tetrachloride.

$$R_2TeCl_2 + 2CH_3MgI \xrightarrow{\qquad} R_2Te + C_2H_6 + MgI_2 + MgCl_2$$

It is possible for the diorganyl tellurium dichlorides to be converted to the telluride via a tetraorganyl tellurium compound. The tetraorganyl tellurium compounds are known to undergo thermal decomposition leading to diorganyl tellurides.[23, 24-26,30] In the reaction between tellurium tetrachloride and a Grignard reagent enough of the former was always present to convert the $TeCl_4$ into tetraorganyl tellurium. The thermal decomposition and hydrolysis of these compounds would give the observed products.

$$TeCl_4 + 4\ RMgX \longrightarrow R_4Te + 4\ MgXCl$$



Grignard reagents will react with arene tellurenyl halides, generated in situ, to give unsymmetric tellurides, e.g. p-$MeOC_6H_4TeC_6H_5$, $C_6H_5TeC_4H_9$, p-$MeC_6H_4TeC_6H_5$ have been prepared by Petragnani using this procedure [72]. Selenotellurides have also been prepared by the reaction of arene tellurenyl halides with R'SeMgBr [72].

Other reactions that are of minor use are the reaction of Grignard reagents with diorganyl ditellurides and diaryl tellurium dihalides.

Aromatic ditellurides are cleaved by aromatic, but not by aliphatic, Grignard reagents in ether solution to give the unsymmetric tellurides in quantative yields based on the equation,

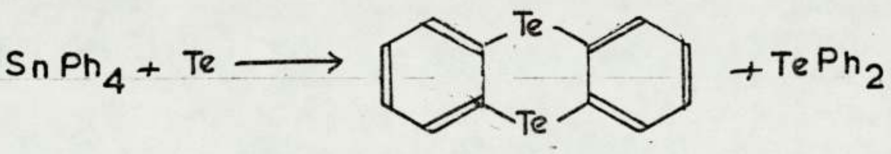
$$R_2Te_2 + R'MgBr \longrightarrow RTeR' + RTeMgBr$$

The aryl telluromagnesium bromide, which is formed in this reaction, precipitates, upon addition of petroleum ether, a syrup. This unstable substance decomposes upon contact with the atmosphere to tellurium and hydrogen telluride [50].

Diorganyl tellurium dihalides react with a two to three fold molar excess of an aromatic Grignard reagent in toluene. The triorganyl telluronium compounds are conveniently prepared by this method in yields as high as 77%. Since aromatic halides do not combine with diorganyl tellurides, the reaction of dichlorides with Grignard reagents is the only easy route to mixed triaryltelluronium compounds $[R_2R'Te]^+X^-$. The dichloride solution must be poured rapidly into the Grignard solution. The stirred mixture must be hydrolysed immediatly. The telluronium salts are best isolated as the iodides after addition of potassium iodide[77].

A number of workers have used tetraaryl tin compounds in the synthesis of organotellurium derivatives.

Schmidt and Schuman [74] reacted tetraphenyl tin with tellurium metal for 80 hours at 240°C in an evacuated tube and isolated diphenyl telluride. Telluranthrene was also produced.



Paul [75] reacted tellurium tetrachloride with tetraphenyl tin in toluene at room temperature to obtain triphenyl tin chloride and phenyl tellurium trichloride.

$$Ph_4Sn + TeCl_4 \xrightarrow[R.T.]{toluene} Ph_3SnCl + PhTeCl_3$$

If triphenyl tin chloride was reacted with phenyl tellurium trichloride in boiling toluene, diphenyl tellurium dichloride was formed.

Srivastava [76] found that tetra p-tolyl tin reacted with tellurium tetrachloride according to the equation,

$$(pMeC_6H_4)_4Sn + TeCl_4 \longrightarrow (pMeC_6H_4)_nTeCl_{4-n} + (pMeC_6H_4)_{4-n}SnCl_n$$

$$n=1 \text{ or } 2$$

It was found that $n = 1$ if the reaction is carried out at room temperature and $n = 2$ if carried out in refluxing toluene.

Srivastava [76] also showed that the tin - aryl bond is cleaved in preference to a tin - alkyl bond in the reaction of $Ph_nSnBu_{(4-n)}$ with tellurium tetrachloride, the tellurium compounds $Ph_nTeCl_{(4-n)}$, $n = 1$ or 2, were formed according to the equation below,

$$Ph_nSnBu_{4-n} + TeCl_4 \longrightarrow Bu_{4-n}SnCl_n + Ph_nTeCl_{4-n}$$

Organolead reagents have only found limited synthetic use for organotellurium compounds. Goddard [77] prepared diphenyltellurium dichloride from tetraphenyl lead and tellurium tetrachloride by refluxing in a mixture of xylene and toluene. Pant [78] repeated this reaction and also carried out the reaction of triphenyl lead chloride with tellurium tetrachloride in dioxan to give phenyl tellurium trichloride. Triphenyl lead chloride also reacted with aryl tellurium trichlorides to give $Ar(C_6H_5)TeCl_2$. $Ar = C_6H_5$ and $p\text{-}C_2H_5OC_6H_4$.

The mixed tetraorganyl lead species $(C_6H_5)_2Pb(CH_3)_2$ when treated with tellurium tetrachloride gave diphenyl tellurium dichloride and dimethyl lead dichloride.

The method of Pant [78] was the only one found to give satisfactory results on a milligram scale. Dance [79a] prepared $R_2{}^{126}TeX_2$ and $R_2{}^{130}TeX_2$ starting from tetraorganyl lead compounds and milligram quantities of TeX_4. X = Cl,Br; R = C_6H_5, o and p tolyl.

A number of other organometallic reagents have only been used either once or twice among these are cadmium, indium, germanium, aluminium, silicon and thallium.

Piette showed that dimethyl cadmium reacted with 2-formyl or 2-cinnamyl phenyl tellurium bromide producing 2-acyl phenyl methyl telluride.[79]

Srivastava [76] showed that diaryl indium chloride and diphenyl thallium chloride transfer organic groups to tellurium tetrachloride when refluxed in benzene producing the diorganyl tellurium dichloride and either aryl indium dichloride or phenyl thallium dichloride.

$$2\ Ar_2MCl + TeCl_4 \longrightarrow 2\ ArMCl_2 + Ar_2TeCl_2$$

M = Tl, Ar = Ph,   M = In, Ar = Ph or p-tolyl.

The same author showed that tetraphenyl germanium behaves in the same way as tetraphenyl tin and tetraphenyl lead in its reaction with tellurium tetrachloride.[76] The reaction was as follows,

$$Ar_4Ge + TeCl_4 \longrightarrow ArTeCl_3 + Ar_3GeCl$$

Ar = Ph or p-tolyl.

Vyazinkin [80] prepared the first compound containing a tellurium - aluminium covalent bond by the reaction of triethylsilane tellurol and triethyl aluminium in hexane.

$$(C_2H_5)_3SiTe\text{-}H + (C_2H_5)_3Al \xrightarrow{\text{hexane}}$$

$$(C_2H_5)_3Si\text{-}Te\text{-}Al(C_2H_5)_2 + C_2H_6$$

Sadekov [81] has shown that aryl trimethylsilanes transfer the aryl group to tellurium tetrachloride in refluxing toluene. This represents a convenient one step process to organyl tellurium trichlorides from the readily available aryl trimethylsilanes

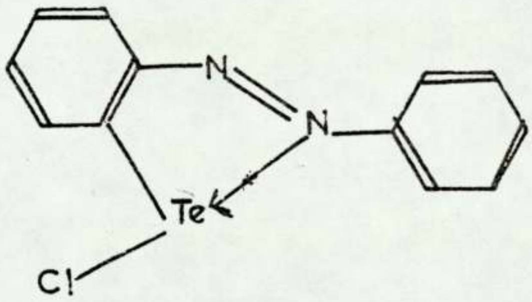
$$RC_6H_4Si(CH_3)_3 + TeCl_4 \xrightarrow[\text{reflux}]{\text{toluene}} RC_6H_4TeCl_3 + (CH_3)_3SiCl$$

R = H, 3-CH_3, 4-Br, 4-CH_3

The only other report of the use of an organothallium reagent besides that of Srivastava [76] is that of Deacon.[82] He reacted bis perfluorophenyl thallium bromide with tellurium metal at 190°C for three days in a sealed tube. Bis perfluorophenyl telluride and thallium I bromide were the products,

$$(C_6F_5)_2TlBr + Te \longrightarrow (C_6F_5)_2Te + TlBr.$$

One of our group has recently reported the synthesis of the compound phenylazophenyl 2C,N'tellurium II chloride.[83]



Phenylazophenyl 2C,N'tellurium II chloride

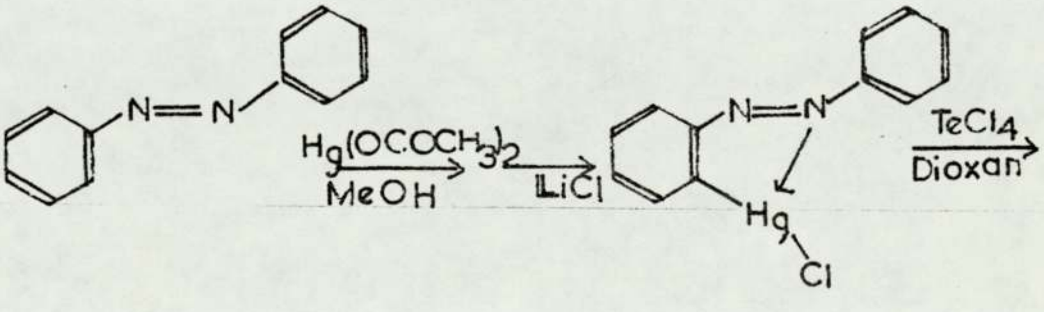
This compound represents one of the few examples of organyl tellurenyl halides and also an example of a nitrogen - tellurium bond, again very few of which are known.

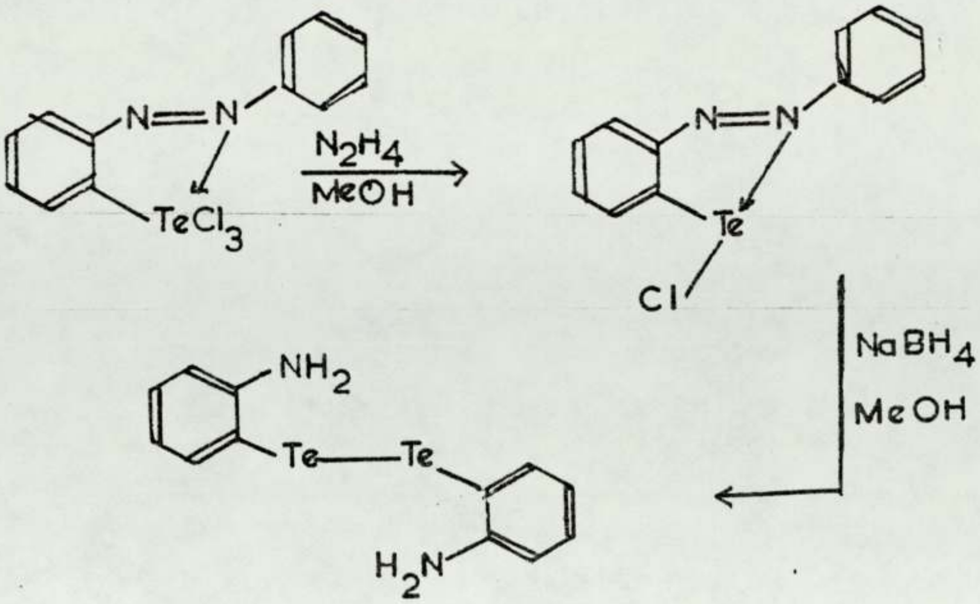
The use of azobenzene was prompted by the work of Cope and Siekman [84,85] who showed that azobenzene reacts with platinum II and palladium II chlorides.

The availability of a potentially coordinating nitrogen atom in the azo group introduced the possibility that monomeric organotellurium trihalides could be formed. It is well known that organyl tellurium trihalides are associated and that this association can be broken down by reaction with Lewis bases such as tetramethylthiourea.[87]

It was thought likely that reduction of the azobenzene derivative of tellurium IV with a mild reducing agent would give tellurenyl compounds, and it was also possible that the use of a stronger reducing agent would lead to an attack on the azo group and give a covenient route to organotellurium compounds with an o-amino group.

The direct combination of tellurium tetrachloride and azobenzene failed to produce the required trichloride. The product phenyl azo phenyl 2C,N'tellurium IV trichloride, $C_{12}H_9N_2TeCl_3$, was prepared via the organomercury compound, made according to the method of Roling [88] The following reaction scheme was adopted. [89]





The reaction of the organomercury compound with tellurium tetrachloride in dioxan afforded the required organyltellurium trichloride which upon reduction with hydrazine in methanol gave the corresponding tellurenyl chloride. Reduction of the latter with sodium borohydride produced bis(o-aminophenyl) ditelluride.

The structure of the tellurenyl chloride has been determined by X-ray crystallography [83] and gives the Te-N bond length as 2.23 Å and the Te-C(2) bond length as 2.04 Å - the shortest known for an organotellurium compound.

Mössbauer data are available for the compound and the following parameters are reported [89]

δ , Chemical Isomer Shift 0.63 ± 0.05 mmsec^{-1} vs Cu/Sb

Δ , Quadrupole Coupling Constant 11.76 mm sec^{-1}

The Quadrupole Coupling Constant was interpreted by the method developed by Jones.[90] The model predicts that for a Te II compound of the type considered here the quadrupole splitting should be of the order of 14 mm sec $^{-1}$. The figure for p-$EtOC_6H_4TeI_2^-$, 13.93 mm sec^{-1}, is in good agreement with this figure.

The figure of 11.76 mm sec^{-1} means that there is some other mechanism for the withdrawal of p-electrons from the tellurium. It is possible that the tellurium p_y orbital could interact with the π- orbital associated with the chelate ring. Such delocalization would decrease the p-orbital imbalance (and hence lower in comparison with a situation where the mechanism for delocalization does not exist, e.g. p-$EtOC_6H_4TeI_2^-$) also the delocalization of p-electron density onto the chelate ring would further deshield the tellurium s electrons and hence enhance δ. It is proposed by Musa[89] that the Mössbauer data supports the view that there is a positive π- interaction between tellurium and the chelate ring.

It was mentioned previously that the azobenzene derivative of TeII is one of the few stable tellurenyl species indeed, with the exception of 2-napthyltellurium iodide it has not been possible to isolate other organotellurium halides which do not have in the ring a stabalizing carbonyl group in the o-position to the tellurium atom. Aliphatic tellurium halides are still unknown, however an alkyl tellurium cyanate has been prepared [91], benzyl tellurocyanate, from benzyl chloride and KTeCN in DMSO as white needles melting at 126-7 °C. The compound is light sensitive and darkens in the presence of air, it is especially unstable in solution. Aromatic derivatives can be prepared in solution from diaryl ditellurides and an equimolar amount of elementary halogen.

$$R_2Te_2 + X_2 \longrightarrow 2RTeX$$

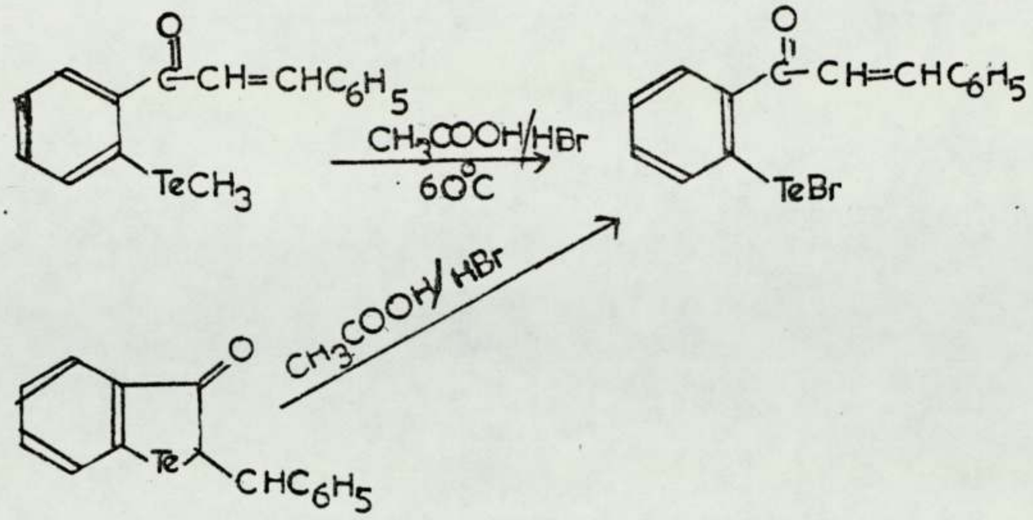
R,X: C_6H_5,Cl [92]; C_6H_5,Br; C_6H_5,I; $4CH_3C_6H_4$,I;
$4CH_3OC_6H_4$,Br; 4 $CH_3C_6H_4$,I; 4 $C_2H_5OC_6H_4$,Br;
4 $C_2H_5OC_6H_4$,I [93].

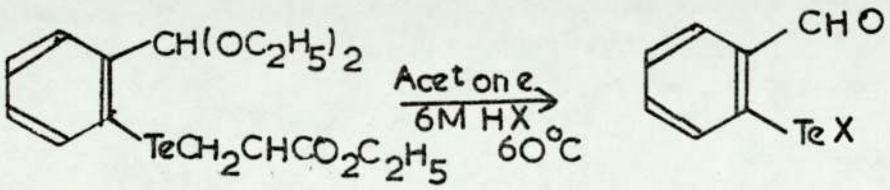
Hauge [92] carried out the preparation of phenyl tellurium halides by adding the required amount of chlorine or bromine dissolved in methanol to an ethanolic or methanolic solution of diphenyl ditelluride containing thiourea, selenourea, or a phosphorus selenide.

The ligands complexed with the organotellurium compounds as follows,

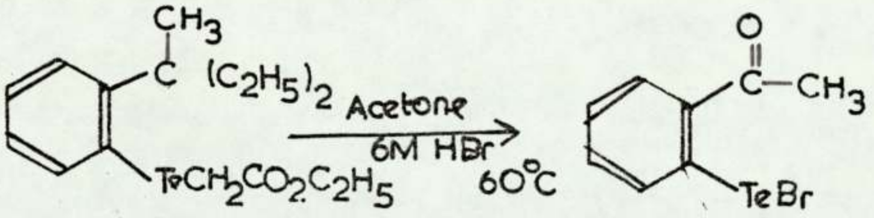
$$C_6H_5TeX + nL \longrightarrow C_6H_5TeXL_n$$

The isolation of aryl tellurium halides becomes possible when a carbonyl group is present in the ortho position to the tellurium atom. These tellurium halides were prepared by Piette and coworkers, examples of which are shown below [94,95].

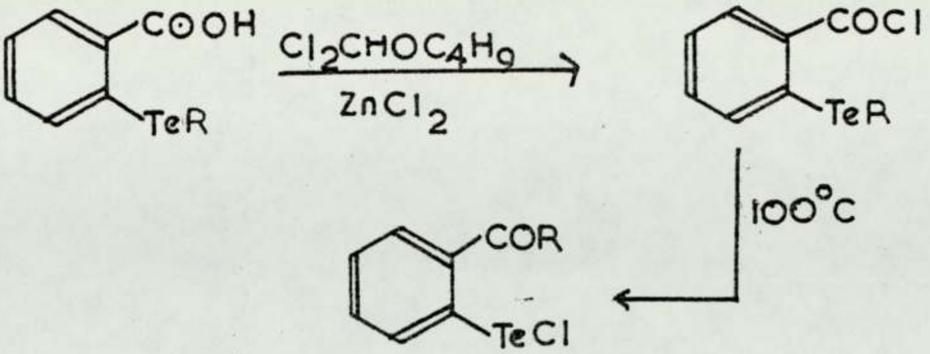




$X = Cl, Br$



When 2 - carboxyphenyl aryl tellurides were treated with dichloromethylbutyl ether at 100°C in the presence of $ZnCl_2$, 2 - benzoylphenyl tellurium chlorides were isolated.[96] The 2 - chloroformyl phenyl aryl telluride, expected in this reaction, was obtained only when the temperature was kept at 50 -60°C.



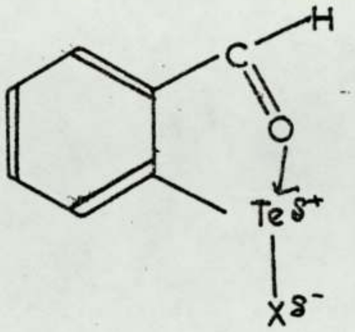
$R = C_6H_5$; 2,4,6,$(CH_3)_3C_6H_2$.

At 100 °C the Cl^- ion migrated to the tellurium atom with a concomicant shift of the aryl group, R, to the carbonyl carbon.

2 acetyl phenyl tellurium halides were isolated in 50% yield after an ether solution of 3-oxo 2,3 dihydrobenzotellurophene had been treated with aqueous hydrohalic acids at room temperature for one hour [97].

The successfull preparation of 2-formyl phenyl tellurium selenocyanate and thiocyanate has also been claimed [98].

An X-ray structural analysis of 2-formyl phenyl tellurium bromide[86] and NMR investigation employing CS_2 solutions of the 2-formyl phenyltellurium derivatives, RTeX (X= Cl, Br, I, CN, SCN, SeCN)[98] showed that the molecules exist in the conformation which permits the Te atom to interact with the carbonyl group. This interaction sufficiently stabalizes the tellurium halide which is now coordinately less unsaturated to allow the isolation of these compounds.



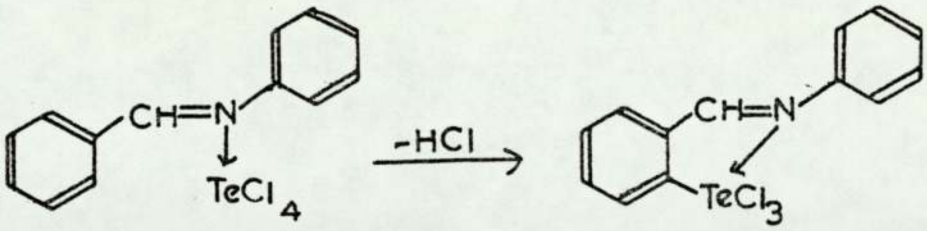
Part of the present study has involved the investigation of the reaction of Schiff bases, isoelectronic with azobenzene, with tellurium tetrachloride. Reactions of the former with transition metals [100] and organotin IV compounds [99] are well documented.

Reactions between N-benzylidene aniline and transition metals lead to metallation of the Schiff Base, which can be proved by spectroscopic techniques e.g. infra-red. Molnor [101] showed that for a series of Schiff bases, RCH=NR', only the mono-substituted compounds have a band at approximately 690 cm^{-1}, which is probably an out of plane carbon - hydrogen bending mode. This band is therefore associated with the presence of at least one unsubstituted phenyl ring attached to either atom of the azomethine linkage. For the complexes with $PdCl_2$ the band at 690 cm^{-1} is present in the spectra of only those complexes which have an unsubstituted phenyl group attached to the nitrogen atom.

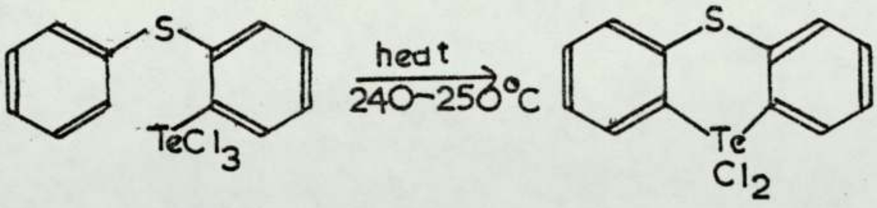
These authors argued that this showed the presence of a sigma bond between palladium and a carbon atom in the phenyl ring which is attached to the carbon of the azomethine group.

It was one aim of the present study to see if Schiff bases could be metallated by tellurium.

Sadekov[102] has investigated the complex formation of tellurium tetrachloride with Schiff Bases. He showed that if a benzene solution of tellurium tetrachloride and N-benzylidene aniline are mixed a yellowish green solid is produced and that an upward shift of ν (C=N) is observed on complexing. No infra-red data in the region of 700 cm^{-1} is given neither was the effect of heat mentioned. It may be that if these coordination compounds are heated then loss of hydrogen chloride could occur giving the o-metallated product which could be proven by IR.

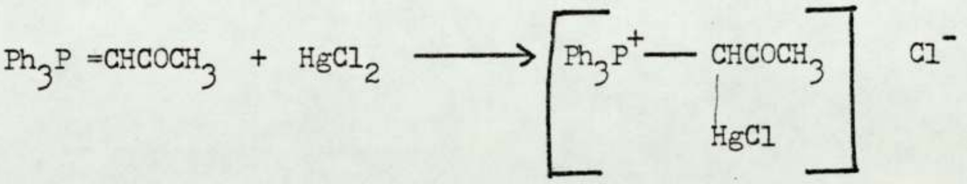


This does not seem unreasonable as coordination is the first step to o-metallation [103] and also certain tellurium compounds are known to evolve HCl on heating producing a closed ring structure e.g. [104] the preparation of the following,



A further class of compound is found to undergo o-metallation, namely ylids [105]. Among the ylids studied was triphenylphosphinebenzoyl methylene ($\mathrm{Ph_3P^+ — \bar{C}HCOPh}$). This ligand was found to be o-metallated by Pd. The reaction was carried out by adding the ylid in methanol, which contained sodium acetate, to a solution of $\mathrm{PdCl_2}$. The resulting mixture was heated for two hours under reflux after which time the product separated out. O-metallation was again proved by the use of spectroscopic techniques namely IR and NMR.

