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A Convenient and General Preparation of Diphenyl Tellurium Dicarboxylates

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Synopsis. A number of diphenyl tellurium dicarboxylates were readily prepared from diphenyl telluroxide and carboxylic acids or anhydrides. Some of them were also derived through the carboxylate exchange from readily available tellurium carboxylates.

While several diaryl tellurium dicarboxylates have been prepared either by the reaction between the corresponding tellurium dichlorides and metal carboxylates[1] or *via* the lead tetraacetate oxidation of tellurides,[2] little attention has been paid to the preparation in which telluroxides serve as starting materials.

$$Ar_2TeCl_2 + 2AgOCOR \longrightarrow Ar_2Te(OCOR)_2 + 2\,AgCl$$

$$Ar_2Te + Pb(OAc)_4 \longrightarrow Ar_2Te(OAc)_2 + Pb(OAc)_2$$

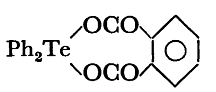
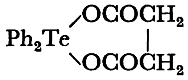
Herein we wish to present facile methods for the preparation of a number of tellurium dicarboxylates from diphenyl telluroxide.

Results and Discussion

Diphenyl telluroxide, easily prepared from diphenyl tellurium dichloride by aqueous sodium hydroxide hydrolysis,[3] was allowed to react with an equiv of acetic anhydride in chloroform for 30 min at room temperature and evaporation of the solvent and recrystallization of the resulting residue from chloroform–hexane gave a crystalline product (I) almost quantitatively.

$$\text{a)}\ Ph_2Te{=}O + Ac_2O \xrightarrow{\text{r.t., 30 min}} Ph_2Te(OAc)_2 \qquad \text{(I)}$$

Table 1. Product yields and physical properties of tellurium dicarboxylates

Dicarboxylate	Method	Yield, %	Mp, °C	IR[d]	NMR[e]	Elemental anal.	
						Found	Calcd
$Ph_2Te(OCOH)_2$	b	95	122—124	1637	8.22(s) 7.25—8.06(m)	C, 45.31 H, 2.99	45.22 3.25
	c	79					
$Ph_2Te(OCOCH_3)_2$	a	89	143—145	1645	7.30—7.95(m) 1.95(s)	lit, mp 138—141 °C[1]	
	b	97					
$Ph_2(OCOPr^i)_2$	a	93	108—109	1637	7.27—7.94(m) 2.20—2.70(m) 1.00(s) 1.12(s)	C, 51.97 H, 5.09	52.68 5.30
	b	91					
	c	68					
$Ph_2Te(OCOBu^t)_2$	b	87	137—140	1642	7.25—7.97(m) 1.08(s)	C, 54.46 H, 5.79	54.59 5.83
	c	56					
$Ph_2Te(OCOPh)_2$	a	88	161—163	1650	8.01—7.30(m)	lit, mp 159—161 °C	
	b	77					
	c	77					
$Ph_2Te(OCOCH_2Ph)_2$	b	92	99—100	1644	7.09—7.79(m) 7.79(m) 7.17(s) 3.49(s)	C, 60.63 H, 4.29	60.91 4.38
	c	79					
$Ph_2Te(OSO_2Tol)_2$	a	79	282—285	1218 1195 1180	7.10—7.95(m) 2.26(s)	C, 48.83 H, 3.80	50.03 3.88
	b	71					
	c	74					
	a	93	181—185	1643	7.20—8.12(m)	C, 54.42 H, 3.25	53.87 3.16
 $Ph_2Te\begin{cases}OCOCH_2\\ \quad\ \mid\\ OCOCH_2\end{cases}$	a	99	115—119	1645	7.25—8.04(m) 2.43(s)	C, 48.36 H, 3.74	48.30 3.55

a) From carboxylic anhydrides. b) From carboxylic acids. c) By carboxylate exchange reaction. The values indicated are unreacted amounts of the starting diacetate, which were determined by NMR measurements 5 minutes after diphenyl tellurium diacetate was mixed with two moles of acids. d) $\nu_{C=O}$ (KBr) cm^{-1}. e) Spectra were measured in $CDCl_3$. Line positions are reported in δ (ppm).

