

CHEMISTRY OF ARYLTELLURIUM(IV)- β -DIKETONATES

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Reactions of aryltellurium(IV) chlorides viz. ArTeCl_3 , Ar_2TeCl_2 and Ar_3TeCl (where $\text{Ar} = \text{C}_6\text{H}_5$, 4-MeOC₆H₄, 4-EtOC₆H₄, 4-HOC₆H₄, 3-Me-4-HOC₆H₃ or 2,4-(HO)₂C₆H₃) with 3,3-bis(chloromercury) pentane-2,4-dione(I) and a variety of β -diketones and their sodium salts have been investigated. The acetylacetonate reacts with ArTeCl_3 only giving C_1 bonded acetylacetonates. A strong intramolecular interaction between tellurium and oxygen linked to C_4 has been evidenced in the C_1 -bonded derivatives by their ^1H and ^{13}C NMR spectra. The reactions with (I) result in C_2 -bonded acetylacetonates of tellurium(IV), but both HgCl groups cannot be substituted, probably due to strong intramolecular interaction of Hg with the neighbouring CO groups. The interaction has been evidenced by ^1H , ^{13}C and ^{199}Hg NMR spectra of the C_2 -bonded derivatives and also indicated by crystal structure of (I). The Ph_3TeCl reacts with sodium- β -diketonates to give telluronium salt type derivatives, which become more ionic when the β -diketone moiety possesses fluorinated alkyl groups. The association between Ph_3Te and β -diketonate anion has been found to be stronger for the pyrazolonate derivatives. The Ph_2TeCl_2 reacts with sodium salts of β -diketones to yield diphenyl tellurium bis(β -diketonates), which are the first examples in which tellurium is chelated with a β -diketonate moiety through oxygens. Some reactions of aryltellurium(IV)- β -diketonates have also been investigated.

Key Words : Aryltellurium(IV)- β -diketonates; C_1 -bonded β -diketonates; Chelated Tellurium β -diketonates

INTRODUCTION

THE β -diketones ($\text{RCOCH}_2\text{COR}'$) constitute an important class of oxygen ligands. Their complexation with metal ions has been extensively studied.¹ Some of these complexes also find interesting applications. The commonest coordination mode of β -diketones in their metal derivatives is the chelation through oxygen atoms. The examples of linkage of a β -diketone moiety with the metal through its central carbon atom are very few. When R or R' is methyl, the metal can replace one of its hydrogen resulting $\text{CH}_2\text{-M}$ type linkage. The chelation through one oxygen and carbon of methyl group is also possible.

The β -diketonates of metalloids are relatively less explored and differ generally from that of metals. The extent of their resemblance with the metal analogues can be best understood by examining the β -diketonates of tellurium because it is among the noblest metalloids. The survey of literature reveals that β -diketonates of tellurium are little explored. Morgan and coworkers² were the

first to carry out the reaction of TeCl_4 with β -diketones and isolate $R\text{TeCl}_3$ (I) and $R_2\text{TeCl}_2$ (II) type derivatives (where $R = (-\text{CH}_2\text{COCH}_2\text{COCH}_3)$ or $(-\text{CH}_2\text{COCH}_2\text{COC}_6\text{H}_5)$). In the reaction of acetylacetone (*acacH*) another product identified later by NMR spectra³ and X-ray⁴ as telluracyclohexane-3, 5-dione dichloride was also obtained. Morgan and coworkers² also carried out the reaction of TeCl_4 with dibenzoylmethane and isolated an unstable $R\text{TeCl}_3$ type derivative in which the linkage of tellurium was considered to be with the C_3 -carbon of β -diketone. The syntheses of Ar_3TeL_2 and ArTeL_3 type compounds (where $L = \text{dibenzoylmethane}$; $\text{ArTe} = \text{PhTe}$ or $(4\text{-C}_6\text{H}_5\text{OC}_6\text{H}_4)$ Te and $\text{Ar}_2\text{Te} = \text{Ph}_2\text{Te}$ or phenoxtellurine) have been reported but their structural features not examined.⁵

