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TRIPHENYLTELLURONIUM β-DIKETONATES; SYNTHESIS AND SPECTRA

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Summary

Triphenyltelluronium β-diketonates, $RC(O)CH=C(O)R^1$ (where $R = CH_3$, Ph or CF_3 and $R^1 = CH_3$, Ph, CF_3 or 2-thienyl) have been prepared. Spectral data (IR, ^1H and ^{13}C NMR, mass spectroscopy) are presented and discussed in conjunction with molecular weight and conductivity data. It is concluded that weak coordination of the β-diketonate to the tellurium atom is a common structural feature of the compounds.

Introduction

Triorganotelluronium salts have been known for many years [1,2] and have been the subject of several recent papers [3–6]. It has been suggested that a solvent-dependent "covalent-ionic" equilibrium may exist, and factors affecting the stability of the covalent form have been identified [6]. Triorganotelluronium carboxylates show interesting behaviour [5], and it therefore seemed worthwhile to investigate a series of triphenyltelluronium β-diketonates. The results of this study are presented here.

Experimental

Triphenyltelluronium chloride was prepared as previously described [7]. The 2,4-pentanediones (β-diketones) were used as the sodium salts.

Synthesis of triphenyltelluronium β-diketonates

A solution of triphenyltelluronium chloride (2 mmol) in the minimum amount of warm water (50–60°C) was mixed with an aqueous solution (minimum quantity of water) of the sodium β-diketonate (4 mmol). The precipitate was separated, washed

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TABLE 1

ANALYSES AND PHYSICAL PROPERTIES OF TRIPHENYLTELLURONIUM β-DIKETONATE

β-Diketone	M.p. (°C)	Colour	Yield (%)	Analysis (Found (calcd.) (%))		
				C	H	Te
Acetylacetone (AA)	121–122	light yellow	52	60.9 (60.3)	4.91 (4.81)	26.98 (27.68)
Benzoylacetone (BA)	104–106	Pale yellow	60	64.31 (64.86)	5.61 (5.63)	24.38 (24.32)
Dibenzoylmethane (DBM)	135–136	yellow	90	68.10 (68.27)	4.76 (4.48)	21.38 (21.72)
Benzoyltrifluoroacetone (BTA)	136–137	light	90	58.15 (58.74)	3.58 (3.67)	21.96 (22.03)
Theonyltrifluoroacetone (TTA)	118–119	Brownish yellow	55	53.58 (53.91)	3.54 (3.29)	21.70 (21.80)

with 2–3 small aliquots of water, and recrystallised from methanol. Analytical data are gathered into Table 1.

Physical measurements Conductivity measurements were made on ca. 1 m*M* solutions in methanol, acetonitrile, nitrobenzene and nitromethane. Molecular weights were determined cryoscopically in nitrobenzene.

IR spectra (4000–200 cm^{-1}) were obtained for KBr discs with Pye-Unicam SP1200 and Perkin–Elmer instruments. ^1H NMR (100 MHz) and ^{13}C NMR (25 MHz) were obtained with a Jeol FX 100 instrument. Mass spectra were determined at 70 eV (1eV 96.5 kJ mol^{-1}) with an AEI MS9 instrument. Source temperatures were in the range 150–200°C.

Tellurium analysis was by a standard procedure [8]. Table 2 contains molecular weight data, Table 3 lists the major IR bands and Tables 4 (^1H) and 5 (^{13}C) list the NMR data.

Discussion

The new compounds $Ph_3Te(RCOCH{=}C(O)R^1)$ were shown to be pure by TLC, they are reasonably soluble in common organic solvents (not CCl_4) but all are sparingly soluble in water. In more polar organic solvents conductivity data indicated dissociation as 1/1 electrolytes. Molecular weight data in nitrobenzene also indicate dissociation at lower concentration levels, but at higher concentrations (5–10 mmol) the molecular weights are close to those expected for a monomer. These data suggest significant ionic character with appreciable association at higher concentrations.

IR data (Table 3) in the ν(CO) region for the solid compounds rule out a chelating mode for the β-diketonate since a band in the range 1625–1665 cm^{-1} is present [9]. Thus either an ionic formulation is suggested or interaction of tellurium with $>$C–O is plausible. The absence of a band at 1720 cm^{-1} rules out the possibility of a Te–C bond involving the middle carbon atom of the anion. The observation of a band at 340–390 cm^{-1} is consistent with a weak tellurium–oxygen interaction.

