“Studies on Vinyl- and Alkoxy carbonyl methyl tellurium Compounds”

Summary

Systematic studies in the field of ‘Organotellurium Chemistry’ initiated at the beginning of twentieth century were hit by the myth about the foul-smell and sensitivity of organotellurium compounds towards air and light. However, the extensive studies by Petragnani in 1950s and 1960s on the reactivity of inorganic and organotellurium compounds established that barring the lower alkyl derivatives majority of the organotelluriums are completely odorless and can be stored in a laboratory for long time. Since 1970, organotellurium chemistry has seen a great renaissance as is evidenced by the prodigious growth of literature in form of research papers, review articles, monographs and books. Besides, the anomalous interesting chemistry of tellurium compounds among organochalcogens, their potential utility in the fields of material science and organic syntheses appears to be responsible for the current interest.

The presence of functional groups with electron-rich center(s) viz. nucleophilic atoms, N, P, O or olefinic bonds with \( \pi \)-electrons, in the organic ligands bound to Te atom among the ‘Functionalized Organotellurium Compounds’ influences appreciably stability, reactivity as well as their supramolecular association in the crystalline state. While each Te atom among diorganoditellurides or organotellurium(II) derivatives is laden with two lone pairs of electrons, the hypervalent Te atom among organotellurium(IV) compounds possesses one lone pair. The attractive force, existing between two such electron-rich centers, namely the central Te atom and a neighboring functional group, coined as secondary bonding interaction (SBI), is now regarded as a delocalized three center – four electron (3c-4e) \( \sigma \) bond with directional characteristics but has significant electrostatic component as well.

The utility of vinyl group in organic synthesis and ubiquity of carbonyl functionality among organic and biological systems has provided an impetus in recent years, to develop newer synthetic protocols to obtain organotelluriums derivatives affording these electron-rich centers. Introduction of Te, the heavy chalcogen atom imparts characteristic features that are advantageous in characterization. It would provide a \( ^{125} \) Te NMR probe and also the single site heavy atom that may substantially facilitate the protein crystallographers in the determination of three-dimensional structures of many important biomacromolecules.
It has been noticed that subtle changes in electronic and steric factors of ligands bound to tellurium atom can bring about substantial differences in the molecular geometry and self-assembly, at least in the crystalline state of organotellurium compounds. For instance, both the carbonyl functionalized organic ligands among, bis(acylmethyl)tellurium(IV) dihalides and bis(amidomethyl)tellurium(IV) dihalides are found to act as (C, O) chelating agents via intramolecular Te···O secondary bonding interaction, only one of the ester functionalized organic ligands in bis(methoxycarbonylmethyl)tellurium(IV) dibromide adopts the bidentate mode and the O atom of the second ligand prefers intermolecular over the intramolecular Te···O interaction. A survey of the existing literature on functionalized organotelluriums reveals that role of aforesaid factors in the syntheses and on the stereochemistry of the resulting vinyl- and alkoxy carbonylmethyltellurium derivatives remains unexplored.

The present thesis is an attempt to examine (a) the regio- and stereoselectivity of electrophilic addition reaction of tellurium tetrahalides, TeX₄ and aryltellurium trihalides, ArTeX₃ (X = Cl, Br) to the terminal acetylenes. 1-Naphthyl and mesityl groups, with specific electronic and steric influence, are the aryl ligands bound to Te among the electrophiles being used and 1-alkynes chosen for the purpose bear a phenyl, p-tolyl or sterically demanding tertiary butyl substituent and (b) nucleophilic substitution reaction of the esters of 2-haloacetic acids with an aryltellurolate as well as their oxidative addition to elemental tellurium as synthetic routes to obtain alkoxy carbonylmethyltellurium derivatives.

The dissertation, thus describes the experimental details, characterization data for the new compounds together with the inferences arrived at. The details of procured chemicals and solvents, syntheses of organotellurium compounds used as precursors and that of the employed analytical and spectroscopic techniques are summarized in form of a chapter entitled, ‘Materials, Analytical Methods & Experimental Techniques’.