Likewise, other commercially available acid anhydrides could be employed for the synthetic purposes and the treatment of diphenyl telluroxide with sulfonic anhydride such as *p*-toluenesulfonic anhydride afforded diphenyl tellurium bistoluenesulfonate (II) in good yield.

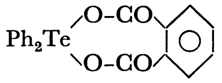
$$Ph_2Te{=}O + (TolSO_2)_2O \longrightarrow Ph_2Te(OSO_2Tol)_2 \qquad (II)$$

Various dicarboxylates thus obtained were satisfactorily characterized by elemental analyses, and IR and NMR spectra. The data are summarized in Table 1.

When desired carboxylic anhydrides are not available on hand, instead the corresponding carboxylic acids may be used as well. Thus, treatment of the telluroxide with 2 equiv of acetic acid in chloroform at room temperature resulted in the formation of the tellurium diacetate (I) quantitatively.

$$\text{b)}\ Ph_2Te{=}O + 2AcOH \xrightarrow{\text{r.t., 30 min}} I + H_2O$$

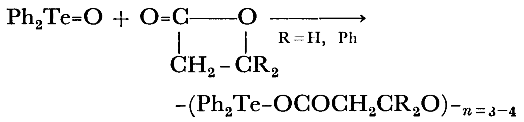
Quite recently McWhinnie *et al.*[4] have reported that sodium salt of ortho-phthalic acid reacts with diaryl tellurium dichlorides to give dimeric tellurium phthalates. It is of particular interest, however, that the methods described here are applicable to dicarboxylic anhydrides and acids such as phthalic, maleic, malonic, and succinic acids giving quantitative yields of monomeric or oligomeric esters. Especially, the melting point of monomeric compound III (mp: 181—185 °C) is markedly different from that of the dimeric ester (mp: 108—110 °C) provided by McWhinnie *et al.*



(III)

MW(obsd): 438

The application of this method to propiolactones failed to give discrete monomeric compounds, but led to the formation of oligomeric compounds with molecular weight larger than 1000.



$$Ph_2Te{=}O + \underset{CH_2-CR_2}{O{=}C{-}O} \xrightarrow[R=H,\ Ph]{} {-}(Ph_2Te{-}OCOCH_2CR_2O){-}_{n=3-4}$$

Meanwhile, although McWhinnie's attempt to obtain a pure product from formic acid was unsuccessful, the preparation of diphenyl tellurium diformate was attained in a nearly quantitative yield by the reaction of the telluroxide with a slight excess of formic acid. Alternatively, the same formate ester could be given by the ligand exchange reaction of the corresponding diacetate with a large excess of formic acid. In general, less acidic carboxylic acids tend to be more readily expelled from the tellurium center than more acidic ones do.

$$\text{c)}\ Ph_2Te(OAc)_2 + 2HCOOH \xrightarrow{\text{r.t., 10 min}} Ph_2Te(OCOH)_2$$

The methods described are quite simple and hence convenient because a variety of carboxylic acids and anhydrides is commercially available and can be directly used without conversion into their sodium or silver salts.

Experimental

A typical procedure was as follows: diphenyl telluroxide and an equimolar amount of carboxylic anhydrides or acids were dissolved in dry chloroform. The reaction mixture was allowed to react at room temperature for 30 min. After evaporation of the solvent, the residue was recrystallized from chloroform-hexane. A similar procedure was also employed for carboxylate exchange reactions by using excess of desired carboxylic acids. Yields and physical properties of products are listed in Table 1.

References

1) B. C. Pant, *J. Organomet. Chem.*, **65**, 51 (1974).
2) B. C. Pant, *Tetrahedron Lett.*, **1972**, 4779.
3) F. Kraft and R. E. Lyons, *Ber.*, **27**, 1768 (1894).
4) N. Dance and W. R. McWhinnie, *J. Orgamomet. Chem.*, **104**, 317 (1976).