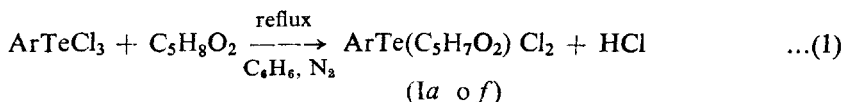
In view of very little information available in literature about the β -diketonates of tellurium and their obvious importance in understanding the extent of similarity between complexation behaviour of metals and metalloids, it was thought worthwhile to explore the reactions of tellurium(IV) and organotellurium(IV) halides with β -diketones with the three main objectives :—

- (a) What is the reactivity of organotellurium(IV) chlorides towards β -diketones?
- (b) Whether tellurium can be linked with C_3 -atom of a β -diketone.
- (c) Whether β -diketones can form chelates with tellurium.

The results of these investigations are the subject of this paper.

C_1 -BONDED β -DIKETONATES OF TELLURIUM(IV)⁶

The ArTeCl_3 reacts with *acacH* according to equation 1.



(where $\text{Ar} = \text{C}_6\text{H}_5(a)$, $4\text{-OHC}_6\text{H}_4(b)$, $4\text{-OCH}_3\text{C}_6\text{H}_4(c)$, $4\text{-OC}_2\text{H}_5\text{C}_6\text{H}_4(d)$, $3\text{-CH}_3\text{-4-OHC}_6\text{H}_3(e)$ or $2,4\text{-(OH)}_2\text{C}_6\text{H}_3(f)$.)

The compound 1a to 1f are non electrolytes in CH_3CN (λ_M 1.45–8.68 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) and behave as diorganytellurium dichlorides. This is supported by their hydrolysis to corresponding $(\text{ArTeO})_2\text{O}$ by 10 per cent sodium carbonate solution. The concentrated hydrochloric acid can liberate *acac* from them (eq 2).



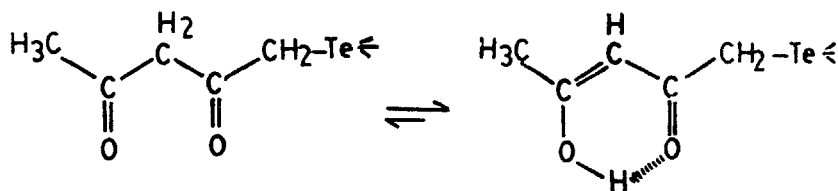
The resorcinol exceptionally reacts with 1c, on heating them in 4 : 1 molar ratio in toluene at 80–90 °C for 12h, resulting highly hygroscopic $(4\text{-CH}_3\text{OC}_6\text{H}_4)$ $(2,4\text{-(OH)}_2\text{C}_6\text{H}_3)$ $(\text{C}_5\text{H}_7\text{O}_2)$ TeCl. On reduction of 1c and 1f with fused $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ or $\text{Na}_2\text{S}_2\text{O}_5$, the elemental tellurium is precipitated whereas Ar_2Te_2 is obtained in other cases.

The chemical shifts observed in ^1H NMR spectra (Table I) suggest that in all the compounds (*Ia* to *If*) tellurium moiety is bonded with terminal carbon (C_1) atom of *acac* and the keto-enol tautomerism, as depicted in Scheme 1, exists in solution. Our assignments of $\text{CH}_2\text{-Te}$ protons agree well with the literature reports for telluracyclohexane-3,5-dione, its dichloride and $(\text{CH}_3\text{COCH}_2\text{COCH}_2)_2\text{TeCl}_2$. The chemical shifts for protons of phenyl ring and its substituents were in agreement with our earlier reports.^{7,8} However, the OH resonance for *Ib* has been found merged in the phenyl signal. The per cent enol-form of *acacH* increases to 95 when a hydrogen at C_1 is replaced by $-\text{Te}(\text{Ph})\text{Cl}_2$ group. The substitution of an electron donating group on phenyl ring at position para to tellurium reduces the amount of enol form almost to the level of *acacH*. The signals for phenyl protons of keto form could not be identified because of their merging in the phenyl signals of enol form except for *Ib*. In comparison to pure *acacH* the CH_3 (δ 1.92/2.11ppm) and CH/CH_2 resonances (δ 5.5/3.5ppm) are observed to be shielded in the spectrum of *Ia*. This indicates that in *Ia* oxygen has significant secondary interaction with Te made positive by two electronegative chlorine atoms, which in turn brings the CH_3 protons under the influence

