Journal of Organometallic Chemistry, 63 (1973) 305–310
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ORGANOTELLURIUM CARBOXYLATES AND RELATED COMPOUNDS: STRUCTURAL AND SYNTHETIC CONSIDERATIONS

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(Received April 9th, 1973)

SUMMARY

The structures of $Ph_2Te(OOCCH_3)_2$, $Ph_2Te(OOCPh)_2$ and $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$ are considered to be based on a four-coordinate ψ-trigonal bipyramidal arrangement of groups about the central tellurium atom. There is evidence for non-equivalence of carboxylate groups in both the solid state and in solution for $Ph_2Te(OOCPh)_2$ and for $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$. The carboxylate groups are as "ester"-like as in related organotin compounds. Attempts to isolate organotellurium triacetates from solution gave only mixtures of hydrolysis products.

The spectrum of $Ph_2Te(NO_3)_2$ is less readily interpreted but the balance of evidence favours a monomeric structure with unidentate or very unsymmetrically bidentate nitrate groups.

INTRODUCTION

Diaryltellurium dicarboxylates are a well established, though not yet large, class of organotellurium compound[1,2]. The carboxylate group may be introduced by the reaction of the diorganotellurium dichloride with the silver carboxylate[3] or by the more recently reported reaction of a telluride with lead(IV) carboxylates[4]. Organotellurium tricarboxylates are, as yet, unknown as crystalline solids. We have recently become interested in organotellurium carboxylates as synthetic intermediates in organotellurium chemistry and in this paper we discuss the structures of these compounds as determined by vibrational spectroscopy and also report on our attempts to synthesize organotellurium tricarboxylates. We also consider the structure of the known diphenyltellurium dinitrate.

EXPERIMENTAL

Infrared spectra were recorded for nujol mulls supported in caesium iodide plates over the range 4000–200 cm^{-1} using a Perkin–Elmer 225 instrument. Solution spectra were recorded for saturated solutions in carbon tetrachloride contained in potassium bromide (4000–400 cm^{-1}) or polythene (400–200 cm^{-1}) solution cells. Some compounds were examined as nujol mulls in polythene plates in the region 400–40 cm^{-1} using the R.I.I.C. FS 720–FS200 interferometer. Spectra were computed to

TABLE 1

VIBRATIONAL FREQUENCIES OF CARBOXYLATE GROUPS IN DIORGANOTELLURIUM DIACETATES

$Ph_2Te(OOCCH_3)_2$		$Ph_2Te(OOCPh)_2$		Ph_2TeBr_2		$(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$		*Assignment*
Solid	*Solution*[a]	*Solid*	*Solution*[a]	*Solid*	*Solution*[b]	*Solid*	*Solution*[a]	
1641 s	1644 s	1649 1635 s	1652 (sh) 1647 (sh) 1641 s			1654 s	1652 (sh) 1646 s	ν_{as} (OCO) (acetate ν_8)
		1622 1618 s	1622 m 1617 m			1628		
1280 s(br)	1288	1312 s 1295 s	1312 s 1289 s			1280 s(br)	1270 s	ν_s(OCO) (acetate ν_3)
917 ms	918 m					Masked	Masked	Acetate $\nu_4[\nu(C–C)]$
655 s	653 s					660 s	659 s	Acetate $\nu_5(COO_{def})$
490 m	489 m					490 m	484 ms	Acetate $\nu_{11}(COO_{rock})$
280 (sh)	283 (sh)	294 mw				327 m 323 m 320 m		Infrared spectrum 330–200 cm^{-1} Tellurium–oxygen modes underlined
272 s 263 (sh)	274 s 262 (sh)	275 mw 267 m 251 w		272 m 258 ms	260 m 252 m	261 ms		
	240 w	237 wm		243 s	240 m	229 m 224 ms		

[a] Carbon tetrachloride solution. [b] Chloroform solution.

a resolution of 2 cm^{-1}. ^{1}H NMR spectra were recorded using a Perkin–Elmer R 10 instrument and mass spectra were obtained at 70 eV with an AEI MS9 mass spectrometer. The Raman spectrum of $Ph_2Te(NO_3)_2$ was obtained on a Cary 81 instrument using He/Ne laser excitation.