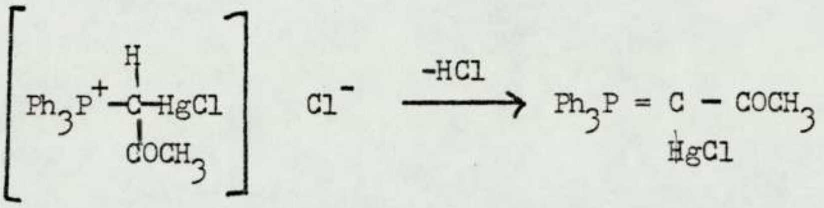
Nesmeyanov has reported the preparation of mercurated phosphorus salts [106]. The reaction of the phosphorus ylid $\mathrm{(C_6H_5)_3P = CHCOCH_3}$ with $\mathrm{HgCl_2}$ gave the mercurated phosphonium salt.



$$\mathrm{Ph_3P = CHCOCH_3 + HgCl_2 \longrightarrow \left[Ph_3P^+ — \underset{\displaystyle HgCl}{\underset{|}{CHCOCH_3}} \right] Cl^-}$$

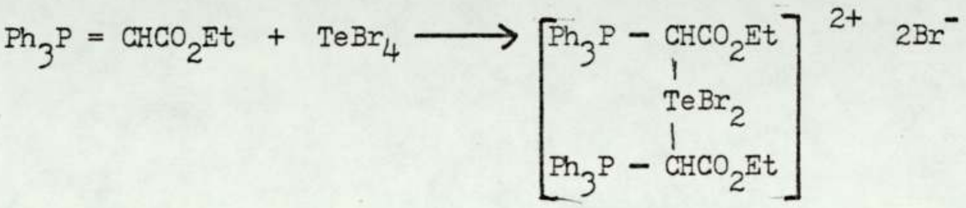
I

Upon reaction of I with sodium methoxide a molecule of HCl is lost giving a mercurated phosphoylid.



$$\left[Ph_3P^+-\overset{H}{\underset{COCH_3}{C}}-HgCl \right] Cl^- \xrightarrow{-HCl} Ph_3P=\underset{HgCl}{C}-COCH_3$$

The only reported reaction of a Wittig reagent with a tellurium halide is that of Petragnani and De Moura Campos [107]. Tellurium tetrabromide reacted with carboethoxymethylene triphenyl phosphorus to give the following product.



$$Ph_3P = CHCO_2Et + TeBr_4 \longrightarrow \left[\begin{array}{c} Ph_3P - CHCO_2Et \\ | \\ TeBr_2 \\ | \\ Ph_3P - CHCO_2Et \end{array}\right]^{2+} 2Br^-$$

The result was later refuted by the same authors [21]. The compound proved to be the diphosphonium hexabromotellurate salt, $2\ (Ph_3P^+CH_2COOC_2H_5)\ TeBr_6^{2-}$.

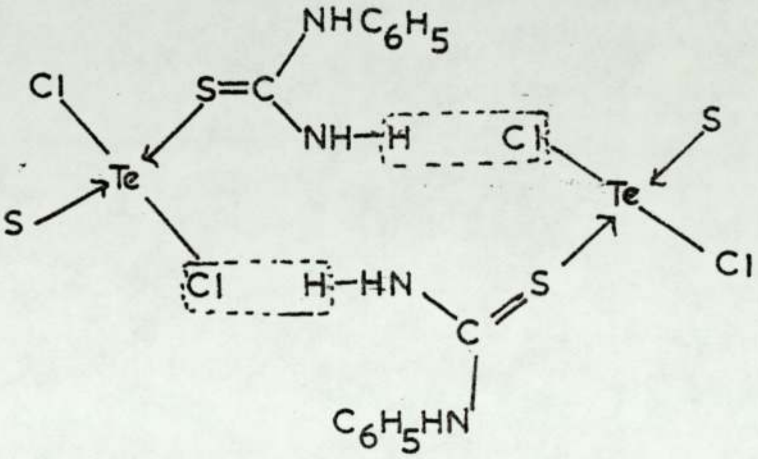
The following mechanism was proposed for the formation of this compound

$$TeBr_4 + H_2O \longrightarrow TeOBr_2 + 2\ HBr$$

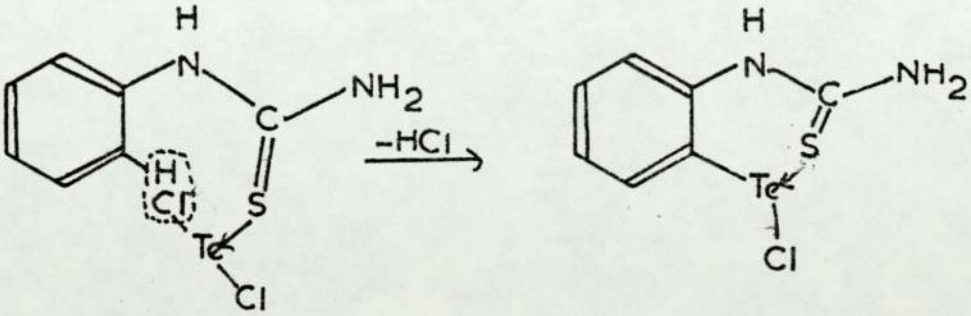
$$2\ Ph_3P = CHCOOC_2H_5 + 2\ HBr \longrightarrow 2\ (Ph_3P^+CH_2COOC_2H_5)\ Br^-$$

$$TeBr_4 + 2\ (Ph_3P^+CH_2COOC_2H_5)Br \longrightarrow 2\ (Ph_3P^+-CH_2COOC_2H_5)\ TeBr_6^{2-}$$

It has been found by Sethuramen [108] that the tellurium II complex of N-phenylthiourea undergoes dehydrochlorination when added to polar organic solvents. The author suggests the formation of an imido complex of tellurium II takes place thus



An alternative idea is that ortho metallation takes place as follows



It should be possible, using infra-red spectroscopy, to determine which mechanism is taking place.

CHAPTER TWO

GENERAL EXPERIMENTAL METHODS

Chemicals:-

All chemicals were obtained from commercial sources and "Analar" grade used when necessary. Tellurium tetrachloride ($TeCl_4$), the starting material for many reactions, was supplied by British Drug House (B.D.H.).

Solvents:-

All solvents were obtained from commercial sources and purified according to literature methods, i.e. Benzene ether, methanol, THF and dioxan [109].

Elemental Analysis:-

Micro analysis for carbon, hydrogen, nitrogen, halogen, sulphur and phosphorous were carried out by the Micro Analytical Laboratories of the Chemistry Department of Aston University. Tellurium analysis was carried out by the method of Clark and Al Turahai[110].

Physical Measurements:-

(a) Infra red spectra:- 4000 cm^{-1} to 250 cm^{-1}

Spectra in this region were recorded on a Perkin-Elmer 457 Spectrometer. Solid specimens were prepared as Nujol Mulls supported between CsI plates or examined as KBr discs. Liquids were run as thin films on CsI plates.

(b) 400 cm^{-1} to 200 cm^{-1}:-

Spectra in this region were recorded on a Perkin-Elmer Spectrophotometer model 519B. Solid samples were prepared as Nujol Mulls and supported between CsI plates.

Nuclear Magnetic Resonance (NMR) Spectra:-

All proton magnetic resonance spectra at 60Hz were recorded on a Perkin-Elmer R14 spectrometer. Tetramethlysilane (TMS) was used as an internal reference.

Mass Spectra:-

The Mass Spectra of all compounds were recorded on the AEI MS9 spectrometer at 70eV.

Melting Points:-

These were determined using a Gallenkamp melting point apparatus.

CHAPTER THREE

AN ATTEMPT TO INTRODUCE BULKY GROUPS ONTO TELLURIUM.

3.1 INTRODUCTION

It was stated earlier (p. 5) that the initial aim of this project was to prepare and study new tetraorganyl tellurium compounds and that it was hoped that the ideas of Hoffman[42] would be of use.

Hoffman suggests that if the equatorial bond angle in a system of C_{2v} symmetry is made large enough then the axial and equatorial bonds would become more equivalent and also that less electronegative groups would be admitted to the axial position.

The bulky groups that were chosen were trimethylsilylmethyl, $(CH_3)_3SiCH_2$, and diphenylmethyl, $(C_6H_5)_2CH$. These groups have been used by other workers, notably Lappert [111a,b] to prepare stable tin II and transition metal alkyls.

An attempt to introduce cyclopentadiene and ferrocene onto tellurium was prompted by the work of Fitzsimmons who investigated the fluxional behaviour of ferrocene type compounds using Mössbauer Spectroscopy. It was hoped to study the ^{125}Te Mössbauer spectra of a cyclopentadiene derivative and ferrocene would act as a bulky group on tellurium and thus allow Hoffman's conclusion to be tested, also a ^{57}Fe study could supplement the ^{125}Te data.

Diorganothallium III compounds have been used successfully to oxidatively add organic groups to metals in low oxidation states [112] for example,

$$SnCl_2 + R_2TlCl \longrightarrow R_2SnCl_2 + TlCl$$
$$Ph_2TlBr + Hg \longrightarrow Ph_2Hg + TlBr$$

So far only two examples of the use of organothallium reagents have been reported for the synthesis of organotellurium compounds (p.42), because of this it was decided to investigate the reaction of diorganothallium III compounds with tellurium in a low oxidation state.

3.2. EXPERIMENTAL

All reactions were carried out under dry nitrogen unless otherwise stated.

3.2.1 Attempted Introduction of Cyclopentadiene or Ferrocene onto Tellurium.

3.2.1.1 Preparation of Sodium Cyclopentadienide.

A 250ml, three necked flask was fitted with a reflux condenser together with a dropping funnel, a nitrogen inlet and a magnetic stirrer. 0.91g (0.04M) of finely cut sodium chips were added to 15ml of dry THF contained in the flask. To this suspension was added 2.6g (0.04M) of freshly distilled cyclopentadiene in 15ml of dry THF, dropwise, over a period of time necessary to sustain the solvent at reflux temperature. The mixture was stirred throughout the reaction.

3.2.1.2 Preparation of Cyclopentadienyl Tributyl Tin, Bu_3^nSnCp.

To a solution of sodium cyclopentadienide, prepared as above, was added, dropwise, 13.0g (0.04M) of tri-n-butyl tin chloride. The resulting solution was stirred and refluxed for one hour when a white solid (NaCl) was produced. After refluxing the NaCl was filtered off giving a yellow solution containing the required compound. Removal of the solvent gave a yellow oil.

Analysis;

Found; C = 56.4 %, H = 9.1 %

$C_{17}H_{32}Sn$ requires; C = 57.5 %, H = 9.02 %

3.2.1.3 Reaction of Bu_3^nSnCp with Tellurium Tetrachloride.

To a solution of Bu_3^nSnCp (0.04M) in 20ml of dry benzene was added, dropwise, a solution of 5.39g (0.02M) of tellurium tetrachloride in 150ml of dry benzene. The reaction conditions are described below.

(i) The tellurium tetrachloride was added at room temperature and then the resulting mixture refluxed for varying amounts of time e.g. ½ hr. 1 hr. 2 hr. These reactions yielded a yellow solution and a white solid. The solvent was removed on the rotary evaporator and on reduction of the volume tellurium was seen to be deposited. Tributyl tin chloride was identified as a product.

(ii) The tellurium tetrachloride was added at room temperature but without refluxing. This reaction gave the same results as above.

(iii). The tellurium tetrachloride was added at -6^0C. This gave a red-yellow solution which gave the same products as above on gaining room temperature.

3.2.1.4. Reaction of Ferrocene with Tellurium Tetrachloride in the presence of $AlCl_3$

Ferrocene, aluminium trichloride (anhydrous) and tellurium tetrachloride were reacted together in various molar quantities.

(i) Equimolar quantities of the reactants.

5.39g of tellurium tetrachloride, 2.66g of aluminium trichloride and 3.71g of ferrocene were refluxed in dry carbon tetrachloride for 20 minutes. The solution was filtered under vacuum to give an orange solution and a black solid. The orange solution yielded ferrocene, MP173°C, lit. value [114] 173-174°C and the black solid was shown to be tellurium metal.

(ii) Reaction of 0.02M $TeCl_4$, 0.04M $AlCl_3$ and 0.04M of ferrocene.

These reagents were reacted under the same conditions as above. The same products were obtained.

3.2.1.5. Reaction of Lithioferrocene with Tellurium Tetrachloride

A solution of n- butyl lithium was prepared by adding dropwise, 10.9g (0.08M) of n - butyl bromide to a suspension of lithium chips in dry ether at -10°C. After completion of the reaction the solution was filtered through glass wool under a nitrogen atmosphere. The etherial solution of n - butyl lithium was added dropwise to 7.4g (0.04M) of ferrocene in dry ether. The mixture was stirred for one hour and then allowed to stand overnight. A solution of 2.6g of tellurium tetrachloride in 100ml of dry benzene was added dropwise. A black solid formed immediatly and the solution was refluxed for 1½ hours. A reddish ether / benzene solution was observed which was filtered and the solvent removed to give an almost quantitative yield of ferrocene. The black solid was again identified as tellurium.

3.2.2. The Attempted Introduction of $(CH_3)_3SiCH_2$- onto Tellurium.

3.2.2.1. Preparation of Chloromethyltrimethylsilane.

Into a 500ml two necked round bottomed flask fitted with a reflux condenser, a dropping funnel and magnetic stirrer was placed 6.0g of magnesium metal in 20ml of dry ether. 35g of methyl iodide in 50ml of dry ether were added dropwise. After addition of the methyl iodide the mixture was refluxed for 30 minutes. The solution was allowed to cool and the flask placed in an ice bath. 36g of chloromethyldimethylchlorosilane in 50ml of dry ether was added dropwise to the Grignard reagent. After the addition of all the silane the reaction mixture was stirred at room temperature for eleven hours. The flask was cooled and the mixture hydrolysed with 200ml of concentrated hydrochloric acid. The ether layer was separated and dried over anhydrous magnesium sulphate and then fractionally distilled to give chloromethyltrimethylsilane boiling at 97°C, Lit. 97.1 °C.[114] The product gave an identical infra-red spectrum to that of an authentic sample provided by Dow Corning Chemicals Ltd.

3.2.2.2. Preparation of $(CH_3)_3SiCH_2Li$.

Into a three necked flask (500ml) fitted with a reflux condenser, dropping funnel and a nitrogen (or argon) inlet were placed 2.0g (4molar excess) of freshly cut lithium chips and 15ml of dry ether. 5.0g (0.04M) of chloromethyltrimethylsilane in 20ml of dry ether were added dropwise. The ether suspension of lithium and the silane were stirred vigorously for four hours at room temperature. It was found that the addition of broken glass to the reaction mixture increased the rate of reaction presumably by continually presenting a clean face of the lithium chip to the silane. A white precipitate of lithium chloride was produced during the reaction.

3.2.2.3. Reaction of $(CH_3)_3SiCH_2Li$ with Tellurium Tetrachloride.

To a solution of $(CH_3)_3SiCH_2Li$, prepared as above, were added 5.39g (0.02M) of tellurium tetrachloride in 50ml of dry benzene at 0°C. The solution was stirred continuously during the addition of the tellurium tetrachloride. After the addition the mixture was refluxed for three hours and filtered, under nitrogen, to yield a white powder (LiCl) and a yellow solution The solvent was removed in vacuum to give white crystals which decomposed on contact with air. This observation could not be repeated in future experiments as decomposition to tellurium took place before removal of the solvent. It was noted that the yellow solution, if left to stand, deposited elemental tellurium.

The only products isolated from the yellow solution were tellurium (identified by its reaction with concentrated sulphuric acid) and 2,2,5,5 tetramethyl 2,5 disilahexane, $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$, obtained as a colourless oil.

Analysis;

Found; C = 55.5 %, H = 13,0 %

$C_8H_{22}Si_2$ requires; C = 54.54 %, H = 12.5 %

This experiment was also repeated enclosing the reaction vessel in aluminium foil, to exclude as much light as possible. The same results were obtained.

In case the expected bis(trimethylsilyl)tellurium dichloride had been reduced to the corresponding telluride the following reactions were carried out in order to isolate the telluride.

3.2.2.4. Reaction with Bromine.

To a portion of the reaction mixture contained in a round bottom flask was added bromine. The mixture was left overnight when it was noticed that the bromine colour had disappeared and yellowish crystals were produced. These crystals showed no organic groups in the infra-red spectrum.

3.2.2.5. Reaction with Methyl Iodide.

To a portion of the reaction mixture contained in a round bottom flask was added methyl iodide. An NMR spectrum was taken of the solution and no evidence of Te - H coupling was noted. The NMR was unchanged after twenty four hours.

3.2.2.6. Reaction of Bis p- ethoxyphenyl telluride with Chloromethyltrimethylsilane.

0.44g (0.001M) of bis p - ethoxyphenyl telluride and 0.12g (0.001M) of chloromethyltrimethylsilane were dissolved in 10ml of dry chloroform. The resulting solution was refluxed for six hours after which time the solution was allowed to cool. The NMR spectrum of the solution showed no evidence of Te - H coupling. On removal of the solvent 0.4g of bis p-ethoxyphenyl telluride was recovered.

3.2.3. The Attempted Introduction of $(C_6H_5)_2$CH- onto Tellurium.

3.2.3.1. Preparation of Diphenylmethyllithium.

This was prepared by the method of Moore[113].

To a suspension of 1.04g (0.15M) of lithium metal (finely cut) in 20ml dry THF contained in a 500ml, 3 necked, round bottom flask fitted with a reflux condenser, dropping funnel and nitrogen inlet were added dropwise 10.2g (0.05M) of chlorodiphenylmethane in 50ml dry THF. The solution was continuously stirred during the addition. After about 20 minutes the solution started to change to yellow and after a further 20 minutes to a blood red colour. After formation of the red colour the solution was stirred for 18 hours and then filtered, under nitrogen, through a plug of glass wool to remove unreacted lithium.

3.2.3.2. Reaction of Tellurium Tetrachloride with Diphenylmethyllithium.

A solution of diphenylmethyllithium, prepared as above, was placed into an ice bath. To this solution was added, dropwise, 5,00g (0.19M) of $TeCl_4$ in 150ml of dry benzene. After the addition of all of the tellurium tetrachloride the solution was heated under reflux for 2 hours. During the reaction the red colour of the organolithium reagent disappeared giving rise to a yellow solution and a grey solid. The solid was filtered off, under nitrogen, and extracted with hot methanol to give lithiumchloride and tellurium metal. The solvent was removed from the yellow solution to give white crystals, recrystallised from benzene, melting at 211°C. This product was shown to be 1,1,2,2, tetraphenylethane. Lit. MP = 212°C[114].

Anslysis;

Found; C = 93.69 %, H = 6.66 %

$C_{26}H_{22}$ requires; C = 93.41 %, H = 6.58 %.

This reaction was repeated at -6°C and -70°C and the same results were obtained.

In an attempt to isolate bis (diphenylmethyl) telluride, if it had been formed during the reaction, the following reactions were carried out.

(i) Reaction with mercuric chloride.

A sample of the reaction mixture was added to a methanolic solution of $HgCl_2$ and a green-brown precipitate which showed no organic groups present in the infra-red spectrum, was produced.

(ii) Reaction with bromine in benzene.

A sample of the reaction mixture was added to a benzene solution of bromine producing yellow crystals which darkened at 105°C but did not melt below 250°C. Again the infra-red showed no organic groups present.

(iii) Reaction with chlorine in ether.

Chlorine was bubbled into ether for about 5 minutes and then a sample of the reaction mixture was added. White crystals were produced which blackened at 115°C. The infra-red spectrum was obtained as a Nujol Mull and showed only broad absorptions in the region 3,400cm^{-1}, 1,600cm^{-1}, 600cm^{-1} and 500cm^{-1}.

3.2.3.3. Preparation of PhTeLi and its reaction with Chlorodiphenylmethane.

To a solution of phenyl lithium (prepared from 0.98g of lithium and 11.13g of bromobenzene in 150ml of dry ether) were added 6.38g of tellurium powder. The reaction was carried out in a three necked, round bottom flask fitted with a nitrogen inlet, reflux condenser and a dropping funnel. The mixture was refluxed for two hours to give a grey solution containing C_6H_5TeLi. A solution of 10.2g of chlorodiphenylmethane in 50ml ether was added and the reaction mixture stirred for two hours. A red solution resulted which was filtered to remove a white solid (LiCl). Upon evaporation of the solvent a mixture of red and white crystals were observed. These were extracted with methanol to give a red solution and white crystals, which were shown to be 1,1,2,2, tetraphenylethane MP = 211°C. Lit. 212°C

Analysis;

Found; C = 93.15 %, H = 6.9 %

$C_{26}H_{22}$ requires; C = 93.41 %, H = 6.58 %.

On evaporation of the methanol diphenyl ditelluride was found MP = 64 °C Lit. 65°C [15]

Analysis;

Found; C = 36.0 %, H = 2.39 %

$C_{12}H_{10}Te_2$ requires; C = 35.2 %, H = 24.4 %.

This experiment was again repeated at -6°C and -70°C and similar results were obtained.

3.2.3.4. Preparation of $C_2H_5OC_6H_4TeNa$ and its reaction with $(C_6H_5)_2CHCl$.

To a solution of 12.4g of bis(p-ethoxyphenyl) ditelluride in 7ml ethanol and 3ml of benzene was added 0.35g of sodium borohydride in 8ml of MNaOH. The colour changed from red to yellow showing the formation of $C_2H_5OC_6H_4TeNa$. A solution of 3g of chlorodiphenylmethane in 10ml of ethanol was added. The mixture was stirred during the addition of the alkyl halide and then refluxed for 1 hour. A red solution and a white powder (NaCl) was produced on cooling. The solvent was removed from the red solution to give a mixture of red and white crystals. These were separated using methanol to give p-ethoxyphenyl ditelluride, MP =107°C Lit.107°C [15]

Analysis;

Found; C = 39.0 %, H = 3.9 %

$C_{16}H_{20}Te_2O_2$ requires C = 38.4 %, H = 40.1 %

and 1,1,2,2, tetraphenylethane.

3.2.3.5. Reaction of Ph_2CHLi with $p\text{-}C_2H_5OC_6H_4TeCl_3$.

To a vigourously stirred suspension of 5.6g $p\text{-}EtOC_6H_4\text{-}TeCl_3$ in 50ml of dry THF was added a solution of Ph_2CHLi, (prepared as on page 64) in 50ml THF at -70°C. The deep red colour of the lithium reagent disappeared on contact with the THF suspension of the trichloride. After the addition was complete the solution was allowed to rise to room temperature when a red solution again appeared. On evaporation of the solvent on a rotary evaporator a mixture of red and white crystals was observed. These were separated using methanol to give bis p-ethoxyphenyl ditelluride and 1,1,2,2, tetraphenylethane.

3.2.4. Preparation and Reaction of Organothallium Compounds.

3.2.4.1. Preparation of Thallium III Chloride.

This is the starting material used in the preparation of the organothallium compounds. Two methods were investigated for the preparation, the second was found to be the most suitable.

(i) Chlorine was bubbled through a suspension of thallium I chloride in water, at 60°C, until the solution was clear. Upon clearing the solution was heated for a further period to remove the water until crystallisation occured. This reaction produced $TlCl_3 . 3H_2O$. The water of crystallisation was removed by dissolving the trichloride in ether and standing over anhydrous copper sulphate for 2-3 days with occasional shaking.

(ii) 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 crystallisation allowed to take place. This procedure yielded anhydrous thallium III chloride. For storage the product was dissolved in dry ether and kept over anhydrous copper sulphate.

3.2.4.2. Preparation of Diphenyl Thallium Chloride.

This compound was prepared by the method of Goddard[115]. Equimolar quantities of diphenyl mercury and thallium III chloride were dissolved in ether and the two solutions mixed. A white precipitate was immediately formed which was allowed to stand overnight. The solution was then filtered and the solid extracted with benzene in a Soxhlet apparatus to remove unreacted diphenyl mercury and phenyl mercuric chloride, which is produced as a by-product. The residue left in the extraction thimble was recrystallised from pyridine to give diphenyl thallium chloride MP $>290^{o}$C, Lit.[115] $>290^{o}$C.

Analysis;

Found; C = 36.92 %, H = 2.61 %, Cl = 9.25 %

$C_{12}H_{10}TlCl$ requires; C = 36.68 %, H = 2.59 %, Cl = 9.25 %

3.2.4.3. Preparation of Diphenyl Thallium Bromide.[116]

A 500ml three necked flask was fitted with a dropping funnel, a reflux condenser, nitrogen inlet and a magnetic stirrer. To the flask were added 3.2g of magnesium metal and 15ml of dry ether. 23.8g of bromobenzene in 50ml dry ether was added dropwise over a period of twenty minutes. After the complete addition the solution was refluxed for ½ hour to complete the reaction. To this solution was added, dropwise a solution of 10.3g of thallium III chloride in 50ml dry ether. The mixture was cooled in ice during the addition and after the vigorous reaction had subsided the product was heated on a water bath for ½ hour, cooled and decomposed with hydrobromic acid. After filtering the dried residue was extracted with pyridine when transparent needles were obtained which did not melt at 290^{o}C.

Analysis;

Found; C = 32.4 %, H = 2.34 %, Br = 18.51 %

$C_{12}H_{10}TlBr$ requires; C = 32.8 %, H = 2.28 %, Br = 18.5 %

3.2.4.4 Preparation of Bis thiourea Tellurium Dichloride.

3.0g of tellurium dioxide were dissolved in concentrated hydrochloric acid and added to an aqueous solution of 6.12g of thiourea. The reaction gave an orange precipitate on mixing. The solid was filtered and shown to be $Te(SC(NH_2)_2)_2Cl_2$.

Analysis;

Found; C = 40.9 %, H = 2.35 %, N = 15.8 %, Cl = 20.0 %, S = 18.5 %

$C_2H_8Cl_2N_4S_2Te$ requires; C = 41.14 %, H = 2.28 %, N = 16.0 %,
Cl = 20.2 %, S = 18.25 %

3.2.4.5. Reaction of Diphenyl Thallium Chloride with Bis thiourea Tellurium Dichloride.

1.82g of diphenyl thallium chloride and 2.07g of $(tu)_2TeCl_2$ were suspended in dry benzene and refluxed for two hours and allowed to stand overnight. A lemon coloured solid remained which was filtered off and the benzene evaporated yielding colourless crystals. The colourless crystals sublimed at 210°C on recrystallising from methanol.