TABLE I
Chemical shifts (δ , ppm)⁺ in ^1H NMR spectra of *I* at 25 °C

I	Enol form			Keto form		
	CH_3	CH	$\text{CH}_2\text{-Te}$	CH_3	CH_2	$\text{CH}_2\text{-Te}$
<i>a</i>	1.36	4.89	4.05	1.53	2.87	4.33
<i>b</i>	2.08	5.79	4.64	2.19	3.85	4.82
<i>c</i>	2.08	5.65	4.54	2.13	3.89	4.74
<i>d</i>	2.09	5.65	4.53	2.26	3.76	4.72
<i>e</i>	2.11	5.69	4.58	2.69	3.78	4.74
<i>f</i>	2.07	5.61	4.59	2.39	3.58	4.81

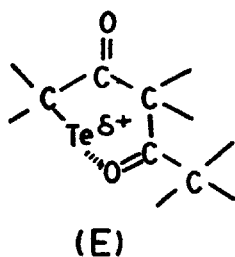
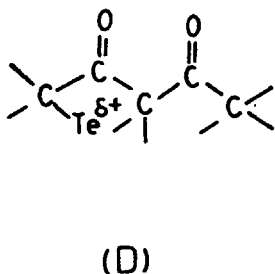
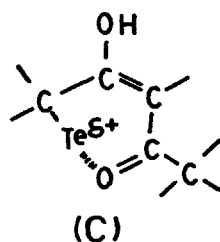
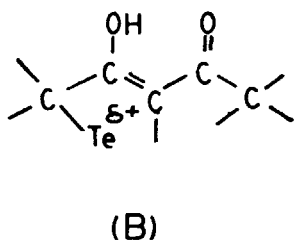
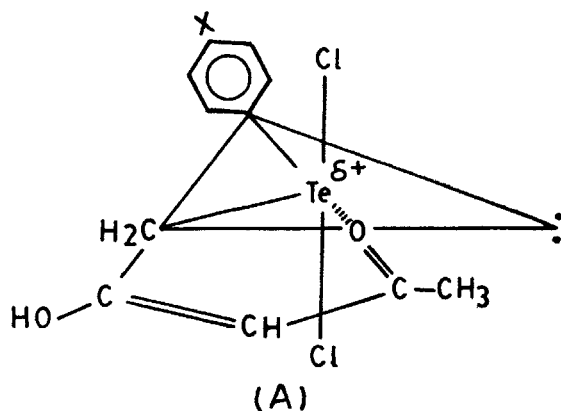
⁺Solvent *b, f* – CD_3CN , *a, c, d, e* – CDCl_3



SCHEME-1

of tellurium lone pair (structure A) and shields them. The shielding of CH/CH_2 also seems to result from the delocalization of electron density arising out of this interaction. When groups para to tellurium make it less positive, this secondary interaction breaks down and configuration B or D results which has CH/CH_2

proton in the vicinity of $\text{Te}^{\delta+}$ and, therefore, these protons are somewhat deshielded in comparison to configuration C or E. In absence of secondary interaction the positive charge on Te affects CH_2 group bonded directly to it more and thus that is also deshielded. The chemical shifts of CH_3 and CH/CH_2 protons observed for *Ib* to *Ic* are in general closer to the values of pure *acacH*, which further support the hypothesis of intramolecular secondary interaction and its breaking.