TABLE 2

MOLECULAR WEIGHT DATA FOR TRIPHENYLTELLURONIUM β-DIKETONATES

β-Diketone	Formula Wt.	Concentration (mM)	Mol.Wt.
AA	457.6	1.15	299.2
		2.76	353.7
		4.61	472.6
		6.17	527.1
BA	519.6	1.89	332.4
		4.00	358.2
		7.20	504.9
		11.02	552.1
DBM	582.6	1.54	300.9
		4.40	430.1
		7.58	593.0
		11.08	618.6
BTA	573.6	1.62	209.6
		3.98	256.8
		6.61	318.5
		9.83	380.1
TTA	567.6	1.61	307.7
		2.90	389.7
		8.69	553.3
		13.61	649.7

The ^{1}H NMR spectrum of the acetylacetonate compound supports the concept of a Te–O interaction since it would be difficult to reconcile two CH signals and a multiplet of CH_3 with either a purely ionic compound or with chelating acetylacetonate. The complexity of the ^{1}H NMR spectra suggests that isomers I and II may

TABLE 3

IR BANDS (in cm^{-1}) [a] OF TRIPHENYLTELLURONIUM β-DIKETONATES

No.	AA	β-Diketone				Assignment
		BA	DBM	BTA	TTA	
1	Complex pattern in 1670–1400	1655	1655	1625	1640	ν(CO)
		1595	1593	1572	1580	Combination of
		1560	1550	1570	1560	$\nu(C{=}O)+\nu(C{=}C)$
		1505	1505	1515	1500	
		1460	1465	1470	1455	$\delta(CH)+\nu(C{=}C)$
		1405	1407	1435	1435	$\delta(CH_3)$ or $\delta(CF_3)$
5	1260	1235	–	1270	1260	$\nu(C\text{–}CH_3)$ or $\nu(CF_3)+\nu(C{=}C)$
6	790	780	775	790	770	π(CH)
	740	730	725	740	735	
7	350	390	340	345	– [a]	ν(Te–O)
8	250	253	250	255	– [a]	ν(Te–C)

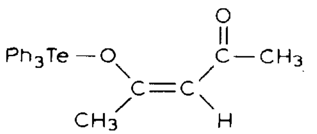
[a] IR spectrum was recorded upto 400 cm^{-1}.

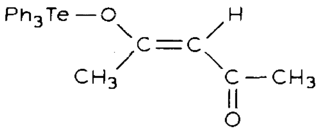
TABLE 4

CHEMICAL SHIFTS IN THE ^{1}H NMR SPECTRA OF TRIPHENYLTELLURONIUM β-DIKETONATES

β-Diketone	Chemical shifts δ (ppm)			
	Phenyl attached to Te	Ligand phenyl	CH	CH_3
AA	7.24–7.70	–	5.47 6.68	1.12–2.21
BA	7.43–7.70	7.25	5.72	1.94
DBM	7.61–7.73	7.22–7.40	6.33	–
BTA	7.35–7.67	7.15–7.28	5.96	–
TTA	7.25–7.70	6.90–6.99	5.88	–

co-exist, as for analogous silicon derivatives [9]:


(I)


(II)

The observation of two ^{13}C signals for carbonyl groups is further support for the Te–O interaction. NMR data for the BA and DBM compounds suggest similar structures.

Mass spectroscopic studies of other telluronium salts [11] have been useful in providing support for the concept of association of cation and anion in the gas phase. It was decided to examine the mass spectroscopic behaviour of the present range of compounds at 70 eV. The spectrum of $Ph_3Te(AA)$ 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* =