Analysis;

Found; C = 23.1 %, H = 1.52 %, Cl = 5.18 %, Te = 39.7 %

The yellow solid was identified as containing thiourea and unreacted starting materials.

3.2.4.6. Reaction of Ph_2TlCl with Tellurium.

2.64g of Ph_2TlCl and 0.76g of tellurium powder were mixed and suspended in benzene. The solution was refluxed for twelve hours to give a grey solid and a colourless benzene solution. Upon evaporation of the solvent colourless crystals subliming at 210°C and having the same composition as those from reaction 3.2.4.5. were produced. Unreacted diphenyl thallium chloride was extracted from the grey solid by hot pyridine.

The above reaction was repeated using THF as solvent where an increased yield was noted.

3.2.4.7. Reaction of Ph_2TlBr with tellurium.

This reaction was carried out under similar conditions as 3.2.4.6. The product was a buff coloured solid, MP = 130°C.

Analysis;

Found; C = 21.1 %, H = 1.42 %, Br = 12.1 %, Te = 36.9 %

3.3 RESULTS

A summary of the reactions in Sections 3.2.1., 3.2.2. and 3.2.3. are presented in Tables 3.1, 3.2. and 3.3.

Analysis

Elemental analysis for compounds used in the thallium study are shown in Table 3.4.

Infra-red Spectra

A comparison of the infra-red absorptions for Ph_2TlCl, Ph_2TlBr, $(PhTe)_2TlCl$ and $(PhTe)_2TlBr$ in the region 1600-250 cm^{-1} is shown in Table 3.5.

Mass Spectra

Mass spectra of $(PhTe)_2TlCl$ and $(PhTe)_2TlBr$ are presented in Table 3.6.

Summary of reactions carried out in order to metallate cyclopentadiene and ferrocene with tellurium.

Reaction	Reactants	Conditions (dry N_2)	Results
3.2.1.3.	Bu^n_3SnCp + $TeCl_4$	Addition in dry benzene at R.T. Reflux for:- (a) 30 mins (b) 1 hour (c) 2hours	Yellow sol^n + white solid Bu^n_3SnCl + Te
		No reflux	As above
		Addition at $-6^\circ C$	Red-yellow sol^n $\longrightarrow$ Bu^n_3SnCl + Te at R.T.
3.2.1.4	(i) 1:1:1 Fc, $AlCl_3$, $TeCl_4$	Reflux in dry CCl_4 for 20 m.	Ferrocene + Tellurium
	(ii) 2:2:1 of above	Reflux in dry CCl_4 for 20m.	Ferrocene + Tellurium
3.2.1.5.	Lithiated Ferrocene + $TeCl_4$	Addition of $TeCl_4$ in dry benzene at R.T. Reflux for 1½ hr.	Tellurium and Ferrocene

TABLE 3.1.

Summary of reactions involving the group $(CH_3)_3SiCH_2$-.

Reaction	Reactants	Conditions (dry N_2)	Results
3.2.2.3.	$(CH_3)_3SiCH_2Li$ + $TeCl_4$	(i) $TeCl_4$ added in benzene at 0°C. Reflux for 3 hr. (ii) Enclosed in Al foil	Yellow sol^n+ LiCl Sol^n gave white crystals, Dec. in air. Prod. Te + $((CH_3)_3SiCH_2)_2$ As above
3.2.2.4.	Yellow sol^n of Prod. + Br_2	Stand Overnight	Yellowish Crystals no Org. groups
3.2.2.5.	Yellow sol^n of Prod. + CH_3I	Room Temp.	No reaction as shown by NMR. No change after 24 hrs
3.2.2.6.	$(p\text{-}EtOPh)_2Te$ + $(CH_3)_3SiCl$	Reflux for 6 hrs in dry $CHCl_3$	No reaction as shown by NMR

TABLE 3.2

Summary of reactions involving the group $(C_6H_5)_2CH$-.

Reaction	Reactants	Conditions (dry N_2)	Results
3.2.3.2.	$(C_6H_5)_2CHLi$ + $TeCl_4$	(i) Addition of $TeCl_4$ in dry benzene at R.T. Reflux for 2 hrs (ii) Addition of $TeCl_4$ in dry benzene at -6°C (iii) Addition of $TeCl_4$ in dry benzene at -70°C	$((C_6H_5)_2CH)_2$ Tellurium LiCl As above As above
3.2.3.3.	PhTeLi + Ph_2CHCl	Ph_2CHCl in dry ether to Li reagent and stir for 2 hrs	$(C_6H_5)_2Te_2$ $((C_6H_5)_2CH)_2$ LiCl
3.2.3.4	p-EtOPhTeNa + Ph_2CHCl	Ph_2CHCl added to Na telluride reflux for 1 hr	$(p\text{-}EtOPh)_2Te_2$ $((C_6H_5)_2CH)_2$ NaCl
3.2.3.5.	Ph_2CHLi + $p\text{-}EtOPhTeCl_3$	Li reagent in dry THF added to a suspension of $p\text{-}EtOPhTeCl_3$ in THF at -70°C	$(p\text{-}EtOPh)_2Te_2$ $((C_6H_5)_2CH)_2$ LiCl

TABLE 3.3

Analyses of Compounds Prepared for the Thallium Study.

	FOUND							EXPECTED						
Reaction	C %	H %	N %	S %	Cl %	Br %	Te %	C %	H %	N %	S %	Cl %	Br %	Te%
3.2.4.2.	36.92	2.61	-	-	9.25	-	-	36.8	2.59	-	-	9.04	-	-
3.2.4.3.	32.40	2.34	-	-	-	18.51	-	32.8	2.28	-	-	-	18.5	-
3.2.4.4.	40.90	2.35	15.8	18.5	20.0	-	-	41.14	2.28	16.00	18.25	20.2	-	-
3.2.4.5.	23.1	1.52	-	-	5.18	-	39.7	22.2	1.54	-	-	5.47	-	39.3
3.2.4.6.	22.6	1.53	-	-	5.40	-	40.1	22.2	1.54	-	-	5.47	-	39.3
3.2.4.7.	21.1	1.42	-	-	-	12.1	36.9	20.8	1.44	-	-	-	11.5	36.8

TABLE 3.4.

3.2.4.2. = $(C_6H_5)_2TlCl$; 3.2.4.3. = $(C_6H_5)_2TlBr$; 3.2.4.4. = $((NH_2)_2CS)_2TeCl_2$

3.2.4.5. = $(C_6H_5Te)_2TlCl$; 3.2.4.6. = $(C_6H_5Te)_2TlCl$; 3.2.4.7. = $(C_6H_5Te)_2TlBr$.

Infra - red Spectra of Organothallium Compounds

1600 - 250 cm^{-1} (KBr Disc)

Ph_2TlCl	$(PhTe)_2TlCl$	Ph_2TlBr	$(PhTe)_2TlBr$
1570	1570	1580	1575
1480	1480	1485	1480
1470			
1435	1435	1440	1435
1330	1330	1330	1330
	1065	1075	1065
		1070	
1020	1020	1020	1020
1015			
1000	1000	1000	1000
995			
725	730	730	735
	725	725	725
690	690		690
650			
455	455	455	455
430		445	
335	330		

TABLE 3.5

Mass Spectra of $(C_6H_5Te)_2TlCl$ and $(C_6H_5Te)_2TlBr$.

$(C_6H_5Te)_2TlCl$		$(C_6H_5Te)_2TlBr$	
m/e	Assignment	m/e	Assignment
414	$(C_6H_5)Te_2^+$	154	$(C_6H_5)_2^+$
284	$(C_6H_5)_2Te^+$	77	$C_6H_5^+$
260	Te_2^+		
244	$C_6H_5TeCl^+$		
207	$C_6H_5Te^+$		
154	$(C_6H_5)_2^+$		
77	$C_6H_5^+$		

m/e values are based on ^{130}Te

TABLE 3.6.

3.4 DISCUSSION

One of the prime objectives of this piece of work was to study the effect on the physical and chemical properties of organotellurium compounds of introducing bulky groups onto tellurium. This work was prompted by the paper of Hoffman [42] dealing with bonding, substitutional site preferences and geometrical distortions in sulphuranes (See Introduction P. 18).

3.4.1.

Work carried out by Fitzsimmons on the Mössbauer spectra of the cation $(C_6H_6)Fe(C_5H_5)^+$ prompted us to look at the possible addition of cyclopentadiene to tellurium and undertake a ^{125}Te Mössbauer study. The addition of ferrocene to tellurium would also be of value in the study of bulky groups mentioned above.

The attempted introduction of cyclopentadiene onto tellurium followed a similar experimental pathway to that used by Green [117] to prepare cyclopentadiene derivatives of niobium and tantalum. This procedure was:-

i) The compound R_3SnCp, R = butyl, Cp = cyclopentadiene, was prepared from tributyltin chloride and sodium cyclopentadienide in dry tetrahydrofuran.

ii) This compound was then reacted with niobium pentachloride at room temperature in either toluene or methylene dichloride to give after ten minutes $Nb(C_5H_5)Cl_4$.

As mentioned in the experimental section no compound containing cyclopentadiene and tellurium could be isolated.

It is known that Bu_3SnCp will undergo radical decompositiion[118] to give $Bu_3Sn\cdot$ and $Cp\cdot$a possible reaction sequence with tellurium tetrachloride could be;

$$
\begin{aligned}
Bu_3SnCp &\longrightarrow Bu_3Sn\cdot + Cp\cdot \\
Bu_3Sn\cdot + Cl - TeCl_3 &\longrightarrow Bu_3SnCl + \cdot TeCl_3 \\
Bu_3Sn\cdot + \cdot TeCl_3 &\longrightarrow Bu_3SnCl + TeCl_2 \\
TeCl_2 &\longrightarrow Te + TeCl_4 \\
TeCl_4 &\xrightarrow{H_2O} TeOCl_2 + 2HCl \\
2\ Cp\cdot &\longrightarrow Cp_2
\end{aligned}
$$

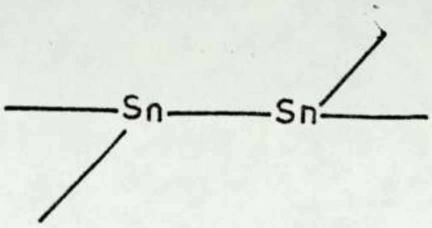
This would account for the presence of the white solid, $TeOCl_2$, tributyltin chloride and tellurium metal. Dicyclopentadiene was not observed but was probably lost on evaporation of the solvent.

The attempted addition of ferrocene to tellurium failed to give the desired product producing only tellurium metal and ferrocene.

3.4.2. Reaction of $(CH_3)_3SiCH_2$- with $TeCl_4$

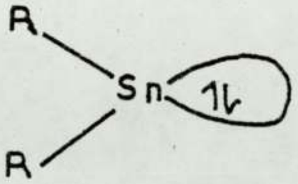
The ligand trimethylsilyl methyl, $(CH_3)_3SiCH_2$-, has been used extensively in transition metal chemistry to produce stable metal alkyls.[119] These compounds can be prepared by reaction of the metal chloride with the lithium or Grignard reagent and are moderately air sensitive although they are thermally stable.[111b] The transition metal alkyls are often relatively unstable and early views attributed this to either an inherently weak M - C bonds and / or to the ready homolysis of the bond to produce free radicals. Furthermore the presence of "stabalizing" π- acceptor ligands such as Cp^-, CO, R_3P were thought to be required. However the M - C bond is not particularly weak compared to the M - N$\equiv$ bond for example also the use of π- acceptor ligands is not always necessary to enhance stability. The simple alkyls $[(CH_3)_3SiCH_2]_4M$ have been prepared for M = Ti, Zr[111b], V and Cr . These are moderatly stable at room temperature, by contrast Me_4Ti decomposes significantly at $- 78^{\circ}$C. As well as the β elimination reaction for transition metal alkyls there is evidence that disproportionation (both inter and intra molecular) is important in the decomposition of tetramethyl titanium[120]. These two routes are of lower activation energy than the simple homolysis of the Ti - C bond. Bulky groups not containing β hydrogens (or leading to thermodynamically unstable olefinic fragments e.g. $Me_2Si{=}CH_2$) will clearly render such routes to decomposition unfavourable.

Recently Lappert et al[111a] have succeded in obtaining dialkyl tin II compounds using bulky groups such as $(Me_3Si)_2CH$-. The compound $((Me_3Si)_2CH)_2Sn$ reacts rapidly with chlorinated solvents but is moderatly soluble in hexane, benzene and diethyl ether. The solutions are extremely air sensitive but the solid is markedly more stable and can be handled briefly in air without significant decomposition. The X-ray crystal structure of the compound has been determined and is found to be a centrosymmetric dimer[111a].

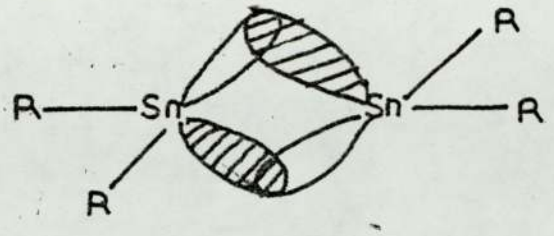


The tin - tin bond is similar to that found in hexaphenylditin, Sn_2Ph_6.

The crystals are found to be diamagnetic at room temperature. This was inferred from a) magnetic susceptability measurements b) sharp NMR spectra and c) the absence of ESR signals under anaerobic and dark conditions. The following bonding scheme was proposed for the monomer (vapour or solution) I and dimer (crystal) II. (An alternative valence bond representation is $R_2\underset{-}{S\ddot{n}}-\underset{+}{Sn}R_2 \longrightarrow R_2\underset{+}{Sn} - \underset{-}{S\ddot{n}}R_2$).



I



II

The dimer is envisaged as formed from the monomer by a pairing orbital overlap scheme involving the filled sp_xp_y non-bonding orbital of one monomer with the vacant p_z orbital of the other i.e. a weak metal-metal double bond is suggested.

As a result of this work and that carried out by Bradley[121] on the ability of bulky groups to stabalize low oxidation states it was decided to use the ligand $(CH_3)_3SiCH_2$- to try and form a stable telluride with a large equatorial bond angle. If this could be made then it would be possible to test Hoffman's Theory.

The reaction of tellurium tetrachloride with trimethylsilylmethyl lithium did not give the expected bis(trimethylsilylmethyl)tellurium dichloride as a stable solid. The only products isolated from the reaction were found to be tellurium metal and 2,2,5,5, tetramethyl 2,5 disilahexane, $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$.

The isolation of these materials would suggest the formation of the desired product which subsequently undergoes either thermal or photochemical induced radical decomposition thus;

$$((CH_3)_3SiCH_2)_2TeCl_2 \longrightarrow ((CH_3)_3SiCH_2)_2 + Te$$

The tellurides, if present, could not be isolated by reaction with elemental bromine, as the dibromide or methyl iodide, as the telluronium iodide.

During the writing of this thesis it was noted that Gysling [122] has recently succeded in preparing this telluride by a different route. The route chosen was the alkylation of sodium telluride with the alkyl chloride.

$$Te + KBH_4 \xrightarrow{NaOH/H_2O} Na_2Te$$

$$Na_2Te + 2\,(CH_3)_3SiCH_2Cl \longrightarrow Te\,[CH_2Si(CH_3)_3]_2 + 2\,NaCl$$

It was found that 2.5 equivalents of KBH_4 in 20 % aqueous sodium hydroxide completely reduced elemental tellurium to a colourless, very air sensitive solution of Te^{2-} after 3-5 hours at reflux temperature. Subsequent treatment of this solution with a solution of 2 equivalents of the alkyl halide in an equal volume of deaerated methanol gave an essentially quantitive yield of the dialkyl telluride. Gysling states that the diorganotellurides are stored under argon since they slowly deposit tellurium on prolonged storage in air. The telluride was converted to a solid derivative by halogen oxidation or complexation with certain transition - metal ions such as Pd II. These complexes showed no signs of decomposition on prolonged storage in air.

The crystal structure of $Pd(SCN)_2$ $[Te(CH_2CH_2CH_2Si(CH_3)_2]_2$ has been determined by Gysling and the C-Te-C bond angle is 93.04°, not an unexpected value as the bulky $Si(CH_3)_3$ group is too far removed from tellurium to effect the C-Te-C bond angle. Unfortunately the corresponding complex containing $(CH_3)_3SiCH_2$- has not been determined and in this case one would expect a much larger bond angle at the tellurium centre.

It is still felt that if $((CH_3)_3SiCH_2)_2TeCl_2$ is prepared by the above route one would be able to investigate Hoffman's Theory using this compound.

It is possible that the attempted preparation of the above telluride via the organolithium route succeded but due to a component in the reagent, possibly free radicals, decomposition was promoted. This is not unreasonable as organolithium reagents are known to produce free radicals in the pres ence of oxygen. Lappert has reported that the stable copper alkyl $(CH_3)_3SiCH_2Cu$, prepared from RLi and CuI in n-hexane/ether at -10°C as a crystalline solid, is stable as the solid or a solution in a hydrocarbon solvent when stored in the dark but on exposure to light decomposes. Photolysis in toluene or pyrolysis at 80°C, gave Me_4Si, $(Me_3Si)_2CH_2C_6H_4CH_3$, $(Me_3SiCH_2)_2$, $PhCH_2CH_2SiMe_3$ and $(PhCH_2)_2$. These results are in agreement with a free radical decomposition pathway.So it is feasible that $((CH_3)_3SiCH_2)_2Te$ would decompose in the pres ence of free radicals, possibly initiated by light, or heat, to the product isolated namely $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ and tellurium.

3.4.3. Reaction of Ph_2CH- group with Te containing Species.

Another bulky group that could be of use in this study is diphenylmethyl or benzhydryl and this has been studied in transition metal chemistry by Lappert and co-workers [123]. This investigation involved the reaction of some d^0 or d^1 metallocene dichlorides with the sterically hindered, β hydrogen free lithium alkyl $LiCHPh_2$, to give thermally stable crystals.

The reaction of diphenylmethyl lithium with tellurium tetrachloride, at various temperatures, resulted in the loss of the blood red colour of the lithium reagent and the isolation of lithium chloride, tellurium metal and 1,1,2,2, tetraphenylethane. The isolation of these products again suggests the presence of radical decomposition of the desired product, bis (diphenylmethyl) telluride (or the dichloride). More evidence for radical decomposition of the required product comes from the following experiments.

I) Reaction of PhTeLi and chlorodiphenylmethane gave only diphenyl ditelluride and 1,1,2,2, tetraphenylethane.

II) Reaction of p-EtOC_6H_4TeNa with chlorodiphenylmethane gave only the ditelluride and 1,1,2,2, tetraphenylethane.

III) Reaction of Ph_2CHLi with p-EtO$C_6H_4TeCl_3$ again gave only bis p-ethoxyphenyl ditelluride and 1,1,2,2, tetraphenylethane.

In I) the expected product would be $PhTeCHPh_2$ and the observed products would be formed by homolytic fission of the tellurium-alkyl bond, the weaker of the two Te-C bonds, and recombination of the two radicals formed. This radical decomposition could be initiated by heat or light thus,

$$PhTeCHPh_2 \xrightarrow{h\nu} PhTe\cdot + \cdot CHPh_2$$

$$2PhTe\bullet \longrightarrow Ph_2Te_2$$

$$2\bullet CHPh_2 \longrightarrow Ph_2CHCHPh_2$$

Similarly in reaction II) and III) the expected products would undergo decomposition thus;

$$\text{II) p-EtOC}_6H_4TeCHPh_2 \xrightarrow{h\nu} \text{p-EtOC}_6H_4Te\bullet + \bullet CHPh_2$$

$$2\ \text{p-EtOC}_6H_4Te\bullet \longrightarrow \text{p-EtOC}_6H_4TeTeC_6H_4\text{OEt-p}$$

$$2\ Ph_2CH\bullet \longrightarrow Ph_2CHCHPh_2$$

$$\text{III)}\quad (p\text{-EtOC}_6\text{H}_4)(\text{Ph}_2\text{CH})\text{TeCl}_2 \xrightarrow{h\nu} p\text{-EtOC}_6\text{H}_4\text{Te}\bullet + \text{Ph}_2\text{CH}\bullet + (\text{Cl})$$

$$2\ \text{Ph}_2\text{CH}\bullet \longrightarrow \text{Ph}_2\text{CHCHPh}_2$$

$$2\ p\text{-EtOC}_6\text{H}_4\text{Te}\bullet \longrightarrow p\text{-EtOC}_6\text{H}_4\text{TeTeC}_6\text{H}_4\text{OEt-}p$$

This type of radical decomposition is known for a similar compound, dibenzyl telluride and the corresponding dibromide or dichloride all of which deposit tellurium and dibenzyl on standing.[71] The halide derivatives are, however more stable than the telluride.

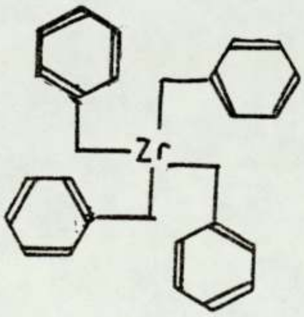
It has been noted[124] that dibenzyl telluride will react with methyl iodide to give the expected telluronium salt, $(PhCH_2)_2CH_3TeI$, which is stable and does not decompose on standing.

An explanation is therefore sought as to why the telluride but not the telluronium salt should decompose on standing.

One explanation may be some form of $n \rightarrow \pi^*$ transition available in the telluride but not the telluronium salt, possibly between a tellurium p orbital and the π system of the aromatic ring. i.e. possibly some type of internal charge - transfer complex.

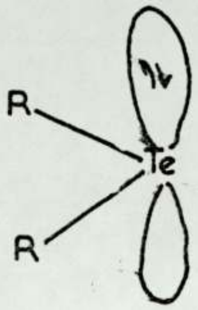
Evidence of interaction between metals and aromatic π systems comes from the following.

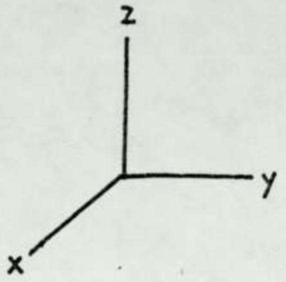
The crystal structure of tetrabenzyl zirconium has been determined[125] and is shown below



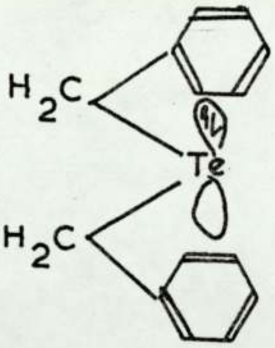
All seven carbon atoms of the benzyl groups are coplanar and nearly perpendicular to the appropriate zirconium - carbon bond. The average angle at the methylene carbon atom is small, $Zr-\hat{C}-C$ average 92°, less than the usual angle at $-CH_2-$. Associated with this the atoms of the aromatic ring bonded to the methylene carbon is closer to the metal than would be expected (av. Zr-----C is 2.74 Å). Thus distortion can be accounted for by an interaction between the aromatic ring and the metal. In the case of tetrabenzyl tin the $Sn-\hat{C}-C$ angle is 103° and no evidence of an interaction is apparent from the X-ray structure, however NMR evidence[126] suggests an interaction. The arguement given is as follows. The benzyl tin derivatives can be considered as derivatives of toluene where a H atom has been replaced by the group SnX_3. The $(Bz)_3Sn$ group will be more positive than the hydrogen although the difference will not be large. The electron inductive effect would thus shift the phenyl group signals of $(Bz)_4Sn$ to higher field than those of toluene, but this shift should be small. The shift of the m-, p- and o- protons is in the right sence. For o- protons the shift is much too large to be attributed to the rather small change in the inductive effect. The explanation is that through orbital interaction between the tin atom and the π electron system of the ring. Only changes in the π electron density of the phenyl ring could be considered as a cause of the relatively large shifts of the o- protons.

As it is known that interactions do occur between aromatic rings and metals in metal- benzyl compounds it is not unreasonable to suggest a similar interaction between tellurium and the aromatic ring in dibenzyl telluride and bis(diphenylmethyl)telluride. The structure of a telluride is as follows with two R groups in the "equatorial" position and a p orbital in the z direction.



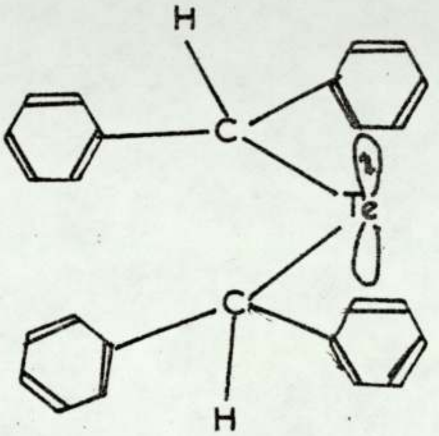


Now in the case of dibenzyl telluride the structure would be,



and thus it would be possible for some type of interaction to occur between the Te p_z orbital and the aromatic ring. In the case of the telluronium salt the Me and I may occupy the axial position and thus remove the p_z orbital and prevent it interacting with the aromatic ring. A crystal structure or a detailed NMR study of dibenzyl telluride would obviously be needed to confirm this hypothesis.

If this explained the instability of dibenzyl telluride then there is no reason why it should not do the same for bis(diphenyl methyl)telluride, or the mixed tellurides. A structure which might be envisaged is



From the above evidence an internal charge transfer complex is proposed for the telluride which might be activated by $h\nu$. The ground state of such a complex would have an electron in the p_z orbital of tellurium and in the excited state in the π^* orbital of the aromatic ring and it is postulated that the excited state is readily accessable and is the precursor for radical decomposition. An example of TeII acting as an electron donor is in its reaction with TCNQ[127] where a deep violet complex is obtained with cyclic tellurides. This compound is paramagnetic.

If the p_z orbital of tellurium can be removed then stability may be conferred on the molecule, e.g. dibenzyl telluride is unstable but the dichloride and the methyl telluronium salt are stable, also complexation of the telluride with a metal such as HgII or CuI would give the same result.