In ^{13}C NMR spectra C_1 signal appears around 60 ppm, supporting the linkage of tellurium moiety with C_1 of *acac*. The variation in the position of methyl carbon (C_5) and C_1 signals with substitution on phenyl group is not much

(0.4–2ppm), suggesting the weak nature of tellurium oxygen interaction. The small deshielding (0.4ppm) of C₅ in *Ib* with respect to *Ia* supports the possibility of above-mentioned hypothesis of weak Te–O secondary interaction.

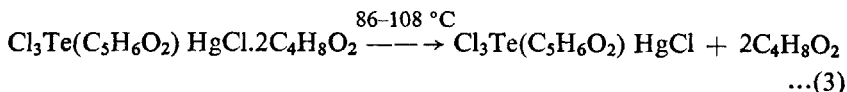
The IR spectra of these Ar(C₅H₇O₂) TeCl₂ type derivatives have broad bands assignable to ν_{OH} , between 3200–3600cm⁻¹ and ν_{CO} bands between 1585–1720cm⁻¹. In pure *acacH* also these bands are observed at similar positions, suggesting that tellurium is not bonded either to oxygen of *acacH* or its C₃ carbon atom. This inference in conjunction with the occurrence of ν_{Te-CH_2} at 490–510cm⁻¹ and $\nu_{Te-C(phenyl)}$ at 205–265cm⁻¹ support the bonding of tellurium with C₁ atom of *acacH*, keto-enol tautomerism represented in Scheme 1 and the predominance of enol form in solid state too.

The mass spectrum of *Ia* has a feature at $m/e = 300$, most probably due to telluracyclohexane-3,5-dione dichloride ion, which further supports the bonding of tellurium moiety with C₁ of *acac*. The reaction of Ar₃ TeCl with *acacH* in accordance to equation 1 probably does not occur due to its ionic nature. The Ar₂TeCl₂ being more covalent also does not react with acetylacetone.

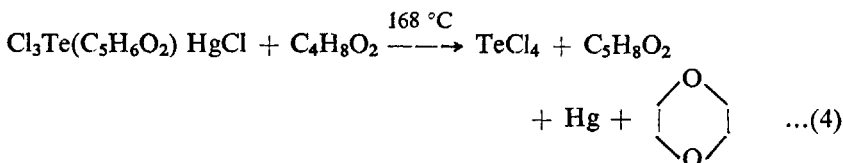
C₃-BONDED β-DIKETONATES OF TELLURIUM(IV)⁹

The 1 : 1 reaction of 3,3-bis(chloromercury)-2,4-pentanedione¹⁰ with TeCl₄ and Ph₂TeCl₂ in dioxane and Ph₃TeCl in methanol gives Ph_{*n*}TeCl_{3-*n*}⁻ (C₅H₆O₂) HgCl (where *n* = 0, 2 and 3) type compounds.

The TeCl₃(C₅H₆O₂) HgCl(II) crystallizes with dioxane (~ 2mol/mol) which is given off slowly on storage. Its TGA curve shows two well defined steps, which can be accounted for in terms of the equations 3 and 4 which reflect the weak bonding of dioxane in it.



(weight loss : Observed 20.19 per cent; Calc 23.65 per cent).



(weight loss : Observed 63.66; Calc 64.73 per cent).

Mass spectral data support the presence of dioxane. The Ph₂TeCl(C₅H₆O₂)-HgCl(III) and Ph₃Te(C₅H₆O₂) HgCl(IV) are fairly stable and do not crystallize with solvent molecules and the greater Lewis acid character of TeCl₃ is probably responsible for the unusual behaviour of II. The reactions of 3,3-bis(chloromercury)-2,4-pentandione with tellurium compounds in 1/2 ratio do not give derivatives of the type (Ph_{*n*}TeCl_{3-*n*})₂ (C₅H₆O₂). For *n* = 0, tellurium metal

separates out, and in other case some ill-defined products containing mercury are obtained.