Preparations

The diaryltellurium dicarboxylates were prepared following a recently reported procedure[4,5]: *Diphenyltellurium diacetate* (n.c.) m.p. 136–138°. (Found: C, 48.2; H, 4.02. $C_{16}H_{16}O_4Te$ calcd.: C, 48.1; H, 4.03%.) *Diphenyltellurium dibenzoate* (nc.) m.p. 156°. (Found: C, 59.6; H, 3.81. $C_{24}H_{20}O_4Te$ calcd.: C, 59.6; H, 3.84%.) *Di(p-ethoxyphenyl)tellurium diacetate* (nc.) m.p. 110–111°. (Found: C, 49.2; H, 4.91. $C_{20}H_{24}O_6Te$ calcd.: C, 49.2; H, 4.95%.) *Diphenyltellurium dinitrate* m.p. 160–161.5° (lit.[6]: 151–160°). All compounds gave satisfactory ^{1}H NMR and mass spectra[5].

Attempts to synthesize organotellurium triacetates. The reaction of diphenyl ditelluride with lead tetraacetate in benzene gives a solution of $PhTe(OOCCH_3)_3$ as proved by ^{1}H NMR spectroscopy[4]. Attempts to isolate the product yielded a white crystalline material of indefinite composition. Infrared analysis revealed the presence of two types of acetate group together with free acetic acid. Hydrolysis occurred rapidly in moist air. Other experiments involving the reaction of $(p\text{-}EtOC_6H_4)TeCl_3$ (1 mole) with silver acetate (3 moles) also gave a white solid of indefinite carbon content. Infrared analysis of this material as a nujol mull gave definite evidence of the presence of a quantity of $[(p\text{-}EtOC_6H_4)TeO]_2O$ as shown by characteristic tellurium–oxygen modes at 680, 555 and 390 cm^{-1} [7]. In addition the presence of coordinated acetate was clearly indicated [ν_{as}(OCO) 1645 cm^{-1}]. It is likely that rapid hydrolysis has led to the formation of a mixture of the anhydride and of $(p\text{-}EtOC_6H_4)Te(O)(OOCCH_3)$ for which other unassigned bands between 500 and 400 cm^{-1} would arise from ν_{11}(acetate) and the oxy-acetate.

RESULTS AND DISCUSSION

Diorganotellurium dicarboxylates

Carboxylate groups may interact in a number of ways with metal centres: they may be unidentate ligands, symmetrical (or unsymmetrical) bidentate ligands; they may act as bridging groups or even be present as free ions. Curtis[8] has given a useful and concise survey of the possibilities for the acetate group in the presence of transition metal compounds and has also discussed the relationship between the mode of interaction and the infrared spectrum.

The vibrational frequencies of the carboxylate groups for the compounds we have studied are isolated in Table 1. Assignments for the acetate group follow Ito and Bernstein[9] and it is noted that the frequencies undergo more (ν_3 and ν_8) or less (ν_4, ν_5, ν_{11}) major shifts, an observation consistent with the view that the acetate group interacts with tellurium to become more ester like.

Solution infrared spectra in carbon tetrachloride are very similar indeed to the mull spectra suggesting that no major change in structure occurs on change of phase. The diorganotellurium dicarboxylates are non electrolytes in nitromethane solution and no evidence for acetate ions is seen in the infrared spectrum, thus ionic structures such as $(\text{–}R_2Te\text{–}O\underset{C}{\cdots}O)^{n+}\text{–}(OOCCH_3)_n^-$ are eliminated. The carbon oxygen stretching frequencies of the acetate group in $Ph_2Te(OOCCH_3)_2$ are similar in position to those of tricyclohexyltin acetate (1645 cm^{-1}), which is known to contain an unidentate acetate group[10], and the separation of ν_3 and ν_8 (Δ) is 361 cm^{-1} in contrast to dimethyltin diacetate (Δ 227 cm^{-1}) for which unsymmetrical bidentate acetato-groups are proposed[11,12]. Thus a reasonable conclusion is that the structure of diphenyltellurium diacetate in both carbon tetrachloride solution and the solid state is monomeric with unidentate acetato-groups. This view is supported by the low frequency infrared spectra which are similar to those of Ph_2TeX_2 (X = Cl, Br, I) for which such structures are well established[13]. It is of interest that, according to the infrared data *i.e.* the position of ν_3 and ν_8, the acetate groups are at least as "ester like" in $Ph_2Te(OOCCH_3)_2$ as in the monomeric form of $Ph_3Sn(OOCCH_3)$ which occurs in carbon tetrachloride solution[14]. Although we are not comparing like with like, the structure envisaged for $Ph_2Te(OOCCH_3)_2$ (ψ-trigonal bipyramidal with acetate in axial positions) might have led to a weaker interaction with tellurium (IV) than with tin(IV) due to the elongation of the axial Te–O bonds.