In the present study, tellurium tetrachloride, TeCl₄ or aryltellurium trichlorides, ArTeCl₃ (Ar = 1-C₁₀H₇, Np; 2,4,6-Me₃C₆H₂, Mes; 4-MeOC₆H₄, Ans) adds across the triple bond of 1-alkynes, RC≡CH (R = Ph, 4-MeC₆H₄, t-Bu) in toluene under reflux to afford very good yields of bis(2-chloro-2-phenylvinyl)tellurium dichloride or aryl(2-chloro-2-phenylvinyl)tellurium dichlorides respectively, as the ultimate addition products (Scheme 1). The addition reaction is compatible with the steric demand of mesityl or 1-naphthyl ligand attached to Te(IV) or that of tertiary butyl terminal substituent at the acetylenic carbon atom.
Scheme 1

Reduction of dichloromethane solutions of the synthesized vinyltellurium(IV) dichlorides with aqueous sodium metabisulfite gives the corresponding vinyltellurides as oils, except for (2-chloro-2-phenylvinyl)mesityl telluride (IB) which was obtained as a crystalline solid. Addition of Br_2 or I_2 to dichloromethane solutions of these tellurides oxidizes them to the corresponding vinyltellurium(IV) dibromides (IBb, ICb, IIIb) and diiodides (IBc, ICc), which are sharp melting solids that are soluble in chloroform and dichloromethane.

The C and H microanalyses correspond to 1:2 and 1:1 (Te(IV) chloride : terminal acetylene) stoichiometry for the adducts of tellurium tetrachloride and aryltellurium trichlorides, respectively. The significant deshielding of ^1H NMR signal due the vinyl proton appearing in the region for aromatic protons in each of the spectrum substantiates telluration at the acetylenic carbon. The deshielding is greater among the compounds bearing sterically demanding Te-bound aryl ligand, viz. 1-naphthyl and mesityl derivatives if compared with their anisyl analogues. Appearance of separate signals for each of the three methyl substituents of the mesityl ligand in the ^1H and ^13C spectra of Te(IV) derivatives, IBa, IBb, IBc and IIBa
indicates a magnetic inequivalence of the ortho methyls. It, thus reveals restricted rotation of the aryl ligand about the Te—C(Mes) bond suggesting thereby the steric congestion about the four-coordinate central Te atom. Presence of only two methyl signals with integration value of one being twice the other in $^1$H spectrum of Te(II) compound (IB) devoid of axial halo ligands is corroborant of the free rotation of the mesityl ring in it.

Structural assignment of the new adducts is based upon single-crystal X-ray diffraction data collected for the compounds IAa, IBa, IBc, IB, ICc, IIIAa, and IIIa. ORTEP views of molecular structures (with thermal ellipsoid probability %) deleting H atoms for want of clarity, are presented below.
The primary geometry around the Te atom in all the diorganotellurium dihalides, is pseudo trigonal bipyramidal with halo ligands at the apical positions and the Te(IV) lone pair at one of the equatorial sites. Steric repulsion due to the presence of bulky aryl ligand among the 1-naphthyl and mesityltellurium(IV) compounds also causes widening of the equatorial C–Te–C angle when compared to the corresponding anisyltellurium(IV) analogue, ICc, bis(vinyl)tellurium(IV) dichloride, IIIa or the arylvinyltelluride IB. The steric influence on the geometry around Te(IV) is more obvious among the mesitylvinyltellurium dihalides. The exocyclic angles \( \angle \text{Te–C9–C10} \) and \( \angle \text{Te–C9–C14} \) at the ipso carbon atom of the mesityl ligand in IBa \( \{114.4(2) ^\circ, 124.3(2) ^\circ\} \) and IBc \( \{111.6(2) ^\circ, 128.4(4) ^\circ\} \) when compared to those in IB \( \{118.8(2) ^\circ, 120.4(2) ^\circ\} \) reveal significant deviation from their putative value of 120°. This substantiates the loss of local \( C_2 \) symmetry of the mesityl group about the Te–C axis and hence the magnetic inequivalence of its ortho methyl substituents, as inferred from the separate signals in their \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra.

The 2-chloro-2-organylvinyl ligand bound to Te atom adopts the customary planar structure and displays (Z) stereochemistry invariably in each of these vinyltellurium derivatives. The addition reactions are, thus, regioselective and obey Markovnikov rule. The shorter interatomic distance between the cis positioned Te and Cl atoms, which varies in the range 3.204(6) (IAa) to 3.362(3) Å (IB), compared to the sum of van der Waals radii of the two atoms, \( \sum r_{vdw}(\text{Te, Cl}) \) of 3.83 Å substantiates the presence of intramolecular 1,4-Te⋯Cl attractive interaction between the two lone pair laden atomic centres. Such an intramolecular Te⋯Cl interactions appears to contribute in the realization of (Z)-conformation to the vinyl group among these compounds.