The chemical shifts for the methyl protons (δ 2.3ppm) of $\text{Hg}_2(\text{C}_5\text{H}_6\text{O}_2)\text{Cl}_2$ agrees well with those reported previously.¹⁰ After crystallization of this compound from methanol two peaks appear in the (δ 2.77 and 2.40ppm) as reported earlier, and can be attributed to the intermolecular interaction of Hg with oxygen of carbonyl group. The replacement of one HgCl by a TeCl_3 or Ph_2TeCl group deshields the methyl protons by ~ 1.3 ppm owing to the higher electronegativity of Te, and this effect is increased by the presence of electronegative chlorine. In IV, where the Te is not linked to chlorine, the deshielding effect is significantly lower (~ 0.5 ppm).

Comparison of the signals for the C_3 carbon atom in ^{13}C NMR spectra (Table II) suggests that the presence of a chlorine-containing Te moiety unexpectedly shields this carbon. This may be attributed to the existence the equilibria shown in Scheme 2, at least in DMSO, and is consistent with the shielding of C(1) and C(5) of the β -diketone moiety.

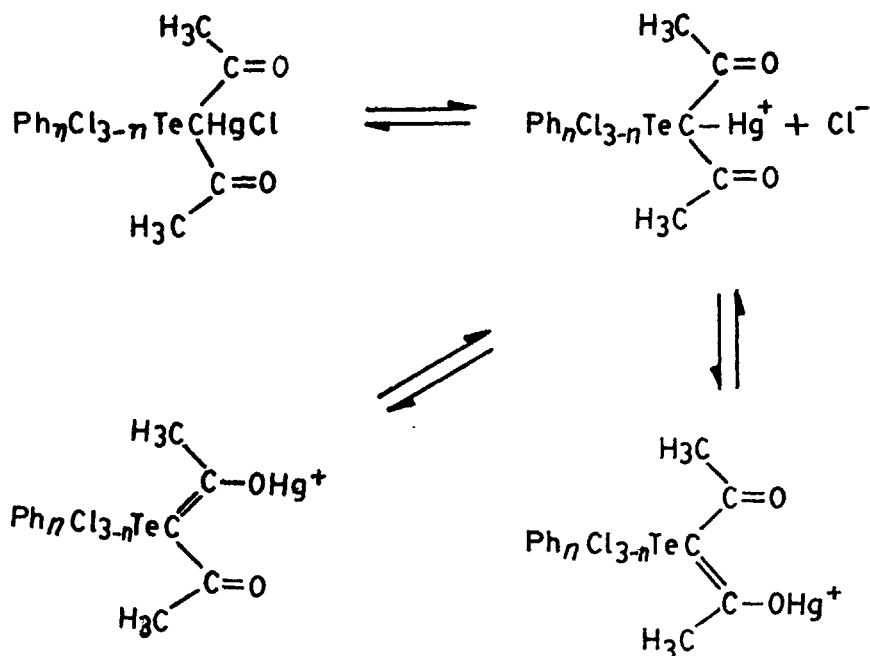
TABLE II
Chemical shifts in ^{13}C NMR

Compound	Chemical shifts (δ , ppm)	
	C_1/C_5	C_3
$\text{Hg}_2(\text{C}_5\text{H}_6\text{O}_2)\text{Cl}_2$	30.62 31.21	70.92
$\text{TeCl}_3(\text{C}_5\text{H}_6\text{O}_2)\text{HgCl(II)}$	29.16	66.52
$\text{Ph}_2\text{TeCl}(\text{C}_5\text{H}_6\text{O}_2)\text{HgCl(III)}$	27.16	66.38
$\text{Ph}_3\text{Te}(\text{C}_5\text{H}_6\text{O}_2)\text{HgCl(IV)}$	30.70	79.13

In IV the ionization of Cl is reduced as the HgCl bond is more covalent and this in turn shifts the equilibrium to left, and so, C(3), C(1) and C(5) all are deshielded relative to II and III.

The larger deshielding (~ 150 ppm) of the ^{199}Hg signal on replacement of one HgCl group by a tellurium moiety also favours the presence of this ionization equilibria. The derivative containing the Ph_3Te group gives the most shielded ^{199}Hg signal since it is the least ionic. The conductivity measurements also show that the compounds are ionized in DMF as 1 : 1 electrolytes (λ_M 67 to 78ohm $^{-1}\text{cm}^2$ mol $^{-1}$), except for III, which being a telluronium salt type derivative, exhibits a higher association between the ions (λ_M 24–27ohm $^{-1}\text{cm}^2$ mol $^{-1}$).