Tin–oxygen stretching vibrations have been assigned for $Me_3Sn(OOCCH_3)$ and for $Me_2Sn(OOCCH_3)_2$ at 306 and 301 cm^{-1} respectively[15]. The similar mass of the tin and tellurium atoms, together with the above evidence of similar strength of interaction of tellurium(IV) and tin(IV) with carboxylate oxygen in these compounds lead us to search a similar region of the spectrum for ν(TeO). Comparison of the low frequency infrared spectra of $Ph_2Te(OOCCH_3)_2$ and Ph_2TeBr_2 reveals a shoulder at 280 cm^{-1} in the diacetate spectrum. This feature is retained in solution and is assigned as the tellurium–oxygen stretching frequency.

The data for $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$ and for $Ph_2Te(OOCPh)_2$ are in general similar to those for $Ph_2Te(OOCCH_3)_2$, they do however differ in some points of detail. A doubling of the ν_s and ν_{as}(OCO) vibrations in the benzoate case is noted, the ν_{as} bands in particular being complex. A doubling of ν_8 in the case of $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$ is also seen. Since these features are retained in solution, with some modification in the case of $(p\text{-}EtOC_6H_4)_2Te(OOCCH_3)_2$, we cannot attribute them entirely to solid state effects, however it is possible that the complex spectra arise from coupling of vibrations of different carboxylate groups in the same molecule. Another possibility is that a slightly different environment for the two carboxylate groups is implied. Thus it is conceivable that the "non-bonded" oxygen atom of one group is closer to the central tellurium atom than the corresponding oxygen atom of the other group. One group therefore approaches an unsymmetrical bicentate situation giving ν_{as} at 1622–1617 cm^{-1} (benzoate) or 1628 cm^{-1} (acetate), the more clearly unidentate group giving ν_{as}(OCO) some 30 cm^{-1} higher.

Diphenyltellurium dinitrate

It seemed logical to include the diphenyltellurium ester of nitric acid in this investigation since it was anticipated that the compound would be structurally related to the dicarboxylates and also that it would present the same problems of interpretation of the spectroscopic data. Infrared analysis of $Ph_2Te(NO_3)_2$ was initially difficult due to reaction of the compound with most common support materials to release ionic nitrate. Satisfactory spectra, which were independent of time were ultimately obtained using silver chloride supports. Bands due to the nitrate group were located at 1531 s, 1269 s, 942 s, 783 m and 700 m cm^{-1}. A band at 716 cm^{-1} may be due to a nitrato-group but could equally be a component of γ(CH) for the phenyl group. The compound is a non-electrolyte in nitromethane.

The nitrate groups are clearly not ionic but it is difficult to obtain a definitive interpretation of the spectrum in structural terms since both uni- and bidentate nitrato-groups give six infrared active fundamentals and the band positions vary according to the strength of the covalent interaction. Comparison with stoichiometrically similar tin(IV) compounds can be useful on occasion. A suitable source of comparative data would appear to be dimethyltin dinitrate which does indeed give a similar spectrum[16]. The crystal structure of this molecule has recently been published[17] and it contains unsymmetrically bidentate nitrato-groups. A feature of the structure is that the two longer tin–oxygen contacts are different. This compound well illustrates the difficulty that can arise in the interpretation of the solid state spectral data for nitrato-complexes since a paragraph in another paper[18] implied that the consensus of opinion was beginning to favour a polymeric structure. We believe it is probable that $Ph_2Te(NO_3)_2$ is monomeric and note that the observed frequencies for the nitrato-groups are also closely similar to those observed for $K[Au(NO_3)_4]$[19] which is an authentic example of a compound containing unidentate nitrato-groups[20]. The rather low frequency of the band at 945 cm^{-1} is, in our opinion, suggestive of unidentate or very unsymmetrically bidentate coordination to the tellurium atom.

In principle, Raman spectroscopy is more powerful than infrared methods in resolving the type of problem encountered here[21]. We were unable to obtain a good quality Raman spectrum and were able to locate only one nitrate band at $\Delta\nu$ 1526 cm^{-1}. If this is assumed to be the most intense band arising from the nitrate groups in the Raman effect, the observation is more consistent with bidentate than with unidentate nitrate since it is normally the second band which is the more intense for the unidentate case[19,21].

The Raman results thus confuse rather than clarify the issue. However until more complete Raman data, or an X-ray crystallographic structural determination become available we regard the infrared data as more reliable and express our preference for the monomeric structure with unidentate or very unsymmetrically bidentate nitrato-groups comparable to the situation discussed above for the diorganotellurium dicarboxylates.

ACKNOWLEDGEMENT

We thank the Chemistry Department, University of Nottingham, for access to the Raman spectrometer.

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