Returning to the work on trimethylsilylmethyl derivatives of tellurium a similar sort of mechanism can be postulated for the instability of the telluride, in this case a possible interaction between the tellurium p_z orbital and the vaccent 3d orbitals on the silicon. Gysling[122] reported the stability of the dichloride and the Pd II complex of the telluride and the relative instability of the telluride and this is in agreement with the above arguement, i.e. the former removes the free tellurium p_z electron. Lappert's work on the silyl Sn II derivatives (described in the preceeding section) also lends weight to the arguement. He reports that $((Me_3Si)CH)_2Sn$ is more stable as a solid than either in solution or the vapour phase and showing the compound to be dimeric in the solid state. The bonding scheme proposed the interaction of a filled sp_xp_y orbital of one molecule with the empty p_z orbital of a second molecule.

It is believed that organolithium, and Grignard, reagents in the presence of oxygen produce free radicals and these may help in the decomposition of the expected tellurides of the present study. Therefore if the preparation of the diphenyl methyl telluride is to be accomplished the preparation must not involve a source of free radicals as this will lead to decomposition. Alternatively if methyl iodide could be added at the beginning of the reaction then it may be possible to isolate the desired telluronium salt. Also mercuric chloride may be useful in this respect as this is known to coordinate with tellurides.

3.4.4. Reaction of Ph_2TlX with Tellurium Metal.

As a result of difficulties found with the above work another method was sought for the introduction of organic groups onto tellurium.

Organothallium reagents were decided upon to try and achieve this.

Diorganyl thallium halides are among the most stable organometallic compounds known, they are unaffected by water and oxygen and many resemble the isoelectronic diorganylmercury compounds. Organothallium compounds have been used in organometallic synthesis previously. In these reactions reductive cleavage of the thallium-carbon bond occurs with transfer of the organic group to the recipient metal.

Several reactions have been reported with metallic mercury and tin II halides, e.g. dialkyl thallium chloride reacts with tin II halides to produce a tin IV derivative.[112]

$$SnCl_2 + R_2TlCl \longrightarrow R_2SnCl_2 + TlCl$$

$$Ph_2TlBr + Hg \longrightarrow R_2Hg + TlBr$$

Similarly bis(pentafluorophenyl)thallium bromide has been shown to react with a variety of metal halides to give thallium I bromide and the pentafluorophenyl derivative of an oxidation state two higher than that of the metal in the original compound.[128a]

$$\text{e.g. } (C_6F_5)_2TlBr + SnCl_2 \longrightarrow (C_6F_5)_2SnCl_2 + TlBr$$

and also with zero valent transition metal complexes,[128b]

$$\text{e.g. } (Ph_3P)_2Ni(CO)_2 + (C_6F_5)_2TlBr \longrightarrow (Ph_3P)_2Ni(C_6F_5)_2$$

Reactions of a variety of elements with $(C_6F_5)_2TlBr$ to give the corresponding pentafluorophenyl derivatives have been demonstrated, e.g. $(C_6F_5)_2Hg$, $(C_6F_5)_4Sn$, $(C_6F_5)_3P$, $(C_6F_5)_2S$ and also $(C_6F_5)_2Te$ by heating the reactants in a sealed evacuated tube at 190°C for three days [82]

Diphenyl thallium chloride has been shown to react with tellurium tetrachloride to give diphenyl tellurium dichloride in 94 % yield, but this not an oxidation - reduction reaction [76]

$$2\ Ph_2TlCl + TeCl_4 \longrightarrow 2\ PhTlCl_2 + Ph_2TeCl_2$$

It was hoped during the course of this work to utilize the reductive-cleavage of the Tl-C bond to form tetraorganotellurium compounds as follows,

$$R_2'Te + R_2TlCl \longrightarrow R_2R_2'Te + TlCl$$

Initially a reaction was sought which would give a stable, well known Te IV species whereby one could test the validity of the thallium reagant to undergo reductive-cleavage of Tl-C bonds resulting in a transfer of organic groups to tellurium.

A likely candidate for this seemed to be $(tu)_2TeCl_2$, tu = thiourea, which is a stable Te II compound and would be expected to give diphenyl tellurium dichloride, a well known product, and thallium I chloride, possibly as the thiourea complex, on reaction with diphenyl thallium chloride.

Unfortunately this reaction did not give the desired product but a compound with the analysis $C_{12}H_{10}Te_2TlCl$. This compound was also prepared by the reaction of tellurium metal with the organothallium reagent in benzene or THF. The corresponding bromine containing product was obtained from the reaction of diphenyl thallium bromide and tellurium metal in the same solvents.

The two products differed in appearence, the chloride existing as plates subliming at 210°C and the bromide as a fluffy mass melting at 130°C (no sublimation). This may indicate that the compounds have different structures.

A possible formulation of the two compounds is $(C_6H_5Te)_2TlX$ where X = Cl or Br. and the experimental data can be interpreted based on this structure. The two products were insufficiently soluble to enable molecular weights to be determined and found to be non electrolytes in methanol.

From the formulation it appears that tellurium has inserted in the thallium - carbon bond. This type of reaction is known for other types of organometallic reagents, e.g. the insertion of tellurium metal into sodium acetylides (See Introduction P. 30). Also tellurium will insert between the magnesium and carbon atoms of a Grignard reagent. Petragnani [51] obtained a pasty substance upon addition of petroleum ether to a solution containing phenyl bromomagnesium telluride which had been prepared from a diorganyl ditelluride and phenyl magnesium bromide.

$$R_2Te_2 + C_6H_5MgBr \longrightarrow RTeC_6H_5 + RTeMgBr$$

The highly unstable precipitate was easily hydrolysed and oxidised.

It seems that the $(tu)_2TeCl_2$ is decomposing to tellurium metal and then inserting in the Tl-C bond. To test this hypothesis the reaction was repeated using tellurium metal and diphenyl thallium chloride again using benzene as the solvent. The same product was obtained. In view of the apparent similarity to a Grignard reagent the experiments were further repeated using THF as the solvent where the same product was produced only in higher yield.

3.4.4.1. Discussion of Possible Structures of the new Tellurium Compounds with Thallium.

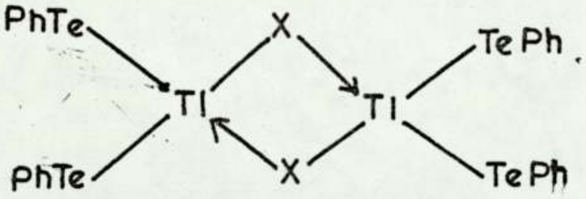
Three possible structures may be suggested for these compounds, two of which are dimers and the third monomeric. The limited solubility of the compounds in solvents suitable for molecular weight determinations makes the problem of differentiation of the monomeric and dimeric structures more difficult and so other methods will have to be relied upon.

It seems that from their appearance the chloride and bromide have different structures, also the fact that one, the chloride, sublimes whilst the bromide has a definite melting point indicates this. A difference in structure is also indicated from mass spectral evidence presented in Table 3.6.

The colour of the compounds, white for the chloride and off white for the bromide suggests that a Te-Te or Te-X bond is not present as this would lead to coloured products. The latter point is borne out by the absence of any absorptions in the infra-red spectrum, 400-200 cm^{-1}, of the chloride.

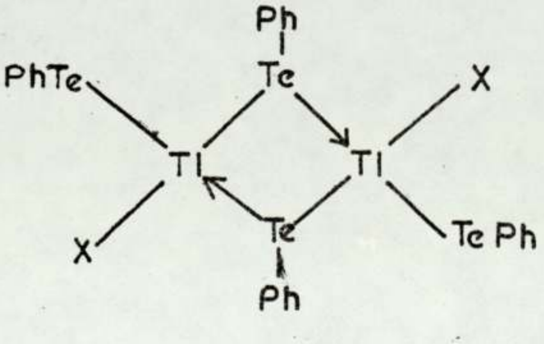
The three possible structures are shown below,

I) Dimer involving halogen bridges between thallium atoms



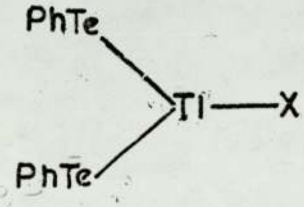
This type of structure is known for the compound $(C_6F_5)_2TlBr$ [129]

II) A dimer involving bridging PhTe groups



This type of structure is known for the compounds $(CH_3)_2TlX$ where X = OMe, OBu, OSiMe$_3$, OPh, SMe, SPh, SePh.[130]

III) A monmeric structure involving three coordinate thallium



A similar structure is known for $PhTlCl_2$ [131]

3.4.4.2. Infra-red Evidence.

The infra-red spectra of the two compounds are shown in Table 3.5 and are very similar in appearence, the only difference being a band at 330 cm^{-1} in the case of the chloride. This band is assigned as a Tl-Cl stretching frequency.

If $(PhTe)_2TlCl$ has the dimeric structure as shown in I) the symmetry of the skeleton is D_{2h} and several examples are known with this type of structure e.g. Ga_2Cl_6 [132] where the bridging Ga-Cl stretching frequency is at 365 cm^{-1}. For a Tl-Cl bridging stretching frequency one would expect a lower value and this is found for the $(C_6F_5)_2TlCl$ dimer where the bands at 215 and 139 cm^{-1} have been associated with the Tl-Cl bridging vibrations.

If the structure is as in II) the symmetry of the skeleton would be C_{2h}. The eighteen fundamental vibrations of the

C_{2h} skeleton are related to those of the D_{2h} skeleton by the relationship:

$$\begin{tikzcd}[column sep=small]
D_{2h} & \underset{(\nu_1\nu_2\nu_3\nu_4)}{4a_g} \arrow[d] & \underset{(\nu_6\nu_7)}{+\ 2b_{1g}} \arrow[dr] & \underset{(\nu_{11}\nu_{12})}{+\ 2b_{2g}} \arrow[dll] & \underset{(\nu_{15})}{+\ b_{3g}} \arrow[dl] & \underset{(\nu_5)}{+\ a_u} \arrow[d] & \underset{(\nu_8\nu_9\nu_{10})}{+\ 3b_{1u}} \arrow[dr] & \underset{(\nu_{13}\nu_{14})}{+\ 2b_{2u}} \arrow[dll] & \underset{(\nu_{16}\nu_{17}\nu_{18})}{+\ 3b_{3u}} \arrow[dl] \\
C_{2h} & 6a_g & + & 3b_g & + & 3a_u & + & 6b_u &
\end{tikzcd}$$

where the numbering of the vibrations for the A_2B_6 skeleton is that used by Nakamoto[133]. The IR active modes for the C_{2h} structure (a_u and b_u) are thus derived from ν_5, ν_8, ν_9, ν_{10}, ν_{13}, ν_{14}, ν_{16}, ν_{17} and ν_{18} of the D_{2h} case. The ν_{13} vibration is a stretching of the bridging bonds whereas ν_3 and ν_{10} are stretching of the terminal bonds. Thus for the $(PhTe)_2TlCl$ dimer with bridging PhTe groups there should be one Te-Tl stretching and one Tl-Cl stretching frequency. This Tl-Cl stretching frequency would be at a higher value than that in the bridging Tl-Cl situation above. If this structure were correct the thallium is in a four coordinate position and one would expect the Tl-Cl stretching frequency at around 300 cm^{-1}[134].

If $(PhTe)_2TlCl$ had the structure as in III) the skeleton would be of C_{2v} symmetry if the C_2TlCl skeleton is planer if not the symmetry would be C_s. Again one Tl-Cl stretching frequency would be expected in the region of 300 cm^{-1}. The figure of 330 cm^{-1} is rather high for four coordinate thallium e.g. $TlCl_4^-$ has bands at 305, 293 and 281 cm^{-1}[134], but would be reasonable for three coordinate thallium, (The lower the coordination number the higher the metal - halogen stretching frequency occurs). The compound $PhTlCl_2$ is believed to be monomeric in the solid state (and solution) and shows Tl-Cl stretching frequencies at 342 and 335 cm^{-1}. The figure of 330 cm^{-1} for the compound $(PhTe)_2TlCl$ is in good agreement with this so it is believed, on the basis of IR evidence that this contains three coordinate thallium and that the structure is monomeric.

No band is observed in the region 400-200 cm^{-1} of the spectrum of the bromide. If the bromide had a similar structure one would expect to see the Tl-Br stretching frequency at approximately ν_{Cl} x 0.76 i.e. 250 cm^{-1}. Again for the structure shown in II) one would expect the Tl-Br stretching frequencies for four coordinate thallium in the region of 230 cm^{-1}. For structure I) the Tl-Br stretching frequency for a bridging structure would be at a lower frequency than the Tl-Br terminal frequency. This would be out of range of the spectrometer used. Based on this evidence it is possible that the bromide has a greater molecular complexity than the chloride e.g. the dimeric structure shown in I).

3.4.4.3. Mass Spectral Evidence.

The mass spectra of the two compounds differ considerably, that of the bromide being much simpler than the chloride. This could imply a difference in structure between the two compounds (It could also be due to differences in the volatility of the two compounds). The main features of the two spectra are shown in Table 3.6.

The spectra of the chloride is essentially that of diphenyl ditelluride, but a ditelluride group is obviously not present in the compound because of the absence of colour, therefore there must be two PhTe groups in close proximity. This can be accounted for by the monmeric structure in I), the structure may be weakly associated in the solid state and this would explain the presence of $PhTeCl^+$. Two possible reactions could be envisaged for the decomposition in the Mass Spectrum

$$\begin{tikzcd} \text{i) } e + (PhTe)_2TlCl \arrow[r] & (PhTe)_2TlCl^+ + 2e \arrow[d, "\text{v. fast}"] \\ & (Ph_2Te_2)^+ + TlCl \end{tikzcd}$$

$$\begin{tikzcd} \text{or ii) } (PhTe)_2TlCl \arrow[r, "\text{heat}"] & Ph_2Te_{2\,(g)} + TlCl_{(s)} \arrow[d, "e"] \\ & (Ph_2Te_2)^+ + 2e \end{tikzcd}$$

The spectrum of the bromide shows only two major peaks at m/e 154 and m/e 77 attributable to Ph_2^+ and Ph^+. There is no evidence of tellurium or bromine in the spectrum. The structure postulated from infra red evidence i.e. bridging bromine will account for this observation with the formation of an involatile Te-Tl-Br compound

3.4.4.4. Mössbauer Spectroscopy.

Samples have been forwarded to Simon Fraser University, British Columbia, for Mössbauer spectra to be recorded but at the time of writing no result had been received.

One would hope that the result may distinguish between the three proposed structures, e.g. for the structure shown in I) one type of tellurium site is expected and a value of 9-10 mm sec^{-1} for Δ Q, comparable with tellurides, this would also be the case for structure III).

Structure II) would be expected to show two tellurium sites with $\Delta Q \approx 5$ mm sec^{-1} for the bridging tellurium comparable to telluronium salts and 9-10 mm sec^{-1} for the terminal TePh group.

3.4.4.5. Conclusions

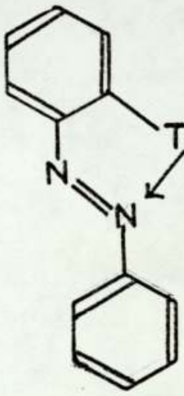
Based on infra-red and mass spectral data compounds with the empirical formula $C_{12}H_{10}Te_2TlX$ where X = Cl or Br are formulated as $(C_6H_5Te)_2TlX$ with the chloride having a monomeric structure with three coordinate thallium and the bromide having a dimeric structure with bridging bromine atoms as opposed to PhTe bridges.

CHAPTER FOUR

ATTEMPTED o- METALLATION REACTIONS WITH TELLURIUM

4.1. Introduction

One of our group has recently prepared the compound (phenyl azophenyl-2C,N') tellurium II chloride [83], and an attempt has been made to interpret the ^{125}Te Mössbauer spectrum of the compound. The Mössbauer data are given below:

	δ mm sec^{-1}(VsCu/Sb)	Δmmsec^{-1}	$\Gamma_{\frac{1}{2}}$
	0.63 ± 0.05	11.76 ± 0.05	6.6
p-$EtOC_6H_4TeI_2^-$	0.46 ± 0.05	13.93 ± 0.05	7.1

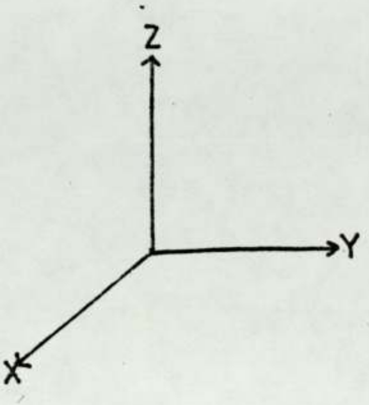
For the ^{125}Te transition the nuclear radius term, $\Delta R/R$, is positive and thus δ, the Chemical Isomer Shift, becomes more positive as the s electron density at the nucleus $|\psi_s(0)|^2$ increases. Removal of 5p electron density from tellurium will result in a deshielding of the s electron from the nucleus and an increase in $|\psi_s(0)|^2$, while removal of s electrons will have a more marked effect in directly decreasing $|\psi_s(0)|^2$.

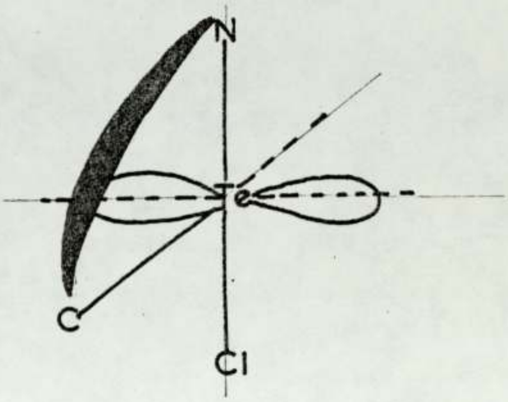
The value of the chemical isomer shift for the azobenzene derivative of tellurium, 0.63 mm sec^{-1} is relatively large compared with other TeII compounds e.g. Ph_2 Te - 0.18 mm sec^{-1} [90], and is also larger than the value of 0.46 mm sec^{-1} obtained for the anion p-$EtOC_6H_4TeI_2^-$.

Jones et al [90] have previously developed a model to account for the quadrupole splitting of a wide variety of organotellurium compounds using the Townes and Dailey Theory [90]. This theory suggests that the electric field gradient, in ^{125}Te, derives predominantly from any imbalance in the tellurium 5p orbital population and that the quadrupole coupling constants are linearly related to the p-orbital imbalance. The model proposed by Jones [90] is that bonding is assumed to occur predominantly through the tellurium 5p orbitals and that this explains the general features of the splitting data obtained for tellurium compounds.

For a compound of the above type a quadrupole splitting of 14 mm sec^{-1} is expected on the basis of the above model. The value of 13.93 for p-$EtOC_6H_4TeI_2^-$ agrees very well with this but that for the azobenzene compound, 11.76, deviates far more from the "calculated" value than has been the case for any other organotellurium compound considered to date i.e. at this juncture there is no reason to question the general validity of the Jones model.

This value of 11.76 mm sec^{-1} means therefore that there is another mechanism for withdrawing p electron density from tellurium. It is possible that the tellurium p_y orbital (See Fig) could interact with the π orbital associated with the chelate ring.



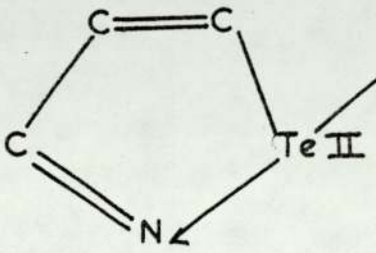


Such delocalization would, if it did occur, decrease the p-orbital imbalance (and hence lower in comparison with a situation where the mechanism does not exist e.g. p-EtOC$_6$H$_4$TeI$_2^-$). This delocalization of the p electron onto the chelate ring would further deshield the tellurium s electron and hence enhance δ

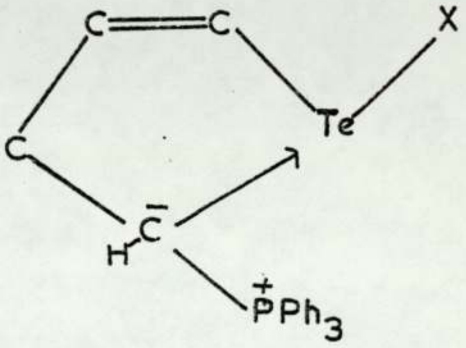
Also the Te-C bond length, 2.04 Å, is the shortest known in an organotellurium compound. This could imply a certain amount of double bond character as would be expected if an interaction between the Te p orbital and the π system of the chelate ring did occur.

It was hoped, as part of the present study, to enlarge on this work, and study a different type of unsaturated chelate ring and also a partially saturated system.

The reaction of mercurated azobenzene with $TeCl_4$ gives the transmetallated product which could be regarded as being formed by o- metallation of the azobenzene with tellurium. Two common groups of compounds would probably satisfy the necessary conditions for this reaction namely Schiff Bases and Ylids both of which are known to undergo o-metallation.



Chelate ring formed with Schiff Base and Te

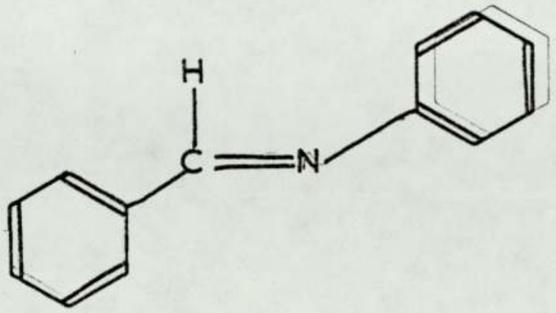


Chelate ring formed with Ylid and Te

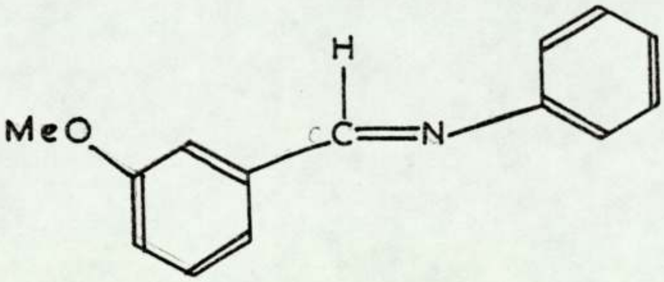
The Schiff Base has a potentially planar structure thus allowing an interaction of a tellurium p orbital and the π system of the chelate ring. If an interaction took place then one would expect the Mössbauer parameters to be comparable with those found for azobenzene and possibly a shorter Te-C bond length.

The Ylid has a non planar structure and there is no π system on the chelate ring. Thus one would not expect any kind of interaction with tellurium. This compound should give a quadrupole splitting constant of about 14 mm sec $^{-1}$ and have a normal Te-C bond length.

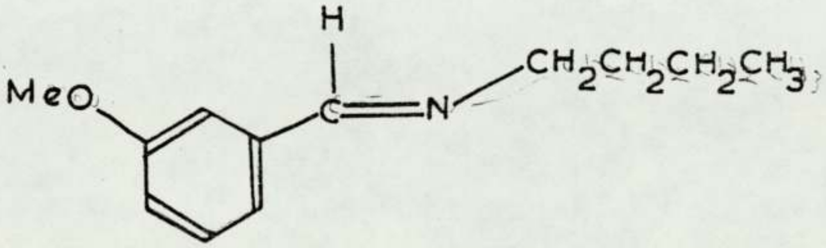
The three Schiff Bases chosen are shown below:



N- Benzilidene aniline



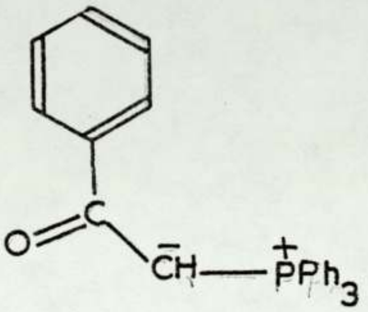
N- (3 methoxybenzilidene)aniline



N- (3 methoxybenzilidene) n-butylamine

The 3- methoxy derivatives were chosen because it is known that this group promotes substitution of $TeCl_3$ in a para position and would hopefully encourage the o-metallation by tellurium. An alkyl derivative was chosen to see if the basicity of the nitrogen affected the reaction.

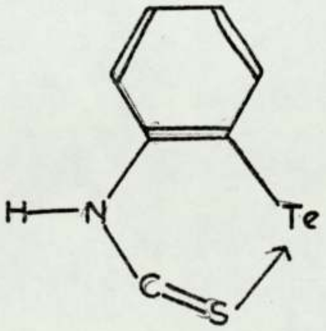
The chosen Ylid was phenacylidene triphenylphosphorane



Phenacylidene triphenylphosphorane

This ligand is relatively easy to prepare and is known to undergo o-metallation.[105]

On searching the chemical literature another possible candidate for o-metallation was N-phenylthiourea, where the chelate ring would be as shown below.



This would produce a six membered ring with the possibility of conjugation of the p-orbital on tellurium with the π system of the double bonds and the lone pair of the nitrogen. The compound $(PhNHCSNH_2)_2TeCl_2$ is known to loose HCl on dissolution in polar organic solvents [108] and it may be that o-metallation has taken place.

4.2. Experimental

4.2.1. Preparation and Reaction of Phosphorus Ylids with $TeCl_4$

4.2.1.1. Preparation of $(Ph_3P\text{-}CH_2COC_6H_5)^+Br^-$

This was prepared by the method of Ramirez[135]

8.35 g (0.04M) of phenacyl bromide was added to a chloroform solution of 10.89g (0.04M) triphenylphosphine. A reaction took place with the evolution of heat. After complete addition of the phenacyl bromide and stirring for ¼ hour the solution was filtered into one litre of anhydrous ether. The resulting precipitate was collected and dried. MP. = 270°C, Lit mpt = 267-9°C.

Analysis;

Found; C= 68.1 %, H = 4.5 %, Br = 18.0 %, P = 6.6 %.

$C_{26}H_{22}BrOP$ requires; C = 67.7 %, H = 4.6 %, P = 6.7 %, Br = 17.6 %.