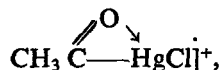
The $\nu_{(\text{CO})}$ band in the present mercury compound (1685cm $^{-1}$) and its triphenyl-tellurium derivative (1690cm $^{-1}$) are very close, indicating the involvement of oxygen in a similar type of interaction in the two compounds. For the other two compounds it is much lower ($\sim 1620\text{cm}^{-1}$), indicating a decrease in double



SCHEME 2

bond character of CO, as suggested by the ^{13}C NMR data. Intermolecular Hg-O interaction seems to be mainly responsible for this. The range of $\nu_{(\text{CO})}$ frequencies however, favours $\text{C}_3\text{-Te}$ bond formation. The $\nu_{(\text{Hg}-\text{C})}$ band is observed in all cases in the region $500\text{-}600\text{cm}^{-1}$ indicating that, at least in solid state, Hg is primarily linked to C_3 , and interaction with the oxygen of CO group is secondary. The IR spectrum of II has bands at $3590, 3530, 800$ and 625cm^{-1} which cannot be accounted for without assuming the presence of dioxane in this compound.¹² The far infrared spectra of II, III, IV and the parent mercury compound show a number of unexpected bands, probably due to strong mercury-oxygen secondary interactions, and so unequivocal assignment in this region is difficult. However, bands indicating $\text{Te}-\text{C}_3$, $\text{Hg}-\text{O}$, $\text{Hg}-\text{Cl}$, $\text{Te}-\text{Cl}$ and $\text{Te}-\text{C}$ (phenyl)¹³ interactions were present.

None of the three compounds gives molecular ion peak, decomposition taking place during the vaporization. The decomposition products exhibit to some extent characteristic fragmentation patterns. In the mass spectra of all three compounds there is a peak at $m/e = 280$ which can be attributed to

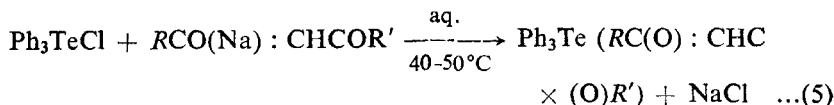


indicating a very significant Hg-O interaction in solid state. The mass spectrum of II is complex. It has ions characteristic of those formed from *acacH*¹⁴ and dioxane,¹⁵ confirming the presence of latter in II. In these C_3 bonded acetyl acetonates the Hg-O secondary interaction seems to be greater than in $\text{HgCl}(\text{C}_5\text{H}_6\text{O}_2)$

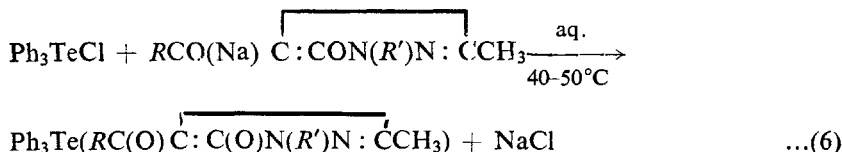
HgCl. On treatment of these compounds with HCl or CH₃I, the tellurium moiety rather than HgCl is replaced by H or CH₃ group, respectively. The higher C-Hg bond energy coupled with the Hg-O secondary interaction seems to be responsible for this. Of the three compounds, III seems to show the most secondary interaction, as expected from its telluronium salt nature. In solution the secondary Hg-O interaction appears to be intramolecular, but in the solid state it may also be intermolecular, as reported for Hg₂(C₅H₆O₂) Cl₂.¹¹

OXYGEN-BONDED β -DIKETONATES OF TELLURIUM(IV)^{16,17}

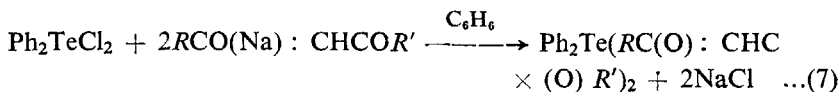
These compounds have been obtained by the reactions (5), (6) and (7)



