

## $\beta$ -Diketonates of aryltellurium(IV) and diaryltellurium(IV)

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Some new diphenyltellurium(IV)-bis- $\beta$ -diketonates,  $\text{Ph}_2\text{Te}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_2$  (I) and 4-methoxyphenyltellurium- $\beta$ -diketonates,  $4\text{-MeOC}_6\text{H}_4\text{TeCl}_3\text{-}_n\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_n$  (II).  $n = 1-3$ ,  $\text{R} = \text{R}' = \text{Me}$ ,  $\text{Ph}$  or  $\text{CF}_3$ , have been synthesized by the reaction of  $\text{RC}(\text{O})\text{Na}\text{:CHC}(\text{O})\text{R}'$  with  $\text{Ph}_2\text{TeCl}_2$  and  $\text{MeOC}_6\text{H}_4\text{TeCl}_3$ . The compounds have been characterized on the basis of elemental analyses, molecular weights, molar conductance measurements and spectral data (IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR). Molecular weight measurements suggest that the compounds of the type (I) are monomeric and those of the type (II) are dimeric in solution. The asymmetric chelation of  $\beta$ -diketonate moiety with tellurium in (I) and bridging of the two tellurium atoms by oxygen atoms of  $\beta$ -diketonate moieties in (II) are inferred from the IR and  $^1\text{H}$  NMR data.

The  $\text{C}_1$  bonded  $\beta$ -diketonates of tellurium(IV)<sup>1,2</sup> are known since long but its  $\text{C}_3$  bonded acetylacetonates<sup>3,4</sup> and oxygen bonded  $\beta$ -diketonates<sup>4-6</sup> have been reported only recently. The oxygen bonded  $\beta$ -diketonates reported so far are of telluronium salt type<sup>5</sup> obtained by the reactions of triphenyltellurium(IV) chloride with sodium salts of  $\beta$ -diketones. Considering that the nature of diaryltellurium dihalides and aryltellurium trihalides is different from that of triaryltellurium halides, we have made an attempt to study the reactions of diaryltellurium dihalides and aryltellurium trihalides with sodium salts of acetylacetone (acac), benzoylacetone (bzac), dibenzoylmethane (dbm), trifluorobenzoylacetone (btfac) and trifluoroacetylacetone (tfac). The results of these investigations are reported in the present note.

### Experimental

Diphenyltellurium dichloride and 4-methoxyphenyltellurium trichloride were synthesized by published method<sup>7</sup>. All  $\beta$ -diketones were used as the sodium salts.

#### Synthesis of $\text{Ph}_2\text{Te}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_2$ (I)

A solution of  $\text{Ph}_2\text{TeCl}_2$  (5 mmol) in benzene was added dropwise to the suspension of sodium  $\beta$ -dike-

tonate (12.5 mmol) in benzene. The mixture was refluxed under dinitrogen atmosphere for 3-4 h and filtered. The filtrate was evaporated to dryness *in vacuo*. The solid obtained was washed with petroleum ether (40-60°) and recrystallized from a 1:1 benzene-hexane mixture.

#### Synthesis of $4\text{-MeOC}_6\text{H}_4\text{TeCl}_2\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}$ (IIa)

A solution of  $4\text{-MeOC}_6\text{H}_4\text{TeCl}_3$  (6 mmol) in hot benzene was added slowly to the suspension of sodium  $\beta$ -diketonate (6 mmol) in benzene. The reaction was worked up as mentioned above for I.

#### Synthesis of $4\text{-MeOC}_6\text{H}_4\text{TeCl}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_2$ (IIb)

$4\text{-MeOC}_6\text{H}_4\text{TeCl}_3$  (6 mmol) in benzene was added to the suspension of sodium  $\beta$ -diketonate (12.4 mmol) in benzene. The reaction was worked up as mentioned above for I. Products of the title composition were isolated in the cases of only acac and bzac. In all other cases, compounds corresponding to only IIa were obtained.