4.2.1.2. Preparation of phenacylidene triphenylphosphorane - $Ph_3P{=}CHCOC_6H_5$.

7.5 g of the above were added to 300ml of a 10 % aqueous solution of sodium carbonate and shaken for 15 hours. This mixture was then filtered and the insoluble portion taken up in 200 ml of hot benzene. Addition of petroleum ether to this solution afforded 5.8g of the required product. MP . = 176 °C, Lit. MP = 178-80 °C.

Analysis;

Found; C = 82.3 %, H = 5.3 %, P = 7.9 %.

$C_{26}H_{21}OP$ requires; C = 82.1 %, H = 5.5 %, P = 8.1 %.

4.2.1.3. Reaction of Phenacylidene Triphenylphosphorane with Tellurium Tetrachloride.

To a stirred solution of 1.84 g (0.007M) $TeCl_4$ in 50 ml dry chloroform contained in a 100 ml round bottom, two necked flask, fitted with a nitrogen inlet and a reflux condenser, were added 2.6 g (0.007M) of the phosphorus ylid prepared as above. The resulting mixture was stirred and heated under reflux for three hours. The solution began to turn green after about 40 minutes.

After the three hours reflux time the solvent was removed on a rotary film evaporator to give a green oil. On mixing with ether the green oil gave a yellow solid melting at 120°C.

Analysis;

Found; C = 48.75 %, H = 3.7 %, P = 6.8 %, Cl = 26.6 %.

This reaction was repeated under various reflux times and gave the same product.

4.2.2. Preparation and Reaction of Schiff Bases with Tellurium Tetrachloride and Tellurium Tetrabromide.

4.2.2.1. Preparation of N-benzilidene aniline.

10.6 g (0.1M) of benzaldehyde were added to 9.3 g (0.1M) of freshly distilled aniline in methanol. An immediate reaction took place and the product crystallised on standing, MP = 31°C.

Analysis;

Found; C = 85.9 %, H = 6.1 %, N = 7.6 %.

$C_{13}H_{11}N$ requires; C = 86.1 %, H = 6.0 %, N = 7.7 %.

4.2.2.2. Preparation of N-(3methoxybenzilidene)aniline.

13.6 g of 3 methoxybenzaldehyde were added to 9.3 g of freshly distilled aniline. An immediate reaction took place. The reaction mixture was heated on a water bath (at 100°C) for one hour after which time the reaction mixture was allowed to cool to room temperature. The aqueous and organic layers were separated and the latter dissolved in benzene and dried over anhydrous magnesium sulphate. The benzene was then removed on a rotary film evaporator to give the desired product. The specimen was checked for purity by infra-red and NMR spectroscopy.

Analysis;

Found; C = 80.4 %, H = 6.4 %, N = 6.6 %.

$C_{14}H_{13}NO$ requires; C =79.6 %, H =6.16 %, N = 6.6 %.

4.2.2.3. Preparation of N-(3 methoxybenzilidene)butylamine.

13.6 g (0.1M) of 3-methoxybenzaldehyde were added to 7.3g of n-butylamine. The reaction mixture was heated on a water bath (100°C) for one hour after which time the reaction mixture was allowed to cool. The aqueous and organic layers were separated and the latter dissolved in benzene and dried over anhydrous magnesium sulphate. The benzene was removed on a rotary film evaporator to give the desired product. The specimen was checked for purity by infra-red and NMR spectroscopy.

Analysis;

Found; C = 76.0 %, H = 8.7 %, N = 7.2 %.

$C_{12}H_{17}NO$ requires; C = 75.4 %, H = 8.9 %, N = 7.3 %.

4.2.2.4. Reaction of N-(3 methoxybenzilidene)aniline with $TeCl_4$ in Chloroform.

4.7 g of N-(3 methoxybenzilidene)aniline and 5.4 g of $TeCl_4$ were added to 20 ml of dry chloroform. The reaction mixture was stirred and refluxed for two hours. During the course of the reaction the solids dissolved to give a brown solution. Yellow crystals were deposited from this reaction mixture during the period of the reflux. After the reaction time 5.0g of the yellow solid was filtered off and dried in vacuum, MP = 120°C.

Analysis;

Found; C= 34.8 %, H = 3.1 %, N = 3.0 %, Cl = 23.5 %.

4.2.2.5. Reaction of $TeCl_4$, aniline and 3-methoxybenzaldehyde.

2.72 g of 3-methoxybenzaldehyde, 5.4 g tellurium tetrachloride and 1.8 g freshly distilled aniline were mixed together in benzene. An immediate reaction took place producing a yellow solid, 9.2g identical to the above. MP = 120 °C.

Analysis;

Found; C = 34.7 %, H = 3.1 %, N = 3.0 %, Cl = 24.0 %.

4.2.2.6. Reaction of N-benzilideneaniline with $TeCl_4$.

20 ml of benzene containing 2.69 g of $TeCl_4$ were added to 1.81 g of the Schiff base in 5 ml of dry benzene. A yellow precipitate was produced immediately this was filtered off and washed repeatedly with dry benzene, MP = 138°C.

Analysis;

Found: C = 36.9 %, H = 2.8 %, N = 3.2 %, Cl = 24.5 %.

4.2.2.7. Reaction of N-(3 methoxybenzilidine)aniline with $TeCl_4$.

20 ml of benzene containing 2.69 g of $TeCl_4$ were added to 2.11 g of the Schiff base in 5 ml dry benzene. A yellow precipitate was immediately formed, This was filtered off and washed repeatedly with dry benzene, MP = 119°C.

Analysis;

Found; C = 35.0 %, H = 3.1 %, N = 3.0 %, Cl = 22.5 %.

4.2.2.8. Reaction of N-(3 methoxybenzilidene)butylamine with $TeCl_4$.

20 ml of benzene containing 2.69 g of $TeCl_4$ were added to 1.91 g of the Schiff base in 5 ml of dry benzene. A yellow precipitate was produced after two days.This was filtered and washed with dry benzene, MP = 99-100°C.

Analysis;

Found; C = 34.0 %, H = 4.2 %, N = 3.4 %, Cl = 24.9 %.

4.2.2.9. Reaction of N-(3 methoxybenzylidene)aniline with $TeBr_4$.

2.11 g of Schiff base in 5 ml of benzene were added to 4.47g of $TeBr_4$ (Prepared from tellurium powder and bromine) in 20 ml of dry ether. An orange precipitate was formed which was filtered off and dried, MP = 130 °C.

Analysis;

Found; C = 32.5 %, H = 2.9 %, N = 2.8 %, Br = 44.0 %.

4.2.2.10. Reaction of N-benzylideneaniline with $TeBr_4$.

1.81 g of Schiff base in 5 ml of benzene were added to 4.47 g of $TeBr_4$ in 20 ml of dry ether. An orange precipitate was formed which was filtered off and dried, MP = 170°C.

Analysis;

Found; C = 32.1 %, H = 2.5 %, N = 2.9 %, Br = 47.4 %.

4.2.2.11. Attempted mercuration of N-(3 methoxybenzilidene) aniline.

A mixture of 5.2 g of the Schiff base and 7.75 g $Hg(OCOCH_3)_2$ in 50 ml of dry methanol was stirred and refluxed under a nitrogen atmosphere for 5 hours. After about thirty minutes the solution turned a reddish orange colour. After the reaction period the solution was allowed to cool to room temperature. 3 g LiCl in hot dry methanol was added and the mixture was stirred for 15 mins. The resulting solution was added to water and a buff coloured solid was filtered off, MP 137-42°C. The solid was found to be insoluble in the common solvents and could not be further purified.

4.2.3. Reaction of Phenylthiourea with Tellurium Tetrachloride and Tellurium Tetrabromide.

4.2.3.1. Preparation of bis N-Phenylthiourea Tellurium Dichloride.

This was prepared by the method of Sethuraman[108].

TeL_2Cl_2 ($L = C_6H_5NHCSNH_2$) was prepared by adding a solution containing 4.0 g (0.025M) of TeO_2 in 25 ml of 2.5 M HCl to a solution of 15.2 g (0.1M) of N-phenylthiourea in 2.5 M HCl. The yellow solid precipitated was filtered, washed with ether/acetone mixture and dried in a vacuum desiccator, MP = 80 °C with evolution of gas. No melting point is given by Sethuramen.

Analysis;

Found; C = 33.5 %, H = 3.16 %, N = 11.2 %, S = 12.81 %, Cl = 14.09 %

$TeCl_2(C_7H_9N_2S)_2$ requires; C = 33.4 %, H = 3.18 %, N = 11.14 %,
S = 12.73 %, Cl = 14.13 %.

4.2.3.2.

If the above experiment is repeated adding the two solutions to each other at 90°C then an orange product is produced melting at 65°C.

Analysis;

Found: C = 36.3 %, H = 3.3 %, N = 11.9 %, S = 14.1 %, Cl = 7.9 %.

4.2.3.3.

If the product from reaction 4.2.3.1. is heated in refluxing benzene then a product identical to 4.2.3.2. is produced.

Analysis;

Found; C = 36.6 %, H = 3.0 %, N = 11.5 %, S = 13.8 %, Cl = 7.8 %.

4.2.3.4. Alternative Preparation of TeL_2Cl_2

5.4 g (0.02M) of $TeCl_4$ dissolved in a minimum of hot benzene was added to 12.4 g (0.08M) of N-Phenylthiourea in hot methanol. The solution turns to a red-orange colour from which crystals of the desired product are obtained on allowing the solution to cool. MP = 80°C with evolution of gas.

Analysis;

Found; C = 33.37 %, H = 3.18 %, N = 11.12 %, S = 12.67.%, Cl = 14.1 %.

4.2.3.5. Preparation of TeL_2Br_2.

2.27 g (0.005M) of $TeBr_4$ were dissolved in ether and added to a solution of 3.1g (0.02M) in methanol. An orange solid, MP = 95°C, was produced on standing.

Analysis;

Found; C = 34.5 %, H = 2.47 %, N = 8.5 %, S = 9.95 %, Br = 23.5 %.

$TeBr_2(C_6H_5NHCSNH_2)_2$ requires; C = 34.6 %, H = 2.5 %, N = 8.6 %,

S = 9.8 %, Br = 24.7 %

4.2.4. Reaction of Selected Tellurides with N-Bromosuccinimide and N-Chlorosuccinimide.

4.2.4.1. Reaction of Diphenyl Telluride with NBS.

To 1.1g of diphenyl telluride (4mmol) in 50 ml of dry benzene were added 0.72g (4mmol) of NBS in 10 ml of the same solvent. The mixture was stirred for three hours. A white crystalline compound separated which was filtered off, MP = 198°C.

Analysis;

Found; C = 41.25 %, H = 2.91 %, N = 3.06 %, Br = 18.4 %

$C_{16}H_{14}O_2NTeBr$ requires; C = 41.7 %, H = 3.04 %, N = 3.04 %,

Br = 17.4 %.

4.2.4.2. Reaction of Diphenyl telluride with NCS

To 2.0g (7mmol) of diphenyl telluride in 50 ml of dry benzene was added 0.95g (7mmol) of NCS in 10 ml of the same solvent. The mixture was stirred for three hours. A white crystalline solid separated which was filtered off and dried in vacuum, MP = 155°C.

Analysis;

Found; C = 45.8 %, H = 3.4 %, N = 3.35 % Cl = 8.7 %.

$C_{16}H_{14}O_2NTeCl$ requires; C = 46.0 %, H = 3.37 %, N = 3.37 %,

Cl = 8.5 %.

4.2.4.3. Reaction of Bis p-Ethoxyphenyl Telluride with NBS.

To 0.74g of the telluride dissolved in benzene were added 0.36 g of NBS in benzene. The mixture was stirred for three hours. A white crystalline solid was filtered off and dried under vacuum, MP = 152 °C.

Analysis;

Found; C = 44.4 %, H = 4.1 %, N = 2.4 %, Br = 13.2 %

$C_{20}H_{22}O_4$TeNBr requires; C = 43.8 %, H = 4.01 %, N = 2.55 %, Br = 14.6 %.

4.2.4.4. Reaction of Bis p-Ethoxyphenyl Telluride with NCS.

0.31g of the telluride, in dry benzene, was added to 0.11g of NCS in the same solvent. The mixture was stirred for three hours and allowed to stand. A white crystalline solid was produced which was filtered off and dried, MP = 167°C.

Analysis;

Found; C = 48.1 %, H = 4.25 %, N = 2.79 %, Cl = 6.9 %

$C_{20}H_{22}O_4$TeNCl requires; C = 47.7 %, H = 4.37 %, N = 2.78 %, Cl = 7.05 %.

4.2.4.5. Reaction of above products with a further mole of N-Halosuccinimide.

0.001 M of the appropriate compound mixed in benzene with 0.001 M of the N-halosuccinimide inbenzene and heated with stirring. This gave a yellow, or colourless, solution which on standing gave a white precipitate which was filtered off to give succinimide,

MP = 126°C

Analysis;

Found; C = 48.3 %, H = 5.1 %, N = 14.1 %

$C_4H_5NO_2$ requires; C = 48.4 %, H = 5.05 %, N = 14.1 %.

The yellow or colourless solution (the colour depends on whether the chloride or bromide is produced) was evaporated to give the appropriate diaryl tellurium dihalide.

4.3 RESULTS

4.3.1. Phosphorus Ylids

(i) The elemental analysis is shown in the experimental section (Page 112)

(ii) The infra-red spectra of the starting compounds and the yellow product are shown in Table 4.1.1.

(iii) The mass spectrum of the compound is shown in Table 4.1.2.

4.3.2. Schiff Bases

(i) Elemental analysis of all compounds prepared are shown in Tables 4.2.1. and 4.2.2.

(ii) Infra-red spectra are shown in Table 4.2.3. and in Figs 4.2.1. to 4.2.9.

Far infra-red spectra are shown in Table 4.2.4.

(iii) Mass spectra are shown in Table 4.2.5.

4.3.3. Thiourea Compounds

(i) Elemental analysis of all compounds are shown in Table 4.3.1.

(ii) Infra-red spectra are tabulated in Table 4.3.2.

4.3.4. Reactions of N-Halosuccinimides

(i) Elemental analysis of all compounds are shown in Table 4.4.1.

(ii) Infra-red spectra are tabulated in Tables 4.4.2., 4.4.3. and 4.4.4.

(iii) Mass spectra are shown in Table 4.4.5.

Infra-red Spectra of $Ph_3P^+CH_2COPhBr^-$, $Ph_3P^+CH^-COPh$ and its Reaction product with $TeCl_4$

$Ph_3P^+-CH_2COPhBr^-$	$Ph_3P^+-CH^-COPh$	$Ph_3P^+-CH^-COPh+TeCl_4$
3060	3050	3060
3040		
2990		
2950		
1660	1620	
1595	1588	1590
1580	1482	1580
1488	1435	1485
1450	1385	1435
1435	1300	1335
1380	1195	1340
1325	1182	1315
1300	1180	1230
1208	1100	1135
1185	1062	1160
1160	1050	1120
1110	1025	1110
1028	1000	1070
990	970	1000
860	920	995
822	890	920
790	870	835
745	840	840
715	800	760
685	745	750
512	710	725
500	688	690
492	560	620
460	550	540
420	510	480
400	460	440
312	430	365
	395	345
	285	285

TABLE 4.1.1.

Mass Spectrum of the Product from Reaction 4.2.1.3.

m/e	Assignment
278	Ph_3PO^+
201	
199	
77	$C_6H_5^+$
38	$H^{37}Cl$
37	^{37}Cl
36	$H^{35}Cl$
35	^{35}Cl

TABLE 4.1.2.

Elemental Analysis of Schiff Bases and their Hydrochlorides

Compound	Found				Calculated			
	C%	H%	N%	Cl%	C%	H%	N%	Cl%
N-Benzilidene aniline $C_{13}H_{11}N$	85.9	6.1	7.6	-	86.1	6.0	7.7	-
N-(3methoxybenzilidene) aniline, $C_{14}H_{13}NO$	80.4	6.4	6.6	-	79.6	6.2	6.6	-
N-(3methoxybenzilidene) butylamine, $C_{12}H_{17}NO$	76.0	8.7	7.2	-	75.4	8.9	7.3	-
N-Benzilidene aniline Hydrochloride, $C_{13}H_{12}NCl$	71.4	5.8	6.5	17.0	72.6	5.5	6.4	16.3
N-(3methoxybenzilidene) aniline.HCl, $C_{14}H_{14}NOCl$	66.9	5.6	5.7	14.9	67.8	5.6	5.6	14.3

TABLE 4.2.1.

Elemental Analysis of Compounds Prepared from $TeCl_4$ or $TeBr_4$ with Schiff Bases.

Reaction	C%	H%	N%	Cl%	Br%
4.2.2.6.	36.9	2.8	3.2	24.5	-
4.2.2.7.	35.0	3.1	3.0	22.5	-
4.2.2.8.	34.0	4.2	3.4	24.9	-
4.2.2.9.	32.5	2.9	2.8	-	44.0
4.2.2.10.	32.1	2.5	2.9	-	47.4

TABLE 4.2.2.

Position of ν C=N in Schiff Bases and Compounds with $TeBr_4$, $TeCl_4$ and $HgCl_2$

Fig	Compound	ν C=N cm^{-1}
	$C_{13}H_{11}N$	1630
4.2.1.	$C_{14}H_{13}NO$	1630
	$C_{12}H_{17}NO$	1645
4.2.2.	$C_{13}H_{11}N.HCl$	1660
4.2.3.	$C_{14}H_{13}NO.HCl$	1650
4.2.4.	4.2.2.6.	1650
4.2.5.	4.2.2.7.	1660
4.2.6.	4.2.2.8.	1670
4.2.7.	4.2.2.9.	1655
4.2.8.	4.2.2.10.	1650
4.2.9.	4.2.2.11.	1630

TABLE 4.2.3.

Far Infra-red Spectra, 400-200 cm^{-1}, of Schiff Bases and compounds with $TeBr_4$ and $TeCl_4$

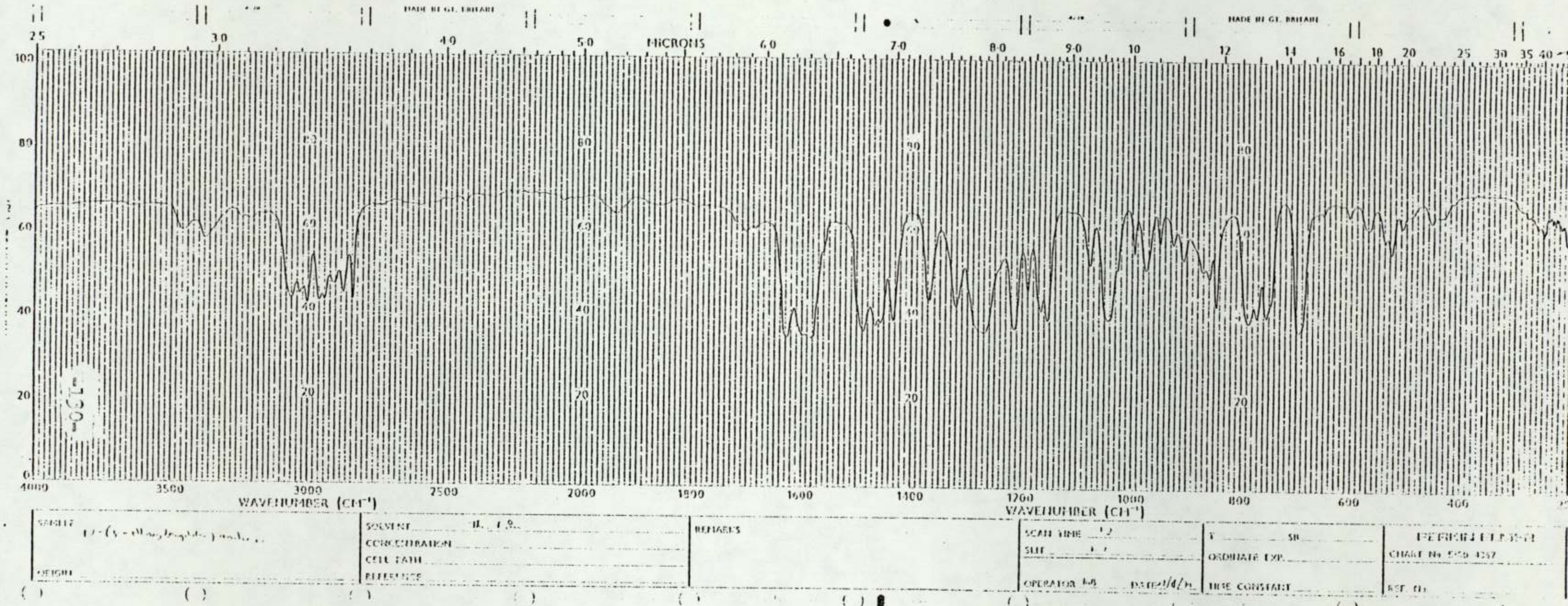
Compound	ν cm^{-1}
$C_{13}H_{11}N$	365, 274, 255
$C_{14}H_{13}NO$	-
$C_{12}H_{17}NO$	-
$C_{13}H_{11}N$ + $TeCl_4$	384, 340, 320, 305
$C_{14}H_{13}NO$ + $TeCl_4$	385, 340, 320, 305
$C_{12}H_{17}NO$ + $TeCl_4$	340, 320, 305
$C_{13}H_{11}N$ + $TeBr_4$	390
$C_{14}H_{13}NO$ + $TeBr_4$	-

TABLE 4.2.4.

Mass Spectra of Schiff Base Compounds with $TeCl_4$ and $TeBr_4$ (m/e).

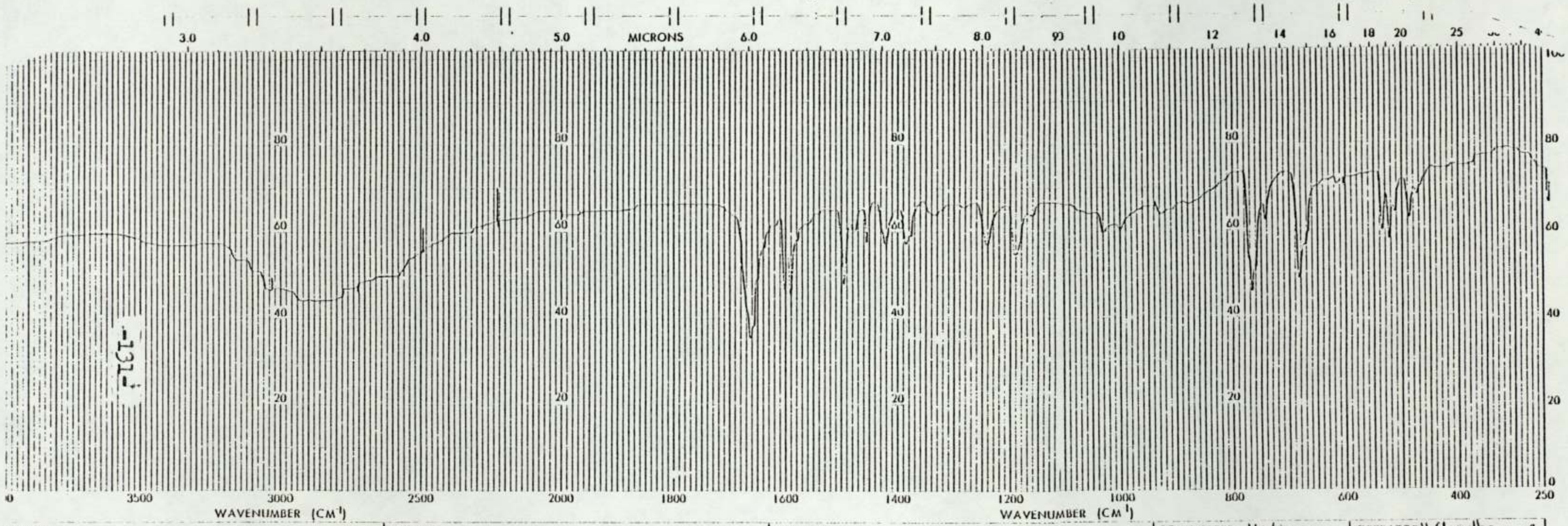
$C_{13}H_{11}N$ + $TeCl_4$	$C_{12}H_{13}NO$ + $TeCl_4$	$C_{14}H_{13}NO$ + $TeCl_4$	$C_{13}H_{11}N$ + $TeBr_4$	$C_{14}H_{13}NO$ +$TeBr_4$	$C_{13}H_{14}N$ HCl	$C_{14}H_{13}NO$ HCl
35	35	35	79	79	35	35
36	36	36	80	80	36	36
37	37	37	81	81	37	37
38	38	38	82	82	38	38
180	190	210	180	210	180	210
181	191	211	181	211	181	211
182	192	212	182	212	182	212
260	260	260	260	290		
			261	291		
			262	292		
			263	293		

TABLE 4.2.5.



Infra-red Spectrum of N-(3 methoxybenzilidene) aniline

Figure 4.2.1.



SAMPLE

ORIGIN

SOLVENT

CONCENTRATION KBr disc approx 10%

CELL PATH

REFERENCE AIR.

REMARKS

SCAN SPEED Medium

SLIT N.