(where $R = \text{CH}_3, \text{Ph}$ or CF_3 , and $R' = \text{CH}_3, \text{Ph}, \text{CF}_3$ or 2-thienyl)



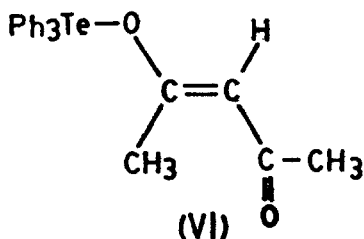
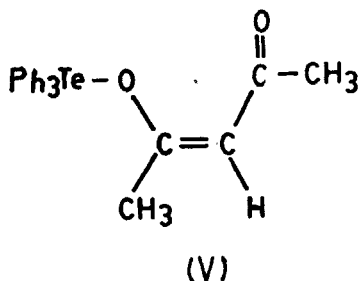
where $R = \text{CH}_3, \text{Ph}, \text{CF}_3$ or 3,5 - (NO₂)₂C₆H₃ and $R' = \text{Ph}$



(where R or $R' = \text{CH}_3, \text{Ph}$ or CF_3).

The Ph₃TeL ($L = \beta$ -diketonate group) type compounds, by molecular weight and conductivity measurements in solvents like nitrobenzene, acetone and methanol, have been found to be ionic in nature. IR data in the $\nu_{(\text{CO})}$ region for the solid compounds rule out a chelating mode for the β -diketonate since a band in the range 1625–1665cm⁻¹ is present.¹ Thus either an ionic formulation is suggested or interaction of tellurium with >C=O is plausible. The absence of a band at 1720cm⁻¹ rules out the possibility of a Te-C bond involving the middle carbon atom of the anion. The observation of a band at 340–390cm⁻¹ is consistent with a weak tellurium-oxygen interaction.

The ¹H NMR spectrum of acac compound supports the concept of a Te-O interaction since it would be difficult to reconcile two CH₃ signals (δ 5.47; 6.68ppm) and a multiplet of CH₃ (δ 1.12–2.21ppm) with either a purely ionic compound or with chelating acac. The complexity of the ¹H NMR spectra suggests that isomers V and VI may co-exist, as for analogous silicon derivatives.¹⁸



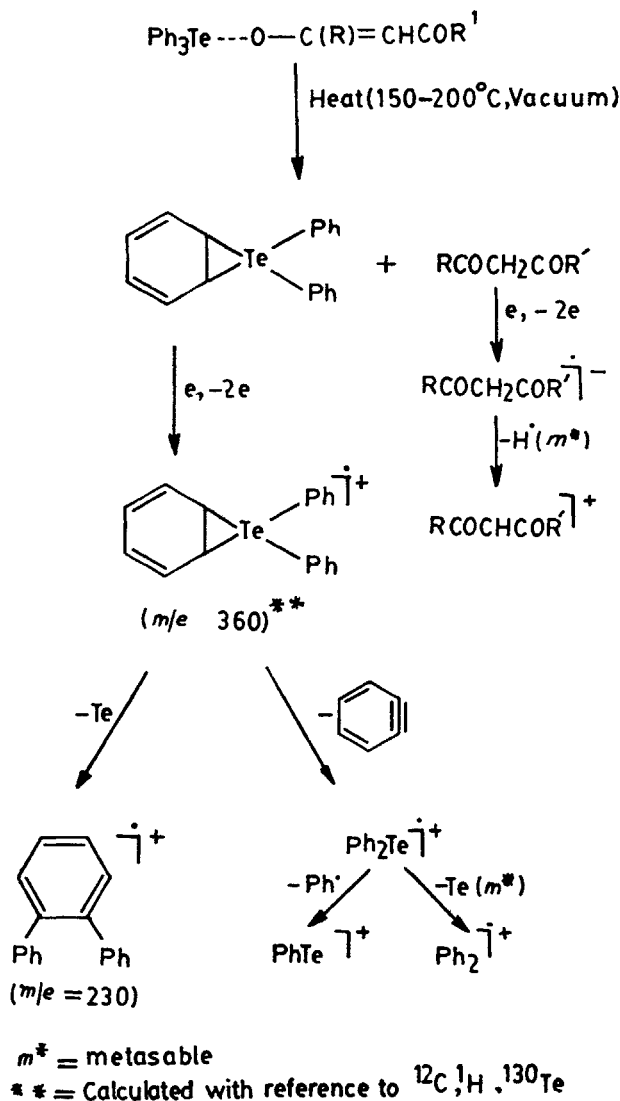
The observation of two ^{13}C signals for carbonyl groups ($\delta 187.63$; 212.00 ppm) further supports the Te-O interaction. NMR data for benzoylacetone and dibenzoylmethane compounds suggest similar structures.