It is apparent from the ORTEP diagrams that the central Te(IV) atom in the arylvinyltellurium dihalides, IAa, IBa, IBC, IB, ICc, and IIIAa enhances its coordination number to five via intramolecular coordination of the Cl atom of the 2-substitued vinyl ligand. However, propensity of Te(IV) to complete its coordination number of six is highlighted among the lattices of 1-naphthyl- and anisyltellurium(IV) derivatives (IAa, IIIAa and ICc), where intermolecular Te⋯X SBI (X = a Te(IV)-bound halo ligand, Cl or I, of the adjacent molecule) give rise to zero-dimensional supramolecular dimeric units (Chart 1).
Chart 1. Zero-dimensional supramolecular unit realized through intermolecular Te···X SBIs in the crystal lattice of ICc, Figure (a); IIIa, Figure (b) and Ia, Figure (c). Hydrogen atoms are omitted for clarity.

In the case of the analogous mesityl derivatives, IBa and IBc, the bulkier aryl group hinders the access of halo ligands of the neighboring molecules to the central five-coordinate tellurium atom; as a consequence, their lattices are devoid of similar supramolecular dimmers. Likewise, in the lattice of, bis[2-chloro-2-(t-butyl)vinyl]tellurium dichloride, IIIa where the central Te(IV) has acquired six coordination via intramolecular Te···Cl secondary bonding interactions, is devoid of dimeric units via intermolecular Te···Cl attractions.

Though, the studies on the electrophillic addition of tellurium tetraiodide, TeI₄ to a C≡C bond are scarce, those of tellurium tetrabromide, TeBr₄ with terminal acetylenes,
RC≡CH (R = Ph, C₅H₁₁) has been studied in the recent past. Isolation of bis(β-bromovinyl)tellurium dibromides, the 1:2 adducts as the ultimate products in these reactions is interesting in view of the fact that TeCl₄ in its reaction with 1-alkynes is known to afford (β-chlorovinyl)tellurium trichlorides as the primary product which gets converted into bis(β-chlorovinyl)tellurium dichloride only when refluxed in glacial acetic acid. It was, therefore, believed that similar to TeBr₄, the intermediate product, a vinyltellurium tribromide, formed in the first step, also undertook syn addition to a triple bond under ambient conditions, to afford bis(2-bromo-2-phenylvinyl)tellurium dibromide (Scheme 2). Reduction of the dibromide with NaBH₄, gave the corresponding divinyltelluride which owing to the presence of double bonds, have great synthetic potential to bring about functional transformation as well as to form carbon – carbon bonds. The (Z) configuration of the β-bromovinyl groups in this bis(vinyl)tellurium dibromide, was established by X-ray diffraction study.

Besides, the studies on the electrophillic addition reactions of organotellurium tribromides and iodides towards 1-alkynes are limited to n-BuTeBr₃, and PhTeX₃ (X = Br, I).

It has, therefore, been envisaged to extend our study on addition reaction of Te(IV) electrophiles to terminal acetylenes and examine the electrophilicity of TeBr₄ and aryltellurium tribromides with different electronic and steric attributes in this context. Phenyl, 4-tolyl and t-butylacetylenes undergo easy regio- and stereo-specific electrophilic addition of tellurium tetrabromide, TeBr₄ or aryltellurium tribromide, ArTeBr₃ (Ar = 1-naphthyl, 1-C₁₀H₇, Np; mesityl, 2,4,6-Me₃C₆H₂, Mes; anisyl, 4-CH₃OC₆H₄, Ans; phenyl, C₆H₅, Ph) when refluxed in stoichiometric amounts in toluene to afford very good yields of divinyltellurium dibromide, (Z)-(t-BuBrC=CH)₂TeBr₂ or arylnvinyltellurium dibromide of general formula, (Z)-[R(Br)C=C(H)]TeArBr₂ [R= Ph, 4-CH₃C₆H₄, C(CH₃)₃] respectively, as the ultimate products (Scheme 3).
Scheme 3

Characterization and structural studies of the new compounds based on elemental analyses and $^1$H, $^{13}$C and $^{125}$Te NMR data indicate that 1,2-addition of Te–Br bond(s) of the tetra- and tribromotellurium(IV) reagents across a triple bond of 1-alkynes in toluene, similar to their chloro analogues, is regio- and stereospecific and proceeds in a syn fashion via a concerted four-centered mechanism to give (Z) isomer exclusively irrespective of the steric bulk of acetylenes or Te(IV) substituents. Solid state structures of the compounds (2-bromo-2-(p-tolyl)vinyl)phenyltellurium dibromide, 2D and (2-bromo-2-(t-butyl)vinyl)phenyltellurium dibromide, 3D have been solved by single-crystal X-ray technique.