No 457 - 5001

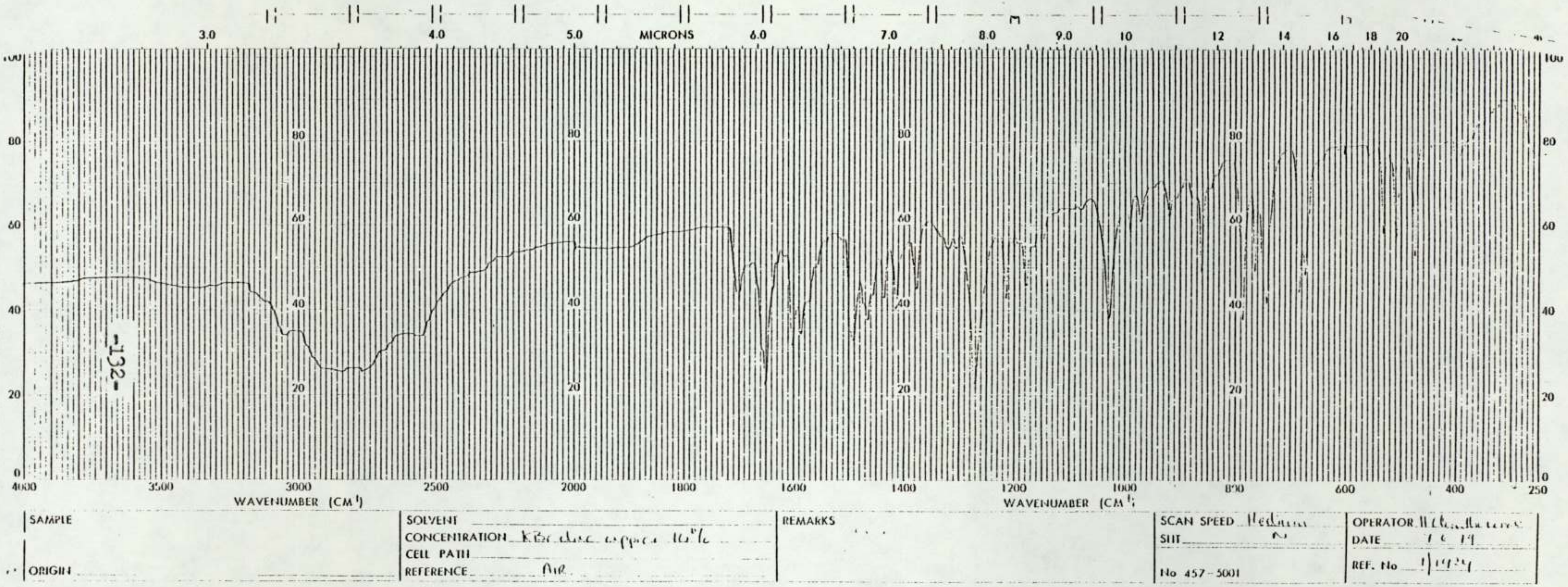
OPERATOR [illegible]

DATE 8/6/79.

REF. No 1925

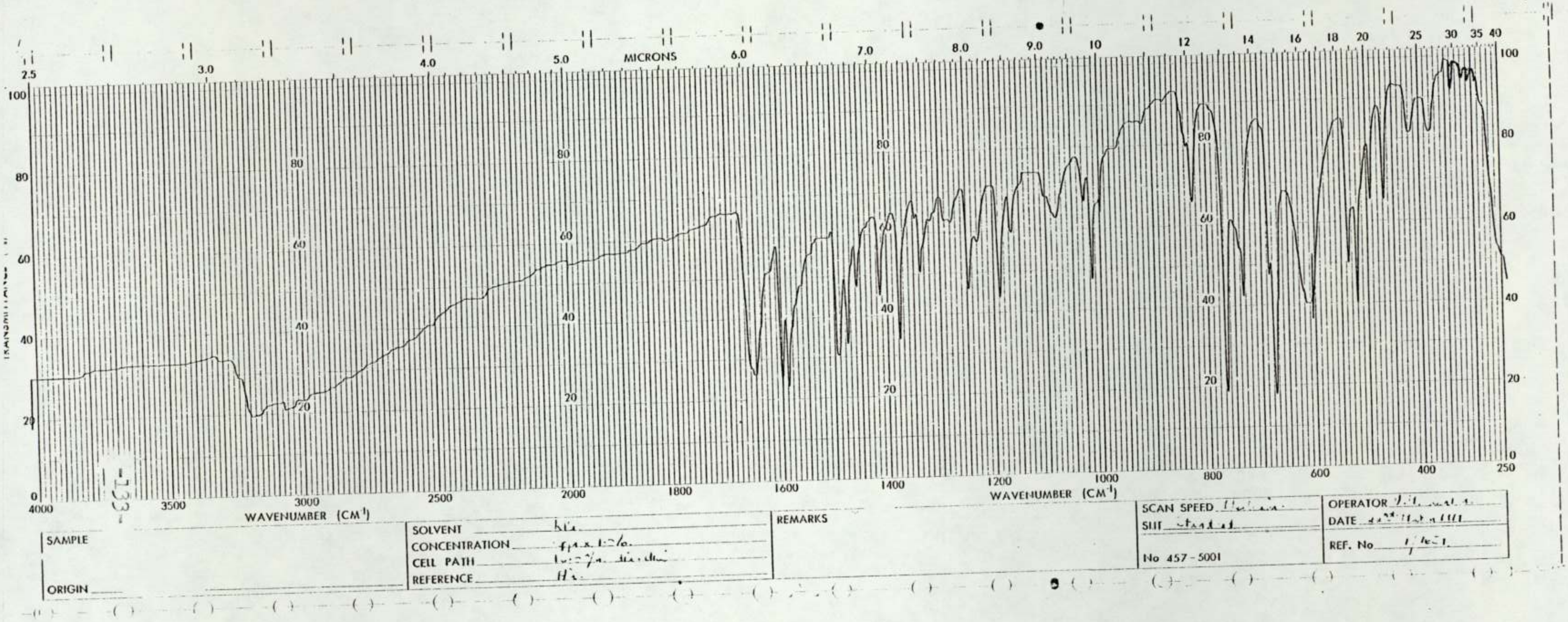
Infra-red spectrum of $C_{13}H_{11}N\ .HCl$

Figure 4.2.2.



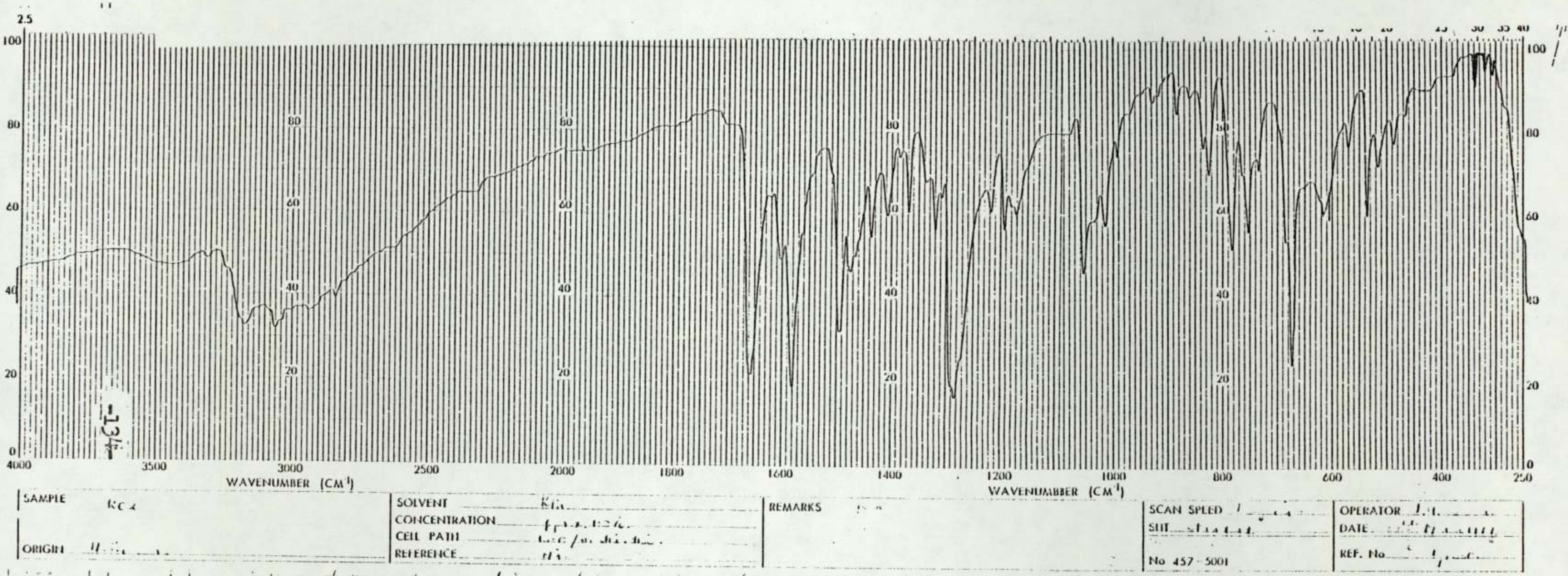
Infra-red Spectrum of $C_{14}H_{13}NO.HCl$

Figure 4.2.3.



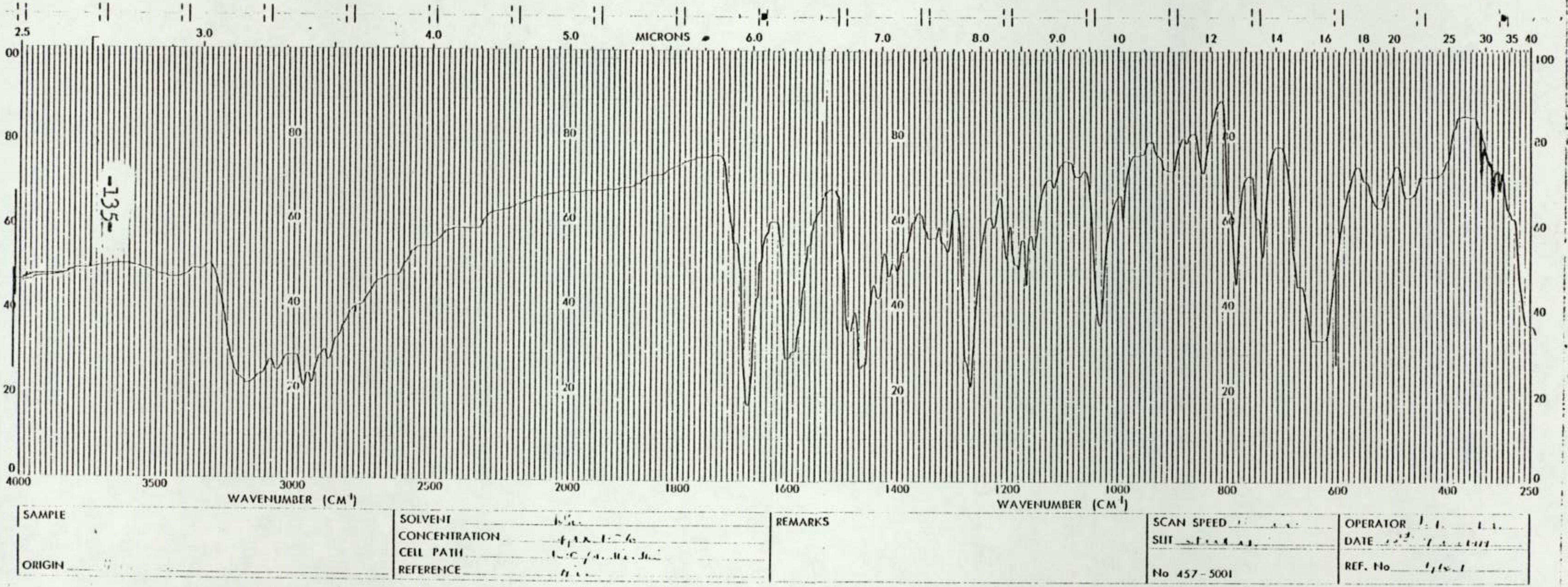
Infra-red Spectrum of Product 4.2.2.6.

Figure 4.2.4.



Infra-red Spectrum of Product 4.2.2.7.

Figure 4.2.5.

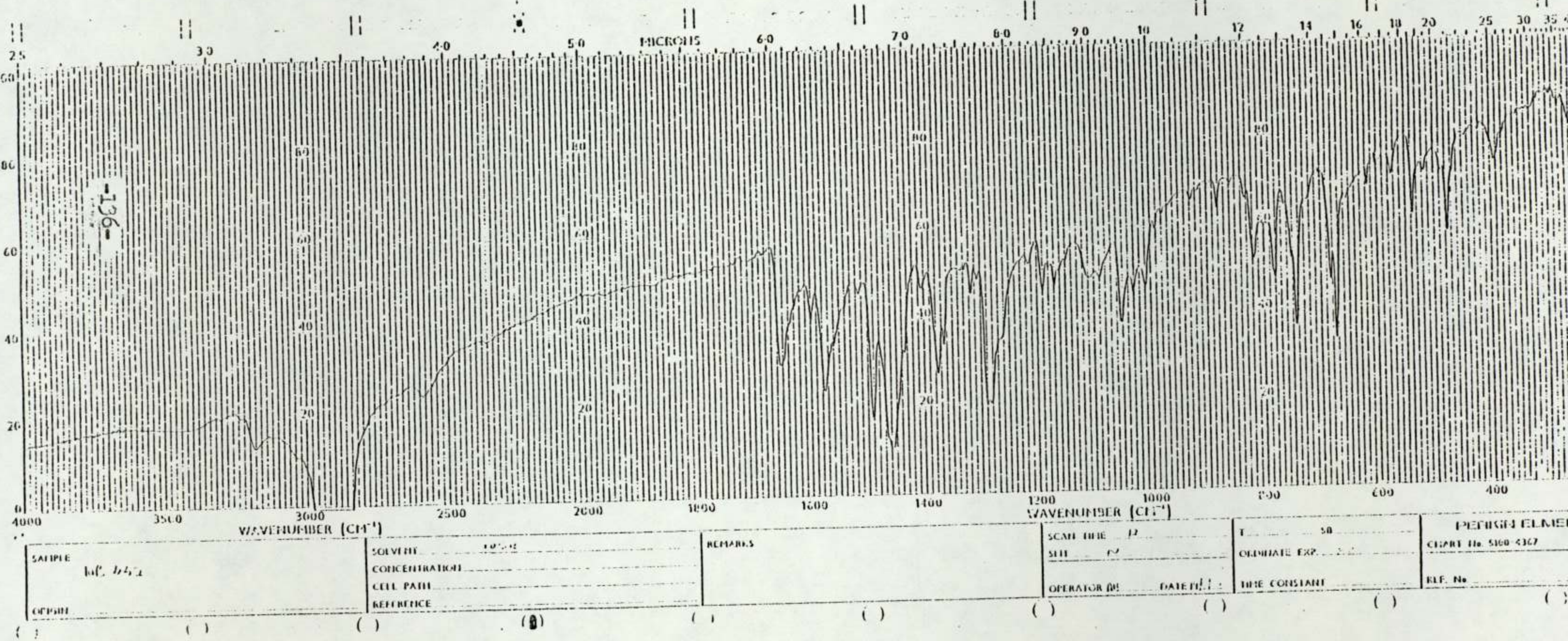


Infra-red Spectrum of Product 4.2.2.8.

Figure 4.2.6.

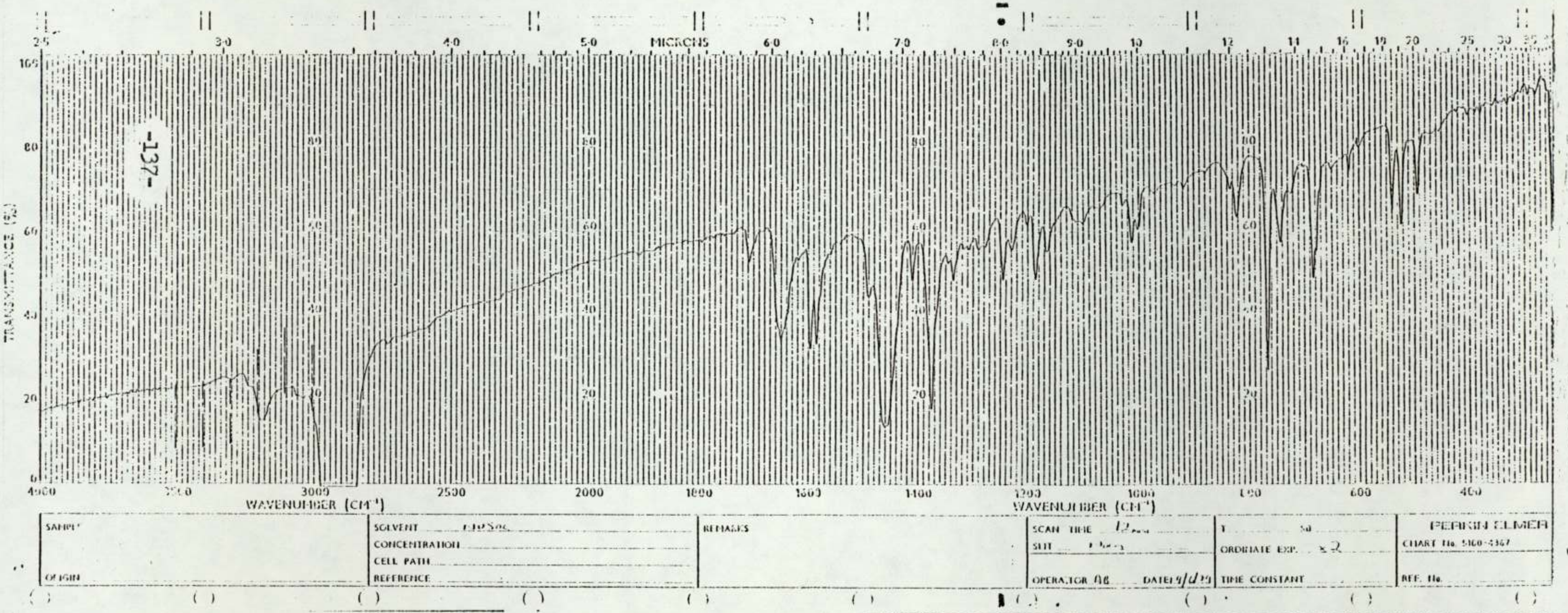
Infra-red Spectrum of Product 4.2.2.9.

Figure 4.2.7.



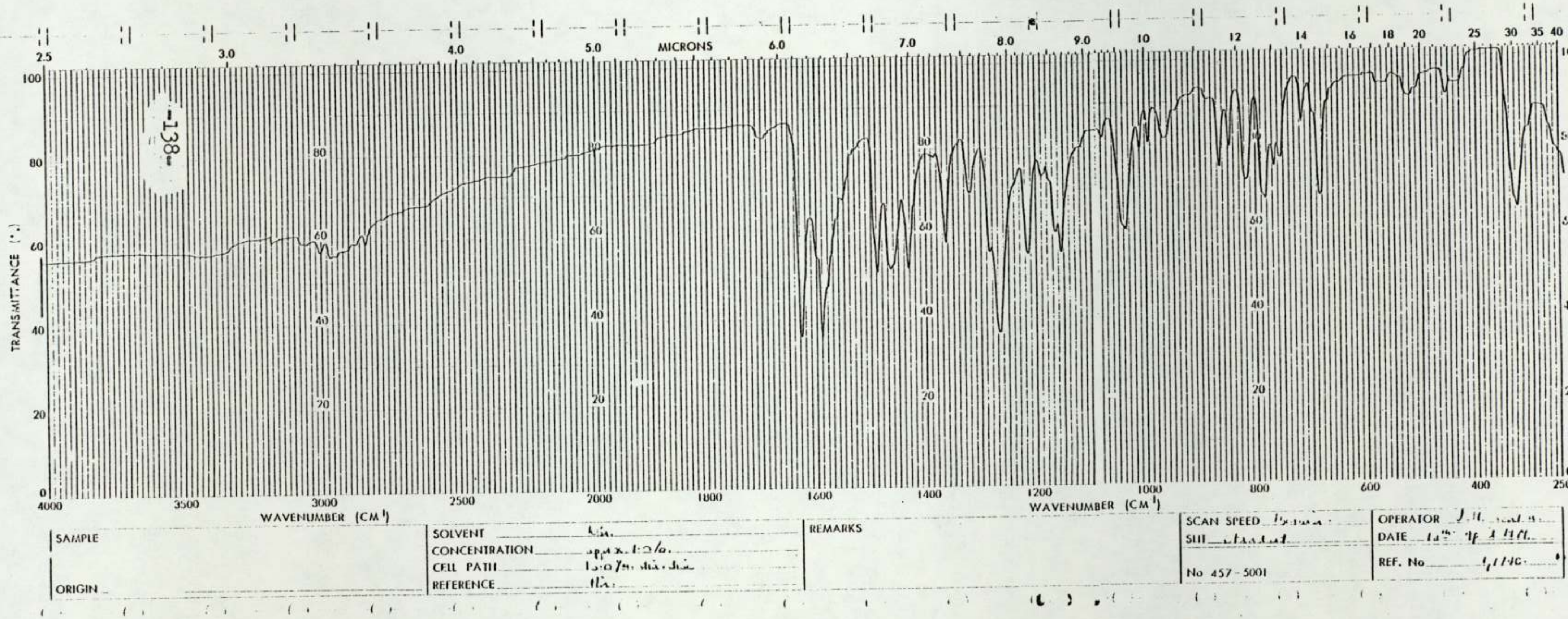
Infra-red Spectrum of Product 4.2.2.10.

Figure 4.2.8.



Infra-red Spectrum of Product 4.2.2.11.

Figure 4.2.9.



Elemental Analysis of N-Phenylthiourea Compounds

	$(Phtu)_2TeCl_2$	$(Phtu)_2TeCl_2$ (heated)	$(Phtu)_2TeBr_2$
Carbon %	33.5	36.3	34.5
Hydrogen %	3.16	3.30	2.47
Nitrogen %	11.2	11.9	8.50
Sulphur %	12.81	14.1	9.95
Chlorine %	14.09	7.9	-
Bromine %	-	-	23.5

TABLE 4.3.1.

Infra-red Spectra of N-Phenylthiourea Compounds

4000--250 cm^{-1}

$C_6H_5NHCSNH_2$	$(Phtu)_2TeCl_2$	$(Phtu)_2TeCl_2$ (heated)	$(Phtu)_2TeBr_2$
3430	3400	3250	3400
3280	3180		3220
3130			3100
	2900		
		1700	
1610	1620	1620	1620
1590	1590	1595	1595
1520	1520	1520	1520
		1495	1495
1445	1450	1450	1450
		1350	
1320	1320	1320	1320
	1300	1300	1300
1290	1270		1265
1230			
1075	1020	1020	1020
1060		1000	920
810	850		850
750	790	790	790
710	750	750	750
690	690	690	690
635			
600			
	590	590	590
	530	530	530
495	495	495	495
460	440	440	440
300	320		

TABLE 4.3.2.

Elemental Analysis of Compounds Formed Between Selected Tellurides and NBS or NCS.

Reaction	C %	H %	N %	Br %	Cl %	Required For	C %	H %	N %	Br %	Cl %
4.2.4.1	41.5	2.91	3.06	18.4	-	$C_{16}H_{14}O_2NTeBr$	41.7	3.04	3.04	17.4	-
4.2.4.3.	44.4	4.1	2.4	13.2	-	$C_{20}H_{22}O_4NTeBr$	43.8	4.01	2.55	14.6	-
4.2.4.2.	45.8	3.4	3.35	-	8.7	$C_{16}H_{14}O_2NTeCl$	46.0	3.37	3.37	-	8.5
4.2.4.4.	48.1	4.25	2.79	-	6.9	$C_{20}H_{22}O_4NTeCl$	47.7	4.37	2.78	-	7.05

TABLE 4.4.1.

Infra-red Spectra of Starting Materials and Products of Reaction Between NCS or NBS and Selected Tellurides

Ph_2Te	NBS	NCS	$(p\text{-}EtOPh)_2Te$	Ph_2TeNBS	Ph_2TeNCS	$(p\text{-}EtOPh)_2TeNBS$	$(p\text{-}EtOPh)_2TeNCS$
3070	3460	3490	3020	3050	3150	3150	3150
3060	3000	3000			3060	3070	
3030						3030	
3020							
3000							
	2950	2950	2940				2980
			2930			2990	2930
						2940	2880
						2880	
1950	1950	1970					
1870	1815		1880				
1775	1785	1785		1770	1770	1770	1775
1750	1735	1745		1700	1700	1700	1705
1630					1695		1630
1580		1550	1585	1575	1575	1590	1590
1560			1570			1575	1575
						1570	1570
1475	1495	1430	1490	1475	1475	1490	1490
1435	1420	1410	1475	1435	1435	1475	1475
	1405		1455	1420	1420	1455	1455
			1445			1445	1440
						1400	1400
1380	1380	1380	1390	1370	1370	1390	1390

TABLE 4.4.2.

Ph_2Te	NBS	NCS	$(p\text{-}EtOPh)_2Te$	Ph_2TeNBS	Ph_2TeNCS	$(p\text{-}EtOPh)_2TeNBS$	$(p\text{-}EtOPh)_2TeNCS$
1325	1315	1330	1300			1305	1305
1300		1300					
1260	1290	1230	1280	1295	1295	1295	1295
	1245		1240	1245	1240	1255	1255
	1235		1235	1240	1245		
	1230						
1180	1165	1165	1175	1180	1185	1180	1180
1160			1155	1155	1155	1175	1175
			1110			1110	1110
			1100				
1095	1005	1010	1060	1055	1055	1085	1085
1065			1040	1050	1050	1050	1055
1015			1000	1020	1020	1045	1045
						1000	1000
985	930	960	955	995	995	930	920
965			920	935	965	920	905
905				915	935	905	
					915		
840	812	818	825	825	850	825	825
			800	815	820	815	815
						805	805
725		700		745	745	795	795
730				730	730	770	775

TABLE 4.4.2. (contd.)

Ph_2Te	NBS	NCS	$(p\text{-EtOPh})_2Te$	Ph_2TeNBS	Ph_2TeNCS	$(p\text{-ETOPh})_2TeNBS$	$(p\text{-EtOPh})_2TeNCS$
690	655	650	630	680	680	695	695
650	640		620	670	660	650	645
650				650	635		
				640			
	565	570	515	555	555	510	510
	545	560	510				
		550					
		525					
460	480	415	440	465	465	450	450
445				440	445	420	425
				415	430		
		340	380			380	380
			340			340	340
						310	310

TABLE 4.4.2. (contd.)