#### Synthesis of $4\text{-MeOC}_6\text{H}_4\text{Te}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_3$ (IIc)

The reactants,  $4\text{-MeOC}_6\text{H}_4\text{TeCl}_3$  and sodium salt of  $\beta$ -diketone, were taken in 1:3 molar ratio in benzene and the reaction was carried out as mentioned above for I. The product obtained corresponded to IIa, except in the case of tfac which gave the title stoichiometry.

Conductivity measurements were made on 1 mM solutions in nitrobenzene and acetonitrile using Metrohm 660 conductometer. Molecular weights were determined in acetonitrile and benzene by Knauer vapour pressure osmometer.

The IR spectra in the range 4000-400  $\text{cm}^{-1}$  were recorded on a Nicolet 5DX FT-IR spectrophotometer in KBr or nujol. Far IR spectra of the compounds in the range 700-30  $\text{cm}^{-1}$  were run as polythene disc on a Perkin Elmer 1700X far IR FT spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FX-100 FT NMR spectrometer at 99.55 and 25 MHz respectively.

Tellurium and chlorine were estimated by standard methods<sup>8,9</sup>. The C and H analyses were carried out on a Perkin Elmer 240 C elemental analyzer. The purity of all the compounds was checked by TLC.

## Results and discussion

$\text{Ph}_2\text{TeCl}_2$  reacts with sodium salt of  $\beta$ -diketone to form  $\text{Ph}_2\text{Te}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_2$  (I). The elemental analyses and some physical properties of the compounds of the type (I) are compiled in Table 1. The analyses support the proposed stoichiometries of the  $\beta$ -diketonate derivatives of tellurium. The compounds, although stable in dry air, were affected by moisture. They were fairly soluble in benzene, chloroform and acetonitrile but insoluble in hexane.

In nitrobenzene, type (I) compounds behaved as non-electrolytes ( $\Lambda_M$  0.2 to  $2.27 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ). The molecular weights measured in acetonitrile revealed their monomeric nature (Table 1). The appearance of an IR band in the  $\nu(\text{CO})$  region at a frequency ( $1575\text{--}1630 \text{ cm}^{-1}$ ) lower than that observed for the telluronium salts<sup>4</sup> strongly suggests the chelating nature of the  $\beta$ -diketonate through oxygen atoms of the carbonyl groups<sup>10,11</sup>. In the far IR region, the compounds exhibited strong bands in the range  $380\text{--}460 \text{ cm}^{-1}$ , attributable to  $\nu(\text{Te}-\text{O})$  vibrations<sup>12-14</sup>. Appearance of more than one  $\text{Te}-\text{O}$  bands in this region suggests the existence of the isomeric forms even in the solid state.

The existence of these compounds in isomeric forms in solution is revealed by their  $^1\text{H}$  NMR spectra (Table 2). Besides phenyl protons ( $\delta$  7.42-7.83 ppm), two signals for CH protons in the region  $\delta$  4.42-6.87 ppm and a multiplet for  $\text{CH}_3$  in the region  $\delta$  1.17-2.97 ppm have been observed. The complex pattern for

CH and  $\text{CH}_3$  protons favours the existence of I as *cis-trans* isomeric mixture. The *trans* isomer (A) may be considered to be more elongated along the Z-axis than *cis*-isomer (B). This is expected on the basis of *trans* effect of phenyl group also.

Attempts to support the existence of A and B in solution by  $^{13}\text{C}$  NMR were not successful due to inadequate solubility of most of the compounds of type (I) in any suitable organic solvent. However, the  $^{13}\text{C}$  NMR spectrum of  $\text{Ph}_2\text{Te}(\text{acac})_2$ , a relatively more soluble compound in  $\text{CDCl}_3$ , besides showing signals for phenyl carbons ranging from  $\delta$  126.6 to 136.9 ppm and CO signals at  $\delta$  176.24 and 176.9 ppm, showed two signals for CH carbon ( $\delta$  108.7 and 113.5 ppm) and three for  $\text{CH}_3$  carbon ( $\delta$  21.31, 22.1 and 28.6 ppm), which were consistent with  $^1\text{H}$  NMR spectral data. These structures A and B for diphenyltellurium-bis-acetylacetonate, which are supported by its  $^{13}\text{C}$  NMR spectrum, may be reasonably presumed for other diphenyltellurium-bis- $\beta$ -diketonates also.