ORTEP views of the two independent molecules of (p-tolylBrC=CH)TePhBr$_2$, 2D and t-BuBrC=CH)TePhBr$_2$, 3D. Hydrogen atoms are omitted for clarity.

The ORTEP views presented above show that the molecular structures of both the compounds possess the putative planar vinyl group, C(Br)C=C(H)Te with (Z) geometry owing to presence of intramolecular 1,4-Te···Br attractive interaction. In the crystal lattices of both
the compounds, six coordination by Te(IV) is attained by the formation of dimeric units via intermolecular Te⋯Br secondary bonding interactions. In compound 2D, pairs of the independent molecules “1” and “2” form dimeric units while in case of 3D, pairs of identical molecules give rise to centrosymmetric dimers by means of intermolecular reciprocatory Te⋯Br\(^{j}\) (i = 1.5-x, -0.5+y, 1.5-z) secondray bonding interaction.

A dimeric unit of independent molecules “1” and “2” of \((p\text{-tolylBrC=CH})\text{TePhBr}_2, \text{2D}\)

A centrosymmetric dimeric unit of identical molecules of \((t\text{-BuBrC=CH})\text{TePhBr}_2, \text{3D}\)

Furthermore, it has been noticed that though, electrophilic substitution at the α-carbon of acylmethanes with tellurium(IV) halides, proceeds smoothly to provide acylmethytellurium(IV) dihalides, attempted telluration of acetic acid esters by electrophilic substitution reaction did not succeed. Consequently, a variety of alternative synthetic routes have been explored in the past to prepare alkoxyacarbonylmethyltellurium derivatives that have increasing importance in organic synthesis. Surprisingly, the oxidative addition of α-acyl/amidomethanes to elemental tellurium has been successfully employed to obtain carbonyl functionalized organotellurium derivatives, but such an insertion of Te\(^0\) into C-X bond adjacent to the carbonyl group in an ester functionality has never been explored as a synthetic mode to prepare symmetrical bis(alkoxyacarbonylmethyl)tellurium derivatives. In this context, it has been envisaged in the present investigation to examine the potential of alkoxyacarbonyl functionality in the activation of α-C\(_{sp3}\)−X (X = I, Br) bond to insert elemental tellurium and to determine the bonding mode of the ester functionalized ligands in the resulting bis(alkoxyacarbonylmethyl)tellurium(IV) dihalides. The mixed (alkoxyacarbonylmethyl)aryltellurium(IV) dihalides have also been prepared for structural comparison.
When a mixture of tellurium powder, ROCOCH$_2$Br and NaI is stirred overnight at room temperature, bis(alkoxycarbonylmethyl)tellurium(IV) diiodides, (ROCOCH$_2$)$_2$TeI$_2$ (R = Me, 1c; t-Bu, 2c) are obtained in very good yields. On reduction in a biphasic medium with Na$_2$S$_2$O$_5$, both the diiodides, 1c and 2c, afford the corresponding tellurides, (ROCOCH$_2$)$_2$Te as yellow liquids which were characterized as their dihalides (ROCOCH$_2$)$_2$TeX$_2$ [X = Cl (1a, 2a), Br (1b, 2b)] after halogenations with SO$_2$Cl$_2$ and Br$_2$ at 0°C (Scheme 4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Product</th>
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<tr>
<td>1a</td>
<td>Te, NaI</td>
<td>(ROCOCH$_2$)$_2$Tel$_2$</td>
</tr>
<tr>
<td>2c</td>
<td>NaS$_2$O$_5$</td>
<td>(ROCOCH$_2$)$_2$Te</td>
</tr>
<tr>
<td>1b</td>
<td>X$_2$</td>
<td>(ROCOCH$_2$)$_2$TeX$_2$</td>
</tr>
<tr>
<td>1c</td>
<td>R = Me, 1c; t-Bu, 2c.</td>
<td></td>
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<tr>
<td>2b</td>
<td>R = Me, 1; t-Bu, 2.</td>
<td></td>
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<tr>
<td>2a</td>
<td>X = Cl. 1a, 2a:</td>
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<tr>
<td>1b</td>
<td>= Br. 1b, 2b</td>
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**Scheme 4**

Compound 1b can also be prepared by the metathetical reaction between 1a and sodium bromide. Attempts to prepare the mixed halide, (CH$_3$OCOCH$_2$)$_2$TeClBr by stirring an equimolar mixture of 1a and NaBr did not succeed, however the isolated sample showed three peaks in its $^{125}$Te NMR spectrum (at 796, 775 and 748 ppm in 3:3:1 ratio) which may be assigned to (CH$_3$OCOCH$_2$)$_2$TeCl$_2$, (CH$_3$OCOCH$_2$)$_2$TeClBr and (CH$_3$OCOCH$_2$)$_2$TeBr$_2$ respectively.