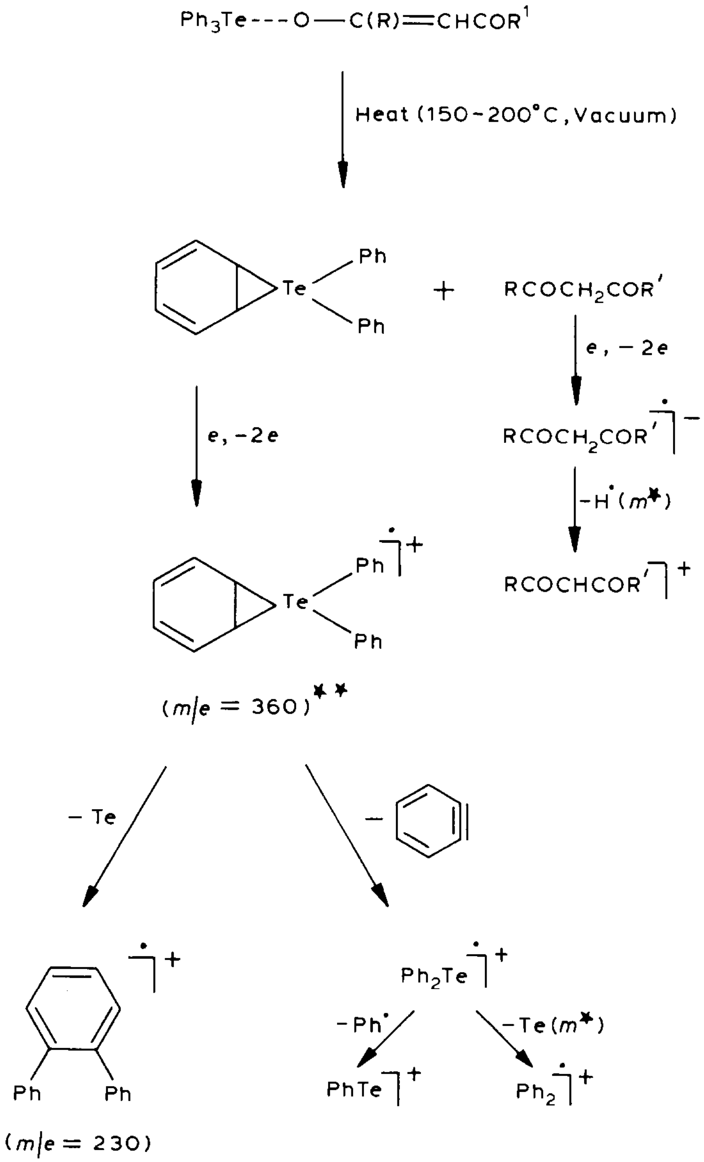
TABLE 5

CHEMICAL SHIFTS IN ^{13}C NMR SPECTRA OF TRIPHENYLTELLURONIUM β-DIKETONATES

β-Diketone	Chemical shifts δ (ppm)					
	Ring carbon	CH_3	CF_3	CH	C–O	C–O–Te
AA	128.21–134.88	28.79	–	99.27	187.63	212.00
BA	126.82–142.90	29.52	–	96.70	180.50	190.20
DBM	126.75–143.27	–	–	94.07	182.90	210.00
BTA	126.89–141.84	–	[a]	89.67	170.12 168.95	186.76
TTA	126.97–135.25	–	[a]	88.94	168.10 179.06 169.70	179.06

[a] Signal of carbon corresponding to CF_3 seems to be merged in the signals of phenyl or thienyl.

445 which could be $Ph_3TeOC(CH_3)=CHC\equiv O^+$ derivable from the parent ion (not observed) for the associated salt. This is a well documented fragmentation for carbonyl compounds [12] but is unfortunately not supported by the observation of either the parent ion or an appropriate metastable.



m^* = metastable ;

** = Calculated with reference to ^{12}C, ^{1}H, ^{130}Te.

SCHEME 1

None of the other compounds show tellurium containing ions beyond $m/e = 370$, however some fragments of higher mass are observed. These do not correlate obviously with the components of the salts and may probably arise from pyrolysis of the material in the source of the instrument. 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. $[RCOCH_2COR^1]^+$ (a metastable transition supporting fragmentation by loss of a hydrogen atom is seen). The following scheme 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 $Ph_3Te(CH_3COCHCOCH_3)$, but no parent ion from acetylacetone at $m/e = 100$ was observed.

It is unwise to infer too much from the mass spectroscopic data since it is difficult to explain the data without involving pyrolysis, however there are some indications that cation–anion interaction may occur in the gas phase at least for $Ph_3Te(AA)$, also a more controlled study of the pyrolysis of the compounds may be rewarding.

A sodium salt like model cannot be ruled out for the salts of BTA and TTA. Replacement of CH_3 by CF_3 in $(CH_3COCHCOR^1)^-$ should reduce the donor capacity of this C=O group and hence the Te–O bond strength [9]. The IR and NMR data offer no conclusive solution but it is noted that, even at higher concentrations, the molecular weight data suggest those compounds to be more dissociated; also it is noted that the ^{13}C shifts for CO in the BTA and TTA compounds are similar to those of the corresponding sodium salts.

Thus it is apparent that the series $Ph_3Te(\beta$-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 groups in $(RCOCHCOR^1)^-$ become more electronegative.

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