The compounds  $4\text{-MeOC}_6\text{H}_4\text{TeCl}_{3-n}\{\text{RC}(\text{O})\text{:CHC}(\text{O})\text{R}'\}_n$  (IIa-IIc) were fairly soluble in benzene and chloroform, partially soluble in acetonitrile but almost insoluble in carbon tetrachloride and hexane. The analytical data support the proposed stoichiometries of these derivatives. In the reaction of tfac with  $4\text{-MeOC}_6\text{H}_4\text{TeCl}_3$ , all the chlorine atoms could be

Table 1—Elemental analysis and physical properties of  $\text{Ph}_2\text{Te}\{\text{RC}(\text{O})\text{:CHO}(\text{O})\text{R}'\}_2$  and  $\text{ArTeCl}_{3-n}(\text{RCOCHCOR}')_n$

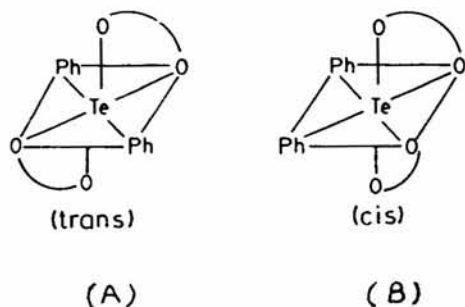
S.No.	Compound	Colour (Yield, %)	M.P (°C)	Mol. wt Found (Calc.)	Found (Calc.), %			
					C	H	Te	Cl
1.	$\text{Ph}_2\text{Te}(\text{acac})_2$	Light orange (45)	79	—	54.39 (55.05)	4.91 (5.01)	25.46 (26.60)	—
2.	$\text{Ph}_2\text{Te}(\text{bzac})_2$	Light orange (65)	94(d)	599.2 <sup>a</sup> (603.6)	62.03 (63.62)	4.33 (4.64)	20.54 (21.14)	—
3.	$\text{Ph}_2\text{Te}(\text{dbm})_2$	Light orange (85)	109	695.2 <sup>a</sup> (727.6)	68.25 (69.26)	4.24 (4.38)	16.23 (17.53)	—
4.	$\text{Ph}_2\text{Te}(\text{btfac})_2$	Yellow (85)	116	701.1 <sup>a</sup> (713.6)	54.02 (53.81)	2.92 (3.08)	16.34 (17.89)	—
5.	$\text{Ph}_2\text{Te}(\text{tfac})_2$	Brownish yellow (90)	89	570.0 <sup>a</sup> (587.6)	43.62 (44.92)	2.83 (3.06)	20.92 (21.71)	—
6.	$\text{ArTeCl}_2(\text{acac})$	Light orange (50)	160(d)	789.0 <sup>b</sup> (809.2)	34.89 (35.59)	3.25 (3.46)	30.09 (31.53)	17.31 (17.55)
7.	$\text{ArTeCl}_2(\text{bzac})$	Light brown (50)	135(d)	927.0 <sup>b</sup> (933.2)	42.79 (43.72)	3.35 (3.42)	26.14 (27.34)	15.16 (15.21)
8.	$\text{ArTeCl}(\text{acac})_2$	Light orange (55)	120(d)	915.0 <sup>b</sup> (936.0)	43.83 (43.58)	4.32 (4.48)	26.63 (27.25)	6.99 (7.58)
9.	$\text{ArTe}(\text{tfac})_3$	Orangish brown (85)	133	1313.0 <sup>b</sup> (1387.2)	37.98 (38.06)	2.70 (2.73)	17.64 (18.39)	—

Ar =  $4\text{-MeOC}_6\text{H}_4$     a = acetonitrile,    b = benzene

Table 2—<sup>1</sup>H NMR data<sup>a</sup> for diphenyltellurium-bis-β-diketonates and aryltellurium-β-diketonates