Mass spectroscopic studies on the Ph_3TeL type compounds at 70eV have shown interesting results. The spectrum of *acac* compounds showed the presence of Ph_3Te^+ , Ph_2Te^+ , PhTe^+ and Ph_2^+ as the major high m/e peaks. However, a feature (weak) containing the characteristic isotope pattern of tellurium was seen at $m/e = 445$ which could be $\text{Ph}_3\text{TeOC}(\text{CH}_3)=\text{CHC}\equiv\text{O}^+$ derivable from the parent ion (not observed) for the associated salt. This is a well-documented fragmentation for carbonyl compounds.

None of the other compounds show tellurium containing ions beyond $m/e = 370$. Some unexpected features are also observed in the spectra. The highest m/e tellurium containing fragment is seen at $m/e = 360$, not $m/e 361$; a significant feature is seen at $m/e = 230$ which does not contain tellurium; the parent ion of the dicarbonyl compound is seen i.e. $[\text{RCOCH}_2\text{COR}']^+$ (a metastable transition supporting fragmentation by loss of a hydrogen atom is seen). The following scheme 3 correlates these observations, although it is speculative in parts in that not all proposed fragmentations are supported by metastables. It should be noted that a feature at $m/e = 230$ was also noted in the case of $\text{Ph}_3\text{Te}(\text{CH}_3\text{COCHCOCH}_3)$, but not parent ion from *acacH* at $m/e = 100$ was observed. These observations indicate that cation-anion interaction occur in the gas phase at least for acetylacetonate. A sodium salt like model cannot be ruled out for the salts of benzoyltrifluoroacetone and theonyltrifluoroacetone. Replacement of CH_3 by CF_3 in $(\text{CH}_3\text{COCHCOR}')^-$ should reduce the donor capacity of the $\text{C}=\text{O}$ group and hence the Te-O bond strength.'

In nut shell the series Ph_3Te (β -diketonate) parallels other telluronium salts in that weak "ionic" interactions, in these instances via Te-O bonds, occur in concentrated solutions and in the solid state. Such interactions become weaker as the *R* group in $(\text{RCOCHCOR}')^-$ become more electronegative. The IR data of $\nu_{(\text{CO})}$ region for pyrazolonates of Ph_3TeL type, however, suggest stronger ionic association than other β -diketonates.

The Ph_2TeL_2 compounds have been found to be non electrolyte by conductance measurements in nitrobenzene as well as molecular weight determinations



SCHEME 3

in acetonitrile, which also indicate their monomeric nature in solution. Two signals for CH and three for CH₃ in ¹H NMR, and $\nu_{(\text{C}=\text{O})}$ around 1585 cm⁻¹ and $\nu_{(\text{Te}-\text{O})}$ absorption at 406, 425 and 460 cm⁻¹ suggest the asymmetric chelation of β -diketonate group with tellurium, resulting in an axially elongated octahedral geometry¹⁷ around it and the presence of *cis* and *trans* isomers. The TGA of these Ph₂TeL₂ type derivatives suggest that by their programmed heating arylated β -diketones or ketones may result.

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