Far Infra-red Spectra of NBS and NCS and their Reaction Products with Selected Tellurides (cm^{-1})

N-Chlorosuccinimide	N-Bromosuccinimide	$(p\text{-EtOPh})_2$Te+ NBS	Ph_2Te + NBS	Ph_2Te + NCS	$(p\text{-EtOPh})_2$Te + NCS
338	278	382	274	272	390
		338	260	260	340
		312	220	238	310
			212	220	
				212	

TABLE 4.4.3.

Position of ν_{sym} C=O and ν_{asym} C=O vibrations for Succinimides and Derivatives.

Compound	ν_{sym} C=O cm^{-1}	ν_{asym} C=O cm^{-1}	$\Delta\nu$
Succinimide	1695	1770	75
NBS	1733	1783	50
NCS	1744	1785	41
$(p\text{-EtoPh})_2Te$ + NBS	1700	1770	70
Ph_2Te + NBS	1700	1770	70
Ph_2Te + NCS	1700	1770	70
$(p\text{-EtOPh})_2Te$ + NCS	1705	1775	70

TABLE 4.4.4.

Mass Spectra of Succinimide and Deivatives (m/e)

NBS	Succinimide	$(p\text{-EtOPh})_2Te$	$(p\text{-EtOPh})_2TeNBS$	Ph_2TeNBS
179	99	372	372	234
151	70	251	251	207
123	56	242	242	179
98	45	130	221	154
81		76	202	151
70			173	130
56			98	123
42			81	81
			70	77
			56	70
			42	56
				42

TABLE 4.4.5.

4.4. DISCUSSION.

4.4.1. Phosphorus Ylids.

The ligand phenacylidene triphenyl phosphorane is relatively simple to prepare and is known to undergo ortho-metallation.[105]

The preparation is a two stage reaction.

(i) Reaction of triphenyl phosphine with phenacyl bromide to give the salt $(Ph_3P\text{-}CH_2COC_6H_5)^+Br^-$

(ii) Reaction of the above with a base to yield the ylid.

Both of these products gave satisfactory elemental analysis and infra-red spectra.

The only reported reaction of a **phosphorus** ylid with a tellurium halide is that of Petragnani and De Moura Campos[107] (see page 52) to produce the diphosphonium hexabromotellurate.

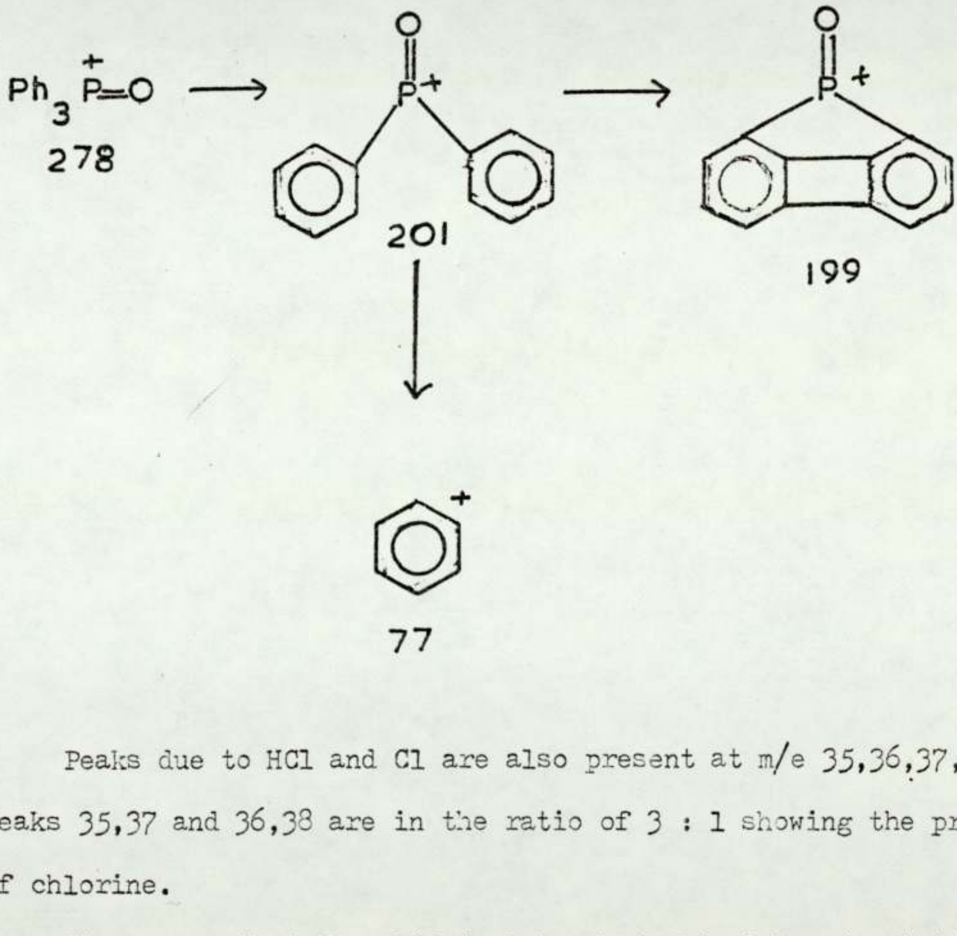
Dias[105] has reported the o-metallation of phenacylidene triphenylphosphorane by palladium. This reaction is carried out by adding $PdCl_2$ in MeOH to a mixture of the ligand and sodium acetate (To promote the removal of the proton) in MeOH and the resulting mixture refluxed for two hours.

The product of the reaction between the phosphorus ylid and tellurium tetrachloride in dry chloroform was a green oil which changed to yellow crystals when ether was added.

Elemental analysis for CHPCl gave an empirical formula of $C_{18}H_{17}PCl_3$. This implies one triphenyl phosphine group to three chlorine atoms in the final product.

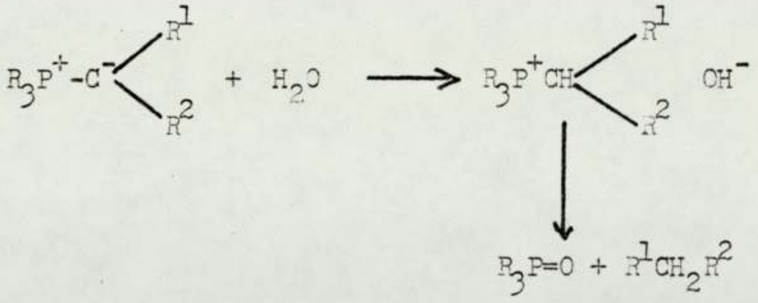
The most striking feature of the infra-red spectrum are the absence of the carbonyl group and the presence of a broad band at ~ 900cm^{-1}. It is obvious from this data that the ylid is no longer present but a compound containing a P-O bond is present. No vibration due to Te-O can be assigned.

The mass spectrum shows the presence of triphenyl phosphine oxide, m/e = 278 and its decomposition products:



Peaks due to HCl and Cl are also present at m/e 35,36,37,38. Peaks 35,37 and 36,38 are in the ratio of 3 : 1 showing the presence of chlorine.

It appears that the ylid is being hydrolized to give triphenyl phosphine oxide. This is a known reaction of phosphorus ylids



The presence of any moisture would also hydrolize the $TeCl_4$ and produce HCl.

$$TeCl_4 + H_2O \longrightarrow TeOCl_2 + 2HCl.$$

It seems that the product obtained from the reaction is produced from a reaction between $Ph_3P = O$ and 1) $TeCl_4$ or 2) $TeCl_4$/HCl.

1) A reaction between $Ph_3P = O$ and $TeCl_4$ could be envisaged to proceed in the same manner as the reaction between $Ph_3P = O$ and PCl_5[136] namely.

$$Ph_3P = O + PCl_5 \longrightarrow Ph_3P^+ {-O-} PCl_5^-$$

The product of the reaction would be:

$$Ph_3P = O + TeCl_4 \longrightarrow Ph_3P^+ {-O-} TeCl_4^-$$

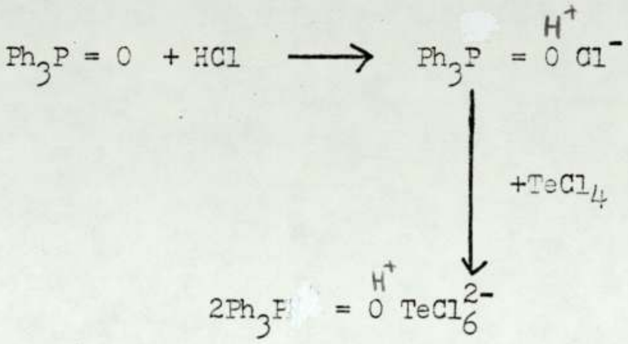
This compound would show a P-O vibration in the region of $850cm^{-1}$ and also TeO. The mass spectrum would also show Ph_3P-O.

The elemental analysis of this compound would be:

$C = 39.4\ \%$, $H = 2.7\ \%$, $P = 5.6\ \%$, $Cl = 25.9\ \%$.

This is in poor agreement with the analysis found and thus this type of compound is thought unlikely.

2) Reaction between $Ph_3P = O$ and $TeCl_4/HCl$ may take place as follows:



$$Ph_3P = O + HCl \longrightarrow Ph_3P = \overset{H^+}{O}\ Cl^-$$

$$\xrightarrow{+TeCl_4}\ 2Ph_3P = \overset{H^+}{O}\ TeCl_6^{2-}$$

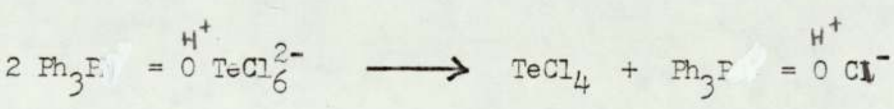
This compound gives an elemental analysis of:

$C = 48.18\ \%$, $H = 3.34\ \%$, $P = 6.9\ \%$, $Cl = 23.7\ \%$.

This is in good agreement with the experimental result.

The $TeCl_6^{2-}$ anion is reasonable as no Te -O vibration is observed in the IR. The P = O vibration is lower than would be expected but the addition of the proton may account for this.

It could be expected that a compound of this type would undergo the following reaction in the mass spectrum following similar hexachlorotellurate structures.[137]



$$2\ Ph_3P = \overset{H^+}{O}\ TeCl_6^{2-} \longrightarrow TeCl_4 + Ph_3P = \overset{H^+}{O}\ Cl^-$$

This would show in the mass spectrum as $Ph_3P=O$ and HCl. as is noted.

CONCLUSIONS

1) The ylid is undergoing hydrolysis under the conditions of the reaction producing $Ph_3P = O$.

2) On the evidence available $Ph_3P = O$ reacts with $TeCl_4/HCl$ to give $2\ Ph_3P = \overset{H^+}{O}\ TeCl_6^{2-}$.

This compound cannot be positively identified but it is the formulation that best fits the available data.

4.4.2. Schiff Bases

The three Schiff bases chosen, N- benzilidene aniline, N-(3 methoxybenzilidene) aniline and N- (3 methoxybenzilidene) n-butylamine, were prepared by standard methods and gave satisfactory analysis, NMR and infra-red spectra.

Reaction of any of the three Schiff bases with $TeCl_4$ in either chloroform or benzene led to yellow products insoluble in either of these solvents. Infra-red analysis of these compounds showed that no o-metallation had taken place.

It is well known that mono and 1,2 disubstituted benzenes have characteristic spectra in the γ(CH) region of the spectrum. Ortho metallation in the phenyl ring of the Schiff base will generate a 1,2, disubstituted benzene and should lead to characteristic changes in the 680-800 cm^{-1} region. This criterion has also been used by other workers. No change in this region of the infra-red spectra were noted. This fact together with the analytical data showed that o-metallation had not taken place.

Examination of the infra-red spectra Figs 4.2.4., 4.2.5., and 4.2.6. shows three main features;

i) Absorptions in the region 3060 and 3200 cm^{-1} characteristic of NH^+ species.

ii) Shift to higher wavenumber of the C=N vibration at $\approx$ 1630 cm^{-1}

iii) A strong, broad absorption at 610 cm^{-1} characteristic of Te-O bonds.

All of the compounds show absorption bands in the far infra-red at 340, 320 and 305 cm^{-1} (Table 4.2.4.) and could be attributed to

Te-Cl vibrations. These would agree with those given by McWhinnie[138] for phenyl tellurium trichlorides, namely at 336,318 and 304 cm^{-1}.

The mass spectra of the compounds are dominated by the peaks attributed to the breakdown of the Schiff base.

The most prominent feature is the parent ion of the Schiff base and also $M-1^+$ and $M+1^+$. The $M-1^+$ is due to the loss of the azomethine proton and is well known in the mass spectra of Schiff bases[139]. The $M+1^+$ ion suggests a protonated structure.

From the available data it seems that the Schiff base has been protonated and an anion is present containing Te, O and Cl.

In order to find more evidence of this the hydrochloride derivatives of two of the Schiff bases were prepared, these being N-benzilidene aniline and N-(3 methoxybenzilidene) aniline. These compounds gave satisfactory elemental analysis and the IR spectra showed similar features to the tellurium containing compounds, namely absorptions due to $C=NH^+$ and a similar shift in the C=N vibration. The mass spectra of the hydrochloride derivatives showed the main features seen previously i.e. peaks at $M-1^+$, M^+ and $M+1^+$.

The above results give support to the idea of protonation of the Schiff base when reacted with $TeCl_4$, due to the similarity in the appearance of the IR and Mass spectra.

The question is now raised as to the nature of the tellurium containing anion.Analysis and IR indicate the presence of O and Cl. The position of the bands assigned to Te-Cl stretching vibration indicates a five coordinate species, these values been similar to those in $PhTeCl_3$ which is believed to be 5 coordinate[138]

The analytical data suggests an empirical formula of the type

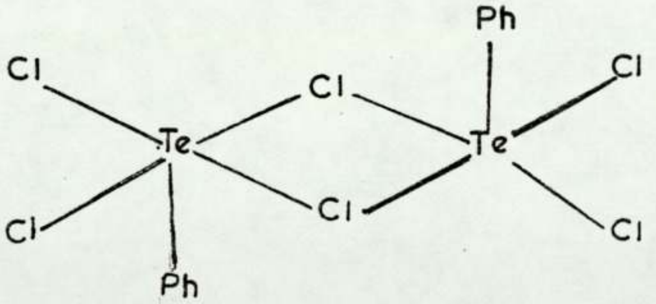
$$(\text{Schiff Base } H^+)\ TeOCl_3^-$$

This anion is known to exist.

The mass spectra of the compounds indicate the presence of Te_2^+ shown as the characteristic isotope distribution for Te in the m/e range 244-60.

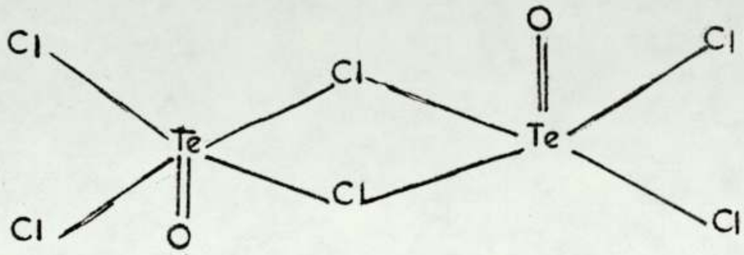
The presence of the ditelluride ion in the mass spectrum indicates a dimeric structure for the anion. The absence of a ditelluride structure is indicated by the colour of the compound i.e. yellow instead of red, the usual colour of ditellurides.

Phenyl tellurium trihalides are known to be dimeric in the solid state [140] with 5 coordinate tellurium as in the figure.



$PhTeCl_3$ has Te-Cl (terminal) vibrations at 336, 318 and 304 cm^{-1} with Te-Cl (bridging) at 180 and 152 cm^{-1}. The former values are very close to the assignments given to the Te-Cl vibrations in the case of the Schiff base compounds and it is reasonable to think that the anion contains 5 coordinate tellurium in the same type of dimeric structure. This would also permit the formation of Te_2^+ detected in the mass spectrum.

It is also possible that there are all terminal Cl and bridging O, however the bridging vibrations would occur out of the range of the instrument used. (For Te-Cl bridges)



In the light of the above evidence the products from the reaction of the Schiff base with $TeCl_4$ are suggested as being ionic (They conduct electricity in acetonitrile solution)

A comparison of calculated elemental analysis and found are shown in Table 4.4.2.1.

Compound	Expected				Found			
	C %	H %	N %	Cl %	C %	H %	N %	Cl %
$C_{13}H_{12}N^+TeOCl_3^-$	36.1	2.7	3.2	24.6	36.9	2.8	3.2	24.5
$C_{14}H_{14}NO^+TeOCl_3^-$	36.3	3.0	3.0	23.0	35.0	3.1	3.0	22.5
$C_{13}H_{18}NO^+TeOCl_3^-$	32.6	4.0	3.1	24.0	34.0	4.2	3.4	24.9

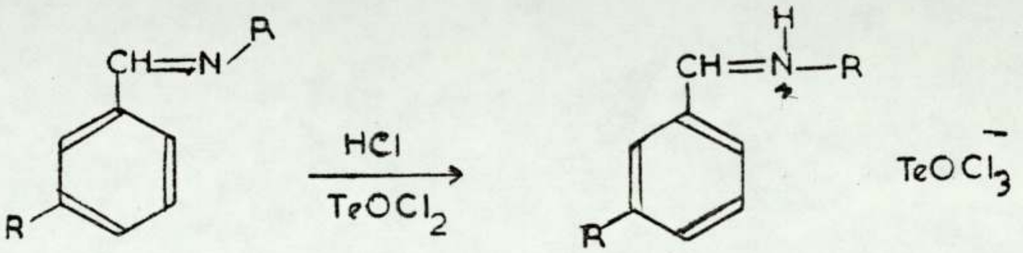
TABLE 4.4.2.1.

The question is now raised to how these compounds can be formed.

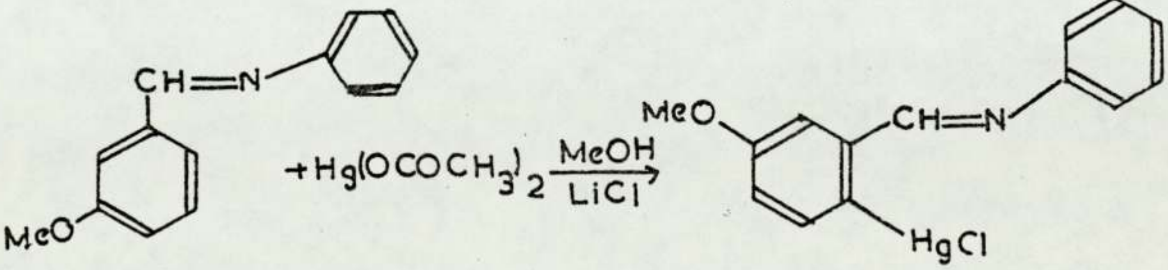
It seems obvious that water has not been completely removed from the system and that the $TeCl_4$ has undergone hydrolysis. Also the base may promote the hydrolysis of $TeCl_4$ if water is present.

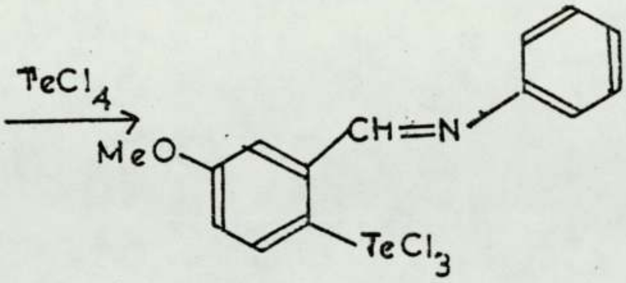
$$TeCl_4 + H_2O \longrightarrow TeOCl_2 + 2\ HCl$$

The Schiff base can then undergo protonation;



In order to try and obtain the o- metallated product as originallly desired an attempt was made to prepare the mercurated Schiff base. This could then be converted to the tellurium compound by the well known reaction of RHgCl compounds with $TeCl_4$ as depicted below





This reaction gave only a solid which gave an incomprehensible analysis result and could not be further purified. Examination of the infra-red spectrum of the product showed a number of interesting features (Fig 4.2. 9.)

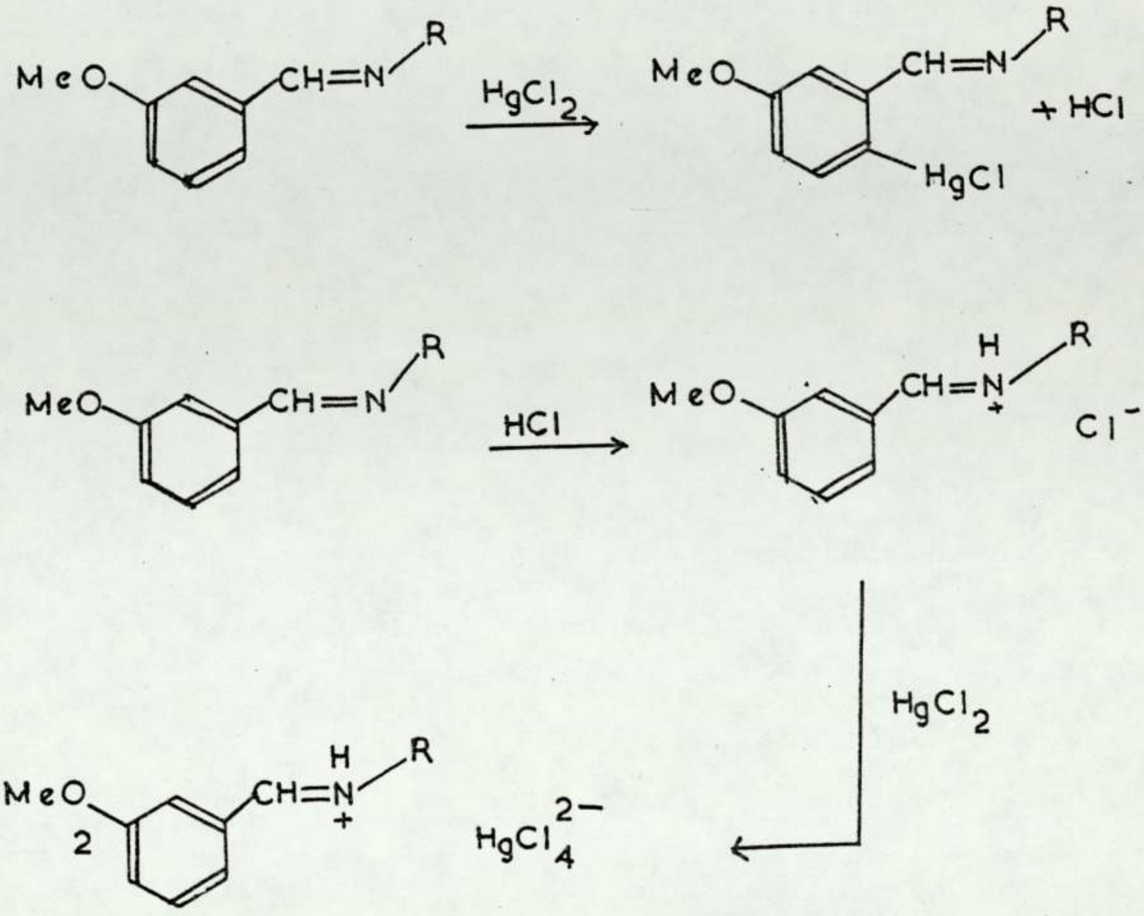
i) The position of C=N at 1630 cm^{-1} i.e. unshifted from the position in the Schiff base

ii) Appearance of a band at 715 cm^{-1} - this is not present in free Schiff base or in any of the tellurium compounds.

iii) The presence of a strong absorption at 325 cm^{-1} assigned as a Hg-Cl stretching frequency, common in organylmercury chlorides.

From the above evidence it seems that o- metallation has taken place, however the mass spectrum shows peaks due to $M-1^+$, M^+ and $M+1^+$ of the Shiff base indicating that a certain amount of the Schiff base salt was present.

A possible reaction scheme is;



It is still felt that the desired o-metallation compound can be prepared if the correct condition can be found.

The reaction of the Schiff bases with $TeBr_4$ gave different compounds to that of $TeCl_4$. The infra-red spectra of these compounds are shown in Figs 4.2.7. and 4.2. 8. The products are orange coloured solids soluble in acetonitrile to give conducting solutions.

The IR spectra show similar features to the chlorides, namely the presense of NH^+ and a shift of the C=N vibration to higher frequency indicating protonation. A notable absence from the spectra is the strong Te=O absorption at 610 cm^{-1}. No band attributable to Te-Br can be identified in the range 400-200 cm^{-1}

The mass spectra of the compounds show the same pattern in the region of the parent ion of the Schiff base as noted previously. Free bromine and HBr are also shown at m/e 79, 80 81 and 82. In addition bromine containing species can be identified at higher m/e numbers corresponding to the hydrobromide compound of the Schiff base.

The elemental analysis of the compounds indicate an empirical formula of,

$$(\text{Schiff Base})^+ \, Te_{\frac{1}{2}}Br_3^-$$

Most probably $2(\text{Schiff Base})^+ TeBr_6^{2-}$

The expected and found analytical data are shown in Table 4.4.2.2.

Compound	Expected				Found			
	C %	H %	N %	Br%	C %	H %	N %	Br %
$(C_{14}H_{14}ON^+)_2TeBr_6^{2-}$	32.6	2.7	2.7	46.5	32.5	2.9	2.8	44.0
$(C_{13}H_{12}ON^+)_2TeBr_6^{2-}$	32.0	2.5	2.9	49.3	32.1	2.5	2.9	47.4

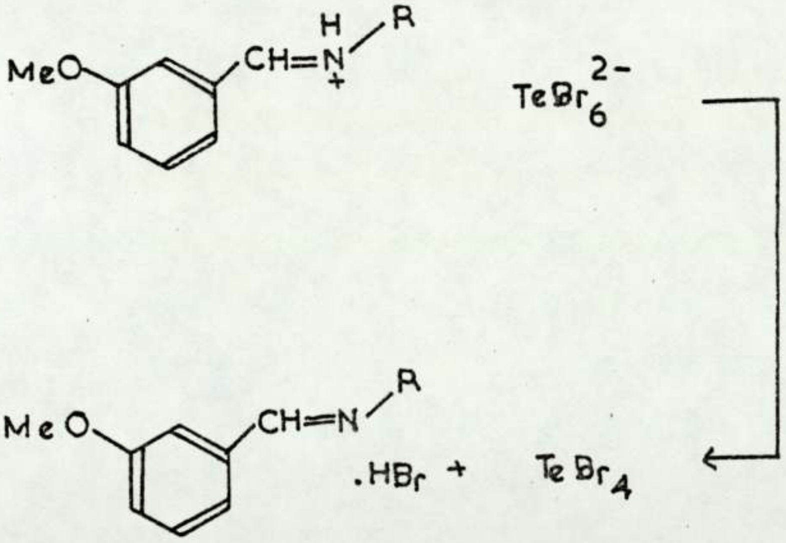
TABLE 4.4.2.2.