S.No.	Compound	Chemical shift δ(ppm)			
		=CH—	—CH <sub>3</sub>	—OCH <sub>3</sub>	Phenyl or Aryl
1.	Ph <sub>2</sub> Te(acac) <sub>2</sub>	4.49	1.18-2.24	—	7.42-7.83
		5.48			
2.	Ph <sub>2</sub> Te(bzac) <sub>2</sub>	4.19	1.17,2.60	—	7.39-8.02
		6.17			
3.	Ph <sub>2</sub> Te(dbm) <sub>2</sub>	4.91	—	—	7.39-8.04
		6.87			
4.	Ph <sub>2</sub> Te(btfac) <sub>2</sub>	4.52	2.02,2.97	—	7.65-7.97
		6.02			
5.	Ph <sub>2</sub> Te(tfac) <sub>2</sub>	4.42	—	—	7.58-7.88
		6.52			
6.	ArTeCl <sub>2</sub> (acac)	—	1.8,2.00, 2.24	3.68,3.84	6.24-7.28
7.	ArTeCl <sub>2</sub> (bzac)	6.36	1.4,1.85	3.7,3.9	6.65-8.1
8.	ArTeCl(acac) <sub>2</sub>	6.30	1.7,20.5,	3.7,3.89,	6.9-8.1
			2.35,2.45,	3.92,3.99	
9.	ArTe(tfac) <sub>3</sub>	5.38	1.75,2.05, 2.4	3.8,3.7	6.99-7.72

<sup>a</sup>Chemical shift in δ(ppm) relative to TMS in CDCl<sub>3</sub>.



substituted by the β-diketonate groups. Contrary to this, acac and bzac could not displace more than two chlorine atoms. All the compounds of the type IIa-IIc in acetonitrile behaved as non-electrolytes ( $\Lambda_M$  6.1 to 20  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) and in benzene showed molecular weights corresponding to twice the value expected from the stoichiometry.

The dimeric nature of these compounds can arise through bridging of two aryltellurium moieties via chlorine atoms or oxygen atoms of the β-diketonate. The absence of  $\nu(\text{Te}-\text{Cl}-\text{Te})$  in the region 180-150  $\text{cm}^{-1}$  and appearance of  $\nu(\text{Te}-\text{Cl})$  around 310-345  $\text{cm}^{-1}$  suggest the absence of bridging Cl and presence of terminal Cl atoms<sup>15</sup>. The assignment of  $\nu(\text{Te}-\text{Cl})$  was substantiated by recording the IR spectra of the corresponding bromo derivatives. IR spectra showed  $\nu(\text{C}=\text{O})$  vibration in the region 1540-1600  $\text{cm}^{-1}$  which neither falls in the range of chelating mode nor of unidentate type of bonding<sup>11</sup>. This suggests the possibility of bridging mode for the β-diketonate

groups. More than one band in the region 380-470  $\text{cm}^{-1}$  attributable to Te-O vibrations<sup>12-14</sup> support the existence of *cis-trans* isomeric forms of the compounds IIa-IIc as reported earlier for oxygen bridged β-diketonates<sup>10</sup>. The bands in the range 230-255  $\text{cm}^{-1}$  are assignable to  $\nu(\text{Te}-\text{C})$  vibrations<sup>15,16</sup>.

The presence of isomeric forms of the compounds IIa,b and c is supported by their <sup>1</sup>H NMR spectra in which multiplets for —CH<sub>3</sub> protons, more than one signal for —OCH<sub>3</sub> protons and a broad signal for CH proton have been observed (Table 2). Attempts to support the above mentioned inferences by <sup>13</sup>C NMR did not succeed due to inadequate solubility of these compounds in suitable organic solvents.

The spectral data indicate that I and II exist in isomeric forms having an asymmetric chelation of β-diketonate group(s) with tellurium. The molecular weight measurements suggest that the compounds of the type Ph<sub>2</sub>Te(β-diketonate)<sub>2</sub> do not polymerize in acetonitrile while structure of the type ArTeCl<sub>3-n</sub>(β-diketonate)<sub>n</sub> seems to be dimeric. In the derivative of Ph<sub>2</sub>Te(IV), due to the *trans* effect of two phenyl groups and reduced electronegativity of tellurium, association through β-diketonate group is inhibited while in ArTeCl<sub>3-n</sub>(β-diketonate)<sub>n</sub> the *trans* effect of one Ar group is unable to check the association and, therefore, dimeric structure results.

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