However, elemental tellurium failed to react directly with α-bromoesters when heated together up to ~100°C in absence of an alkali metal iodide. The oxidative addition of alkyl α-bromoacetates to Te(II) species also did not succeed. Addition of CH$_3$OCOCH$_2$Br to a stirred solution of mesityltellurium bromide in dichloromethane (prepared *in situ* by mixing equimolar amounts of dimesitylditelluride and Br$_2$) separated some elemental tellurium and the isolated product corresponded to dimesityltellurium dibromide.

In addition, nucleophilic substitution reaction of α-bromoesters, ROCOCH$_2$Br, with aryltellurolates, ArTe$^-$ (Ar = 1-C$_{10}$H$_7$, Np; 2,4,6-Me$_3$C$_6$H$_2$, Mes) at room temperature has been used in the present study to obtain mixed diorganotellurium derivatives, the (alkoxycarbonylmethyl)aryltellurides, (ROCOCH$_2$)TeAr (Ar = Np, R = Me, 3; t-Bu, 4; Ar =
Mes, R = Me, 5; t-Bu, 6) as yellow oils or low melting solid 6. Oxidative addition of dihalogens to α-aryltellurated esters, 3 - 6, gave the dihalides, (ROCOCH₂)TeX₂ (X = Cl, 3a-6a; Br, 3b-6b; I, 3c-6c) (Scheme 4). These mixed diorganotellurium(IV) dihalides are crystalline solids stable to air and moisture, except 3c and 5c which decompose on standing at room temperature. Analytical and spectroscopic data obtained for the characterization of all the new compounds together with the diffraction data for 1b, 1c, 3b, 5b, and 6a have been discussed in this chapter on “Alkoxycarbonylmethyltellurium Derivatives: Facile Synthesis and Structural Studies”.

Molecular structures of (MeOCOCH₂)TeNpBr₂, 3b, (MeOCOCH₂)TeMesBr₂, 5b, and (t-BuOCOCH₂)TeMesCl₂, 6a, given below show that the functionalized organic moiety, ROCOCH₂, behaves as a (C, O) chelating ligand. The carbonyl O atom of the ester group in these compounds is involved in a 1,4-Te···O secondary bonding interaction. These structures are comparable to those of analogous compounds, viz., (acylmethyl)aryltellurium dihalides, (RCOCH₂)TeX₂ or (amidomethyl)aryltellurium dihalides, (R₂NCOCH₂)TeX₂ reported earlier.

![Molecular structure of (CH₃OCOCH₂)TeNpBr₂](image1)

![Molecular structure of (CH₃OCOCH₂)TeMesBr₂](image2)

![Molecular structure of (t-BuOCOCH₂)TeMesCl₂](image3)

However, the functionalized ligands in the case of (MeOCOCH₂)₂TeI₂, 1c, unlike (RCOCH₂)₂TeX₂ or (R₂NCOCH₂)₂TeX₂, are devoid of intramolecular Te···O secondary
bonding interaction. Interestingly, in case of (MeOCOCH₂)₂TeBr₂, 1b, the bromo analogue of 1c, one of the two organic ligands takes part in an intramolecular 1,4-Te∙∙∙O interaction, the other appears to involve an intermolecular Te∙∙∙O interaction to result in a one-dimensional array of molecules in its crystal lattice.

Based on the foregoing observations on alkoxytellurium derivatives, it may now be safely concluded that:

- The potential of an ester group to activate the α-C₃–Br bond to insert Te(0) and afford ester-functionalized organotellurium derivatives is poor compared to an acyl or amido group.
- Stirring at room temperature of a mixture of an alkyl ester of α-bromoacetic acid, sodium iodide and tellurium powder however provides a convenient synthetic route to obtain the desired organotellurium compounds.
- The delicate balance between the electronic factors and crystal forces appears to direct the bonding mode of the alkoxytelluriummethyl ligands in the solid state.
- The secondary bonding interactions involving Te(IV) atom with a lone pair, appear to ignore the VSEPR rules at least in the crystalline state of the functionalized organotellurium(IV) halides.