The formation of these compounds as opposed to oxybromides can be explained by the increased hydrolytic stability of $TeBr_4$ compared to $TeCl_4$.

The behaviour in the mass spectra of the compounds can be explained by the fact that hexahalotellurates are known to dissociate under vacuum to give $TeBr_4$ as shown below for 2 $NH_4^+TeBr_6^{2-}$

$$2\ NH_4^+TeBr_6^{2-} \longrightarrow 2\ NH_4Br + TeBr_4$$

So that in the case of the N- (3 methoxybenzilidene) aniline derivative, for example, the following takes place



This gives m/e at 291 and 293 corresponding to ^{79}Br and ^{81}Br. There are also peaks at 290 and 292 corresponding to the loss of the azomethine H.

The anion $TeBr_6^{2-}$ would be expected to show Te-Br vibrations in the region of 195 cm^{-1} and would be out of range of the instrument used.

Conclusions

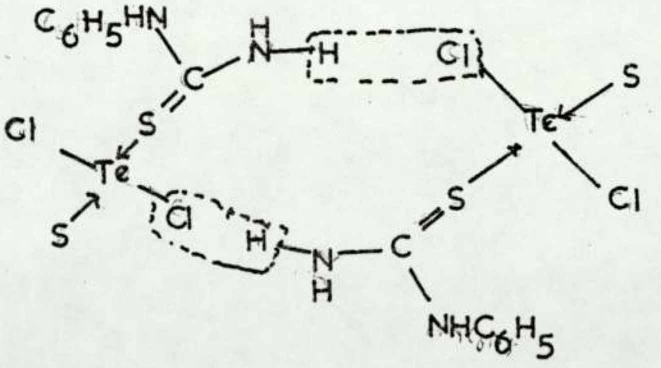
1) $TeCl_4$ or $TeBr_4$ will not directly o-metallate the Schiff bases studied, but give the compounds of general formula (Schiff Base H)$^+$ $TeOCl_3^-$ and 2 (Schiff Base H)$^+$ $TeBr_6^{2-}$.
2) N-(3 methoxybenzilidene)aniline can be o-metallated with Hg but under the conditions used only very small quantities are produced which proved difficult to purify. Perhaps a longer reflux period would be benificial - lack of time prevented further work being carried out on this topic.

4.4.3. N-Phenylthiourea

On searching the chemical literature a possible candidate for o- metallation seemed to be N-phenylthiourea (see page 109).

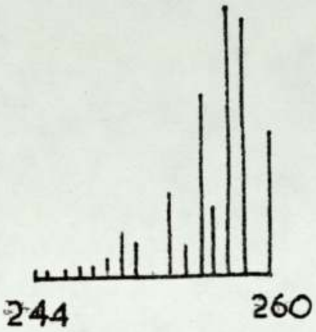
Tellurium II complexes with N-phenylthiourea have been prepared by Sethuraman [108]. The author prepared TeL_2Cl_2 (L = N-phenylthiourea) by adding a solution of TeO_2 in HCl to a solution of N-phenylthiourea in the same solvent. This experiment was repeated and found to give the same product. An alternative synthesis was derived using $TeCl_4$ and N-phenylthiourea in organic solvents. In this reaction the TeIV is reduced to TeII by the N-phenylthiourea producing the same product.

Sethuramen showed that on dissolution in a polar organic solvent the TeII compound loses HCl to give a glassy Te II imido chloro complex (See below).

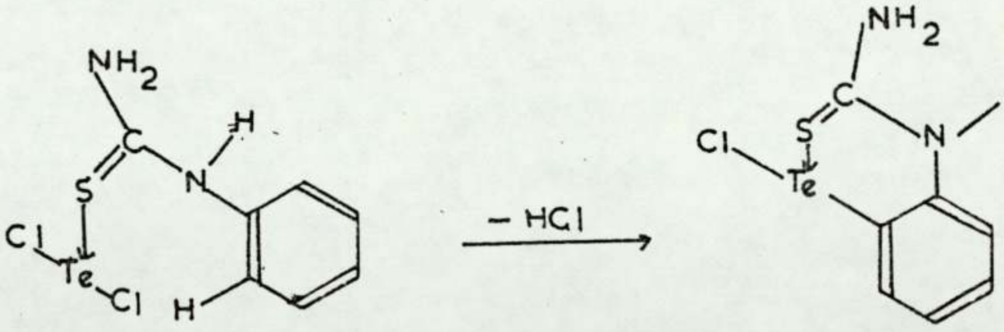


This process was also shown, during the present study to, occur on heating the solid to 80°C. Evidence of HCl loss was also found in the mass spectrum together with Te_2^+ which could be formed from the above structure due to the close proximity of the two Te atoms.

The presence of Te_2^+ was confirmed by a comparison of the mass spectrum in the region 244-60 with that calculated for Te_2^+ [141] The calculated isotopic distribution is shown below.



An alternative mechanism for loss of HCl could be the o-metallation of the phenyl ring as follows,



Examination of the IR spectrum (Table 4.3.2.) of the heated phenylthiourea complex shows no peaks at ~ 700 cm^{-1} and so o-metallation is unlikely to have taken place also one of the N-H vibrations of the complex had disappeared on heating.

The complex TeL_2Br_2 (L=N-phenylthiourea) has been prepared for the first time during this study by the addition of $TeBr_4$ to N-phenylthiourea in organic solvents. This could not be prepared by Sethuraman using TeO_2/HBr and N-phenylthiourea.

Conclusions

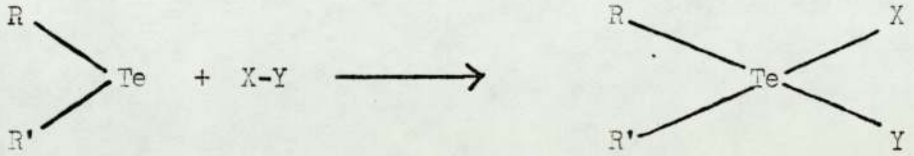
i) On heating bis(N-phenylthiourea)tellurium dichloride l oses HCl producing a dimeric tellurium imido complex and not o-metallation.

ii) Bis(N-phenylthiourea)tellurium dibromide has been produced for the first time.

4.4.4. Reactions of N-Chloro and N-Bromosuccinimide with Selected Tellurides.

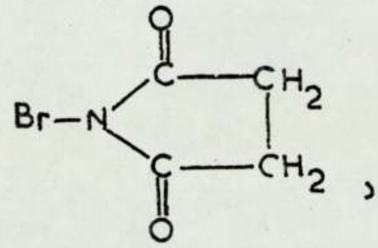
In the present chapter work has been carried out on the attempted o metallation of various types of molecules among them Schiff Bases. One of the attractions of using the Schiff bases is the possibility of forming Te-N bonds. Work by Musa on azobenzene derivatives of tellurium (See page 104) also produced a compound containing a Te-N bond and an attempt made to assign an infra-red frequency to this vibration, and so it would have been useful to study the Te-N system in the Schiff base. As a result of this interest the literature was searched for evidence of Te-N systems. One of these is the N-Phenylthiourea tellurium compounds, see section 4.4.3., and a paper by Srivastava [142] concerning the insertion of Te II into N-Hal bonds. This latter paper was of interest because of two reasons (i) The presence of Te-N bonds and (ii) the apparent disagreement of the work with that of Dance [143] carried out at this University.

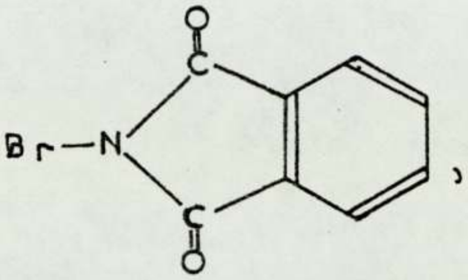
The work described in Srivastava's paper involves the reaction of diaryl tellurides RR'Te with compounds X-Y as follows;

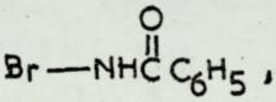


R = R' = Ph, p-MeOPh; R = Ph, R' = p-MeOPh

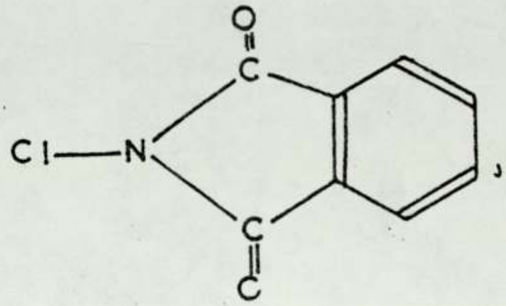
X-Y =

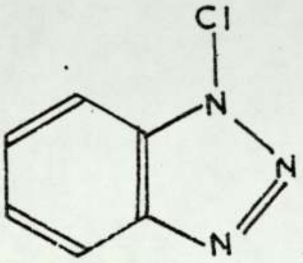






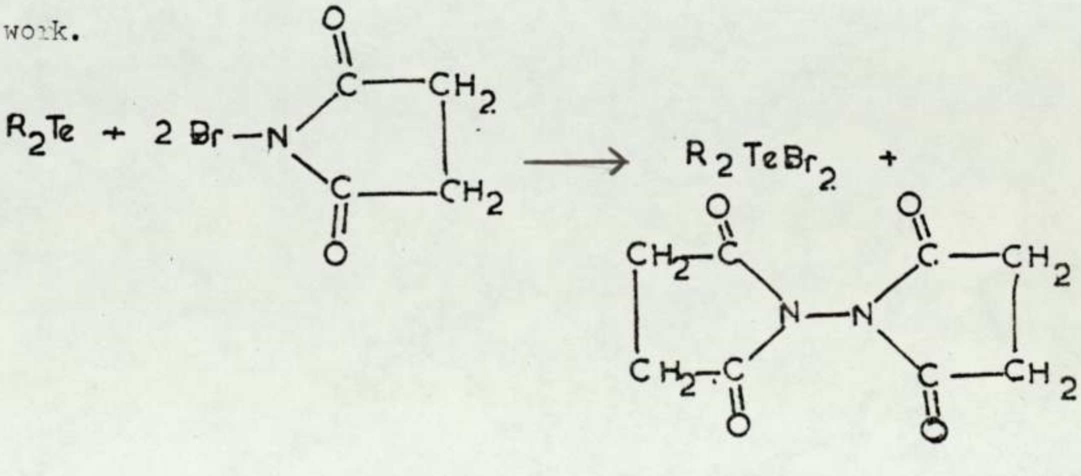
$Br-NHC(=O)C_6H_5$

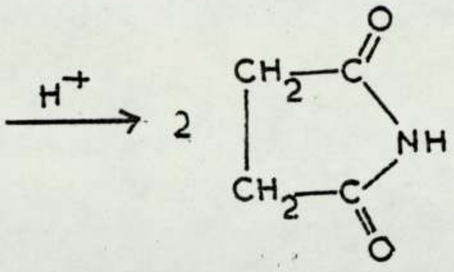




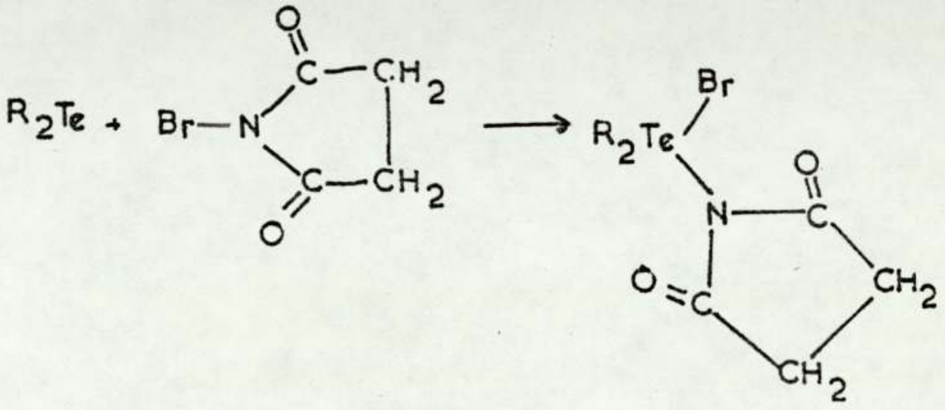
These reactions are further examples of the well known oxidative addition to Te II other examples being Cl_2,Br_2 I_2 and $(SCN)_2$ and the products are white solids giving conducting solutions in CH_3CN.

The reaction of NBS with diaryl tellurides has previously been studied by Dance who could not obtain the oxidative-addition product but instead obtained the diaryl tellurium dihalides and succinimide (or the dimer). He proposed the following reaction scheme, postulating as an intermediate the compound proposed by the latter work.





This reaction going via the following intermediate,



followed by reaction with a further mole of NBS to give the observed products.

So the aim of this particular piece of work was to try and find out which of the workers was correct and, if the latter, to try and identify a Te-N vibration in the infra-red.

The same preparative route as Srivastava was used (See section 4.2. 4.). Namely addition of equimolar quantities of a benzene solution of telluride to a solution, in the same solvent, of either NBS or NCS. The tellurides chosen for the study were diphenyl telluride and bis p-ethoxyphenyl telluride. The results of these reactions were the products similar to those produced by Srivastava, furthermore the reaction of the products with a further mole of either NBS or NCS gave the diphenyl tellurium dihalide and succinimide. So infact both workers were correct, Dance suggesting the correct mechanism for the appearance of products identified by him.

All the products gave satisfactory analysis, See Table 4.4.1., and a useful method of characterisation is infra-red spectroscopy.

One of the most prominent features of the infra-red spectra is the presence of two absorptions between approx. 1700 and 1800 cm^{-1}. The higher one of the two being due to the asymmetric stretching of the two carbonyl groups, the lower to the symmetric stretching, of the succinimide molecule. These absorptions are shown in Table 4.4.4. for succinimide, NBS, NCS and all the products prepared. It can be seen that the splitting of the two vibrations varies with the substituent on the nitrogen i.e H, Br, Cl, or Te

Work has been carried out by Popov[144] concerning the splitting of the vibrational frequencies of the multiple bonds of symmetric molecules.

Considering a symmetrical molecule containing two identical groups of atoms and two frequencies, corresponding to the symmetrical (ν_s) and antisymmetrical (ν_{as}) vibrations of the two equivalent groups The value of the splitting ($\Delta\nu$) depends to a considerable degree on the mechanical parameters of the intermediate units. In molecules in which the multiple bonds are separated by less rigid ordinary bonds, C-C, $\Delta\nu$ drops rapidly as the number of intermediate bonds is increased. Examples are unsaturated hydrocarbons with two C=C bonds, dicyanides and dicarbonyl, the latter gives splitting of about 7 cm^{-1}.

An entirely different situation exists when an oxygen or nitrogen bridge is present between carbonyl or other similar groups. In anhydides of organic acids the splitting of the C=O frequencies is large e.g. succinic anhydride it is 77 cm^{-1}. In the case of nitrogen bridges large splittings are also noticed e.g. N-methylsuccinimide $\Delta\nu = 69\ cm^{-1}$.

Popov suggests that the splitting of the vibrational frequencies of equivalent groups separated by different bridges should depend on the electronic properties both of the equivalent groups and of the bridging group. It is thought that splitting would be greatest in those cases when there is a strong interaction of the bridging group with each of the two equivalent groups adjoining it. This condition is observed when the bridging group possesses pronounced electron donor properties, while the two groups connected to it belong to the opposite type - electron acceptors:. A decrease in $\Delta\nu$, compared to N-Me and N-H compounds, is noted for N-Halo groups due to the weakening of the electron donor properties of the bridge nitrogen. Also the value of the splitting would depend upon the electronegativity of the group attached to N e.g. N-iodosuccinimide $\Delta\nu = 70\ cm^{-1}$; N-bromosuccinimide $\Delta\nu = 50\ cm^{-1}$ and N-chlorosuccinimide $\Delta\nu = 41\ cm^{-1}$.

The tellurium compounds have a splitting of 70 cm^{-1} and would therefore seem to have similar electron acceptor properties as carbon e.g $\Delta\nu$ for N- methylsuccinimide is 69 cm^{-1}.

This does not seem unreasonable as shown by evidence from another spectroscopic technique, namely Mössbauer spectroscopy. The quadrupole splitting, which in the case of tellurium relates to the p-orbital imbalance and hence the orbital population of a bond, is similar for diaryl tellurides and ditellurides i.e. for Te-Te bonds and Te-C bonds, e.g. ΔQ for Ph_2Te = 10.5 mm sec $^{-1}$ and for Ph_2Te_2 ΔQ = 10.7 mm sec^{-1}. Thus it seems that tellurium sees very little difference between another tellurium atom or a carbon atom, the orbital populations of Te-Te and Te-C bonds being very similar.

The foregoing discussion gives good evidence of the formation of a Te-N bond and now an assignment of the vibration may be attempted.

The N-halogen vibration in NBS or NCS has not yet, to my knowledge, been assigned. A paper by Petterson [145] concerned with N-Cl stretching vibration in various molecules did not detect this vibration for NCS in the region 800-650 cm^{-1}. Only compounds with strongly electronegative groups attached to the N-Cl group showed N-Cl vibrations in the region studied. e.g. trichlorocyanuric acid and NCS contain the -CONClCO- group and the fact that the group is bound to a highly electronegative -NClCONCl- group in the former but to the electropositive $-CH_2CH_2-$ in the latter evidently results in a a greater difference in the N-Cl freqency in the expected direction.

The band at 560 cm^{-1} in NCS disappears in NBS but a band at 480 cm^{-1} appears. Both of these bands disappear on reaction with the tellurides. In view of this the N-Cl and N-Br vibrations are assigned as 560 cm^{-1} and 480 cm^{-1} respectively.

On examining the IR spectra of the tellurium containing compounds, particularly those derived from bis(p-ethoxyphenyl) telluride, show the presence of a sharp band of medium intensity at 695 cm^{-1}. This band is present both in $(p\text{-}EtOPh)_2TeN(CO)_2(CH_2)_2Cl$ and $(p\text{-}EtOPh)_2TeN(CO)_2(CH_2)_2Br$ but absent in both of the starting materials. The band is also present in Ph_2Te derivatives but there is also a band at this position in Ph_2Te itself and so a confident assignment cannot be given for this compound.

It seems reasonable from the above data to assign the band at 695 cm^{-1} to a mode to which stretching of Te-N is contributing.

A study of the far infra-red spectra 400-200 cm^{-1} of the compounds Table 4.4.3. shows no absorption which can be assigned to Te-X. This is not surprising in view of the fact that the compounds are electrolytes in CH_3CN and are likely to have the same type of structure as the telluronium salts namely,

$$R_2TeN(CO)_2(CH_2)_2^+ \quad X^-$$

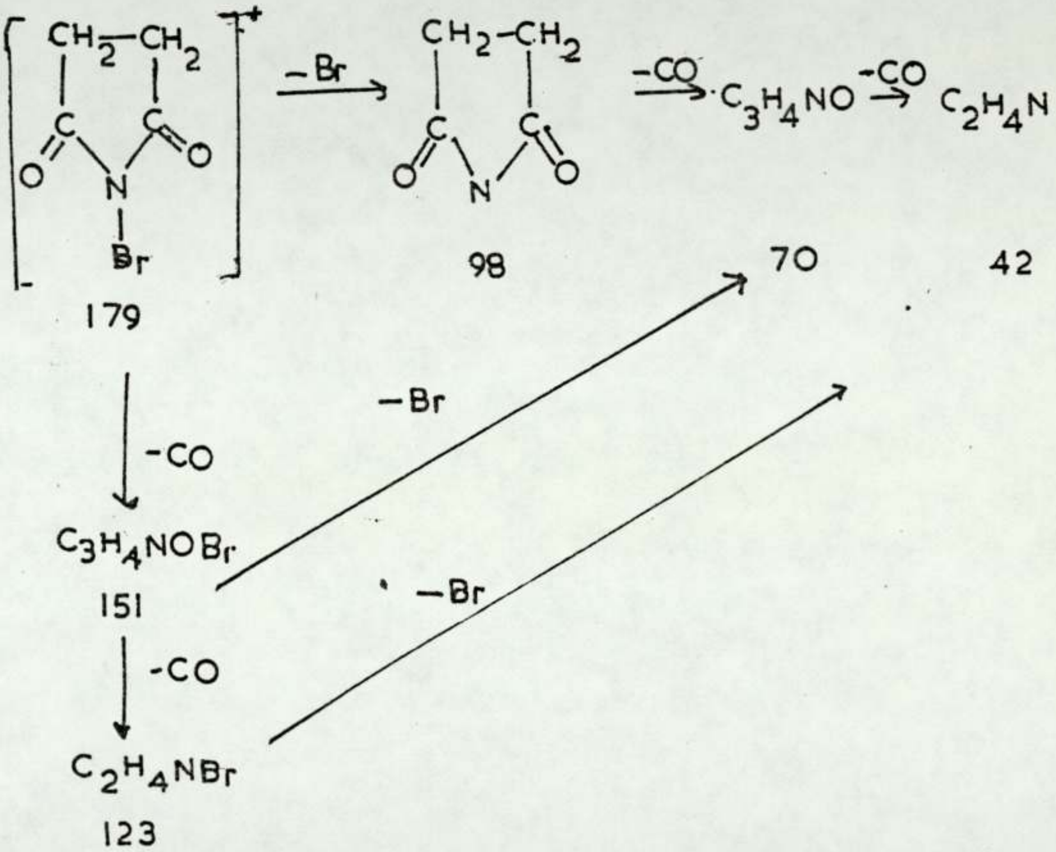
If this were so one would expect similar behaviour i.e. decomposition as follows

$$R_2TeN(CO)_2(CH_2)_2^+ X^- \rightleftharpoons R_2Te + X\text{-}N(CO)_2(CH_2)_2$$

This is a well known reaction of telluronium salts [146] and is confirmed by the mass spectra of the compounds. Similar results are obtained with Ph_2TeMeI where the mass spectrum shows only Ph_2Te and MeI and not Ph_2TeMe^+.

The mass spectra of the compounds are shown in Table 4.4.5. The decomposition scheme for the starting materials are shown below.

1) N-Bromosuccinimide



2) Tellurides are known to under go decomposition as follows;

$$\begin{tikzcd}
R_2Te \arrow[r, "-R"] \arrow[d, "-Te"] & RTe^+ \arrow[r, "-R"] \arrow[d, "-Te"] & Te^+ \\
R_2^+ \arrow[r] & R^+ &
\end{tikzcd}$$

(i) $(p\text{-EtOPh})_2TeN(CO)_2(CH_2)_2Br$

Peaks due to the telluride m/e 372, based on ^{130}Te are the highest found. The decomposition of this is also seen as depicted below

$$\begin{tikzcd}
\begin{array}{c}(pEtOC_6H_4)_2Te^+\\ m/e = 372\end{array} \arrow[r, "- p\text{-}EtOC_6H_4"'] \arrow[d, "-Te"] & \begin{array}{c}p\text{-} EtOC_6H_4Te^+\\ m/e = 251\end{array} \arrow[d, "-Te"] \\
\begin{array}{c}(p\text{-}EtOC_6H_4)_2^{\ +}\\ m/e = 242\end{array} \arrow[r] & \begin{array}{c}(p\text{-}EtOC_6H_4)^+\\ m/e = 122\end{array}
\end{tikzcd}$$

No NBS is seen in the mass spectrum as indicated by the absence of fragments at m/e 151 and 127 (see page 173) but bromine and the succinimide ion are present at m/e 79, 81 and m/e 98 respectively, also the decomposition peaks at m/e 70 and 42. Based on mass spectral evidence a competing mechanism seems to be taking place, namely the ejection of $EtOC_6H_4Br$. This is shown by the peaks at 171 and 173 due to $C_8H_5O^{79}Br^+$ and $C_8H_5O^{81}Br^+$.

(ii) $Ph_2TeN(CO)_2(CH_2)_2Br$

The mass spectra of this compound shows the presence of Ph_2Te and NBS as shown below

$$\begin{tikzcd}
\begin{matrix}\mathrm{Ph_2Te}^+\\ 284\end{matrix} \arrow[r, "-\mathrm{Ph}"] \arrow[d, "-\mathrm{Te}"] & \begin{matrix}\mathrm{PhTe}^+\\ 207\end{matrix} \arrow[r, "-\mathrm{Ph}"] \arrow[d, "-\mathrm{Te}"] & \begin{matrix}\mathrm{Te}^+\\ 130\end{matrix} \\
\begin{matrix}\mathrm{Ph_2}^+\\ 154\end{matrix} \arrow[r] & \begin{matrix}\mathrm{Ph}^+\\ 77\end{matrix} &
\end{tikzcd}$$

The decomposition of NBS is also shown as on page 173

Conclusions

i) New compounds have been prepared from NBS and NCS and selected tellurides, the new compounds are $(p\text{-}EtOC_6H_4)_2TeN(CO)_2(CH_2)_2X$, $X = Cl$, Br and $(C_6H_5)_2TeN(CO)_2(CH_2)_2Cl$.

ii) A Te-N vibration in these compounds as been assigned at 695 cm^{-1}

(N-Cl and N-Br have also been assigned at 560 and 480 cm^{-1} respectively)

iii) The succinimide derivatives are believed to be of similar structure to telluronium salts as indicated by conductivity and mass spectral evidence.

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