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A FACILE AND GENERAL METHOD FOR THE PREPARATION OF DIARYLTELLURIUM DICARBOXYLATES

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Summary

Diaryltellurium dicarboxylates can be prepared by treatment of the corresponding dichlorides with carboxylic acids in the presence of silver oxide. The conversion of the dichlorides to the carboxylates can also be achieved through a more practical method employing a carboxylate anionic exchange resin. IR and PMR data are given.

Introduction

A few years ago we reported [1] the preparation of diaryltellurium dicarboxylates by treatment of the dichlorides with silver carboxylates.

$$Ar_2TeCl_2 + 2\ RCO_2Ag \xrightarrow{\text{solvent}} Ar_2Te(O_2CR)_2 + 2\ AgCl$$

$Ar = p\text{-}CH_3Ph$; $R = Ph, C_3H_7, C_7H_{15}, C_{11}H_{22}$

At that time, only a few examples of this class of organotellurium compounds had been reported [2—5]. Recently Pant [6,7] employed lead tetraacetate to convert diaryltellurides into the corresponding diacetates.

$$Ar_2Te + Pb(O_2CCH_3)_4 \rightarrow Ar_2Te(O_2CCH_3)_2 + Pb(O_2CCH_3)_2$$

The same author also prepared diacetates and a dibenzoate applying our earlier method of reacting dichlorides with silver carboxylates. From spectral data the structure of these compounds was proposed [8].

In this paper we report further development of this method. It now provides a very attractive and inexpensive procedure for preparing any type of diaryltellurium dicarboxylate in high yield.

Results and discussion

An improvement of our method [1] was reached by avoiding the preparation of the separate silver carboxylates which is very time-consuming, especially due to the necessity of drying the salts prepared in aqueous medium. Instead, the direct treatment of the dichloride with the carboxylic acid in boiling benzene was carried out in the presence of silver oxide.

$$Ar_2TeCl_2 + 2\ RCO_2H \xrightarrow{Ag_2O} Ar_2Te(O_2CR)_2$$

$$Ar = p\text{-}CH_3Ph;\ R = Ph,\ C_3H_7,\ C_7H_{15},\ C_{11}H_{22}$$

Two mechanistic pathways could be considered: (a) formation, "in situ" of the silver carboxylate, followed by reaction with diaryltellurium dichloride:

$$2\ RCO_2H + Ag_2O \rightarrow 2\ RCO_2Ag + H_2O \qquad (1)$$

$$2\ RCO_2Ag + Ar_2TeCl_2 \rightarrow Ar_2Te(O_2CR)_2 + 2\ AgCl \qquad (2)$$

(b) Formation "in situ" of diaryltelluroxide followed by its reaction with the carboxylic acid:

$$Ar_2TeCl_2 + Ag_2O \rightarrow Ar_2TeO \qquad (3)$$

TABLE 1

PREPARATION OF DIARYLTELLURIUM DICARBOXYLATES BY REACTION OF Ar_2TeCl_2 WITH AMBERLITE IR 45}OH^- RESIN

$Ar_2Te(OCOR)_2$	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%)	
			C	H
$(CH_3Ph)_2Te(OCOPh)_2$ [a]	230	75		
$(CH_3OPh)_2Te(OCOPh)_2$	210	86	57.67 (57.59)	4.03 (4.11)
$Ph_2Te(OCOPh)_2$ [a]	165	94		
$(CH_3Ph)_2Te(OCOCH_2Ph)_2$	95	80	62.01 (62.13)	3.92 (4.82)
$(CH_3OPh)_2Te(OCOCH_2Ph)_2$	90—91	81	58.50 (58.88)	4.25 (4.57)
$Ph_2Te(OCOCH_2Ph)_2$	86—88	70	61.10 (60.93)	4.47 (4.34)
$(CH_3Ph)_2Te(OCOCHPh_2)_2$	147—149	90	69.06 (68.88)	5.28 (4.95)
$(CH_3OPh)_2Te(OCOCHPh_2)_2$	141	68	66.22 (65.99)	4.91 (4.74)
$Ph_2Te(OCOCHPh_2)_2$	167—168	78	68.22 (68.21)	4.70 (4.57)
$(CH_3Ph)_2Te(OCOCH{=}CHPh)_2$	207—209	86	63.65 (63.61)	4.55 (4.67)
$(CH_3OPh)_2Te(OCOCH{=}CHPh)_2$	162—165	80	60.44 (60.41)	4.55 (4.43)
$Ph_2Te(OCOCH{=}CHPh)_2$	175	82	62.96 (62.54)	4.34 (4.19)
$(CH_3Ph)_2Te(OCOCH_3)_2$ [a]	177	70		
$(CH_3OPh_2Te(OCOCH_3)_2$ [a]	135	98		
$Ph_2Te(OCOCH_3)_2$ [a]	138	70		
$(CH_3Ph)_2Te(OCOCH_2CH_3)_2$	185—187	97	52.36 (52.67)	5.09 (5.30)
$(CH_3OPh)_2Te(OCOCH_2CH_3)_2$	168—170	96	49.26 (49.22)	4.92 (4.95)
$Ph_2Te(OCOCH_2CH_3)_2$	100—103	73	50.13 (50.51)	4.75 (4.71)
$(CH_3Ph)_2Te(OCOCH(CH_3)_2)_2$	140—142	83	54.79 (54.58)	5.80 (5.83)
$(CH_3OPh)_2Te(OCOCH(CH_3)_2)_2$	176—178	99	51.13 (51.20)	5.69 (5.46)
$Ph_2Te(OCOCH(CH_3)_2)_2$	109	70	52.63 (52.67)	5.26 (5.30)
$(CH_3Ph)_2Te(OCOC(CH_3)_3)_2$	140—143	90	56.47 (56.28)	6.59 (6.26)
$(CH_3OPh)_2Te(OCOC(CH_3)_3)_2$	176—178	85	53.00 (52.97)	6.00 (5.92)
$Ph_2Te(OCOC(CH_3)_3)_2$	141	70	54.54 (54.56)	6.19 (5.83)

[a] Known compounds [6,7].

TABLE 2

PMR AND IR ANALYTICAL DATA OF THE COMPOUNDS

	PMR (δ) (ppm)	IR ν(C=O) (cm^{-1})
$(CH_3Ph)_2Te(OCOPh)_2$	2.3 (s, 6H); 7.1–8.1 (m, 18H)	1617s; 1639s [b]
$(CH_3OPh)_2Te(OCOPh)$	3.8 (s, 6H); 7.0 (d, J 9 Hz, 4H); 7.3–8.1 (m, 18H)	1617s; 1637s [c]
$Ph_2Te(OCOPh)_2$	7.2–8.23 (m)	1620s (br) [b]
$(CH_3Ph)_2Te(OCOCH_2Ph)_2$	2.41 (s, 6H); 3.55 (s, 4H); {7.16 (d, J 9 Hz); 7.26 (s): 24H [a]; 7.51 (d, J 9 Hz, 4H)	1644s (br) [c]
$(CH_3OPh)_2Te(OCOCH_2Ph)_2$	3.38 (s, 4H); 3.37 (s, 6H); 6.78 (d, J 9 Hz, 4H); 7.13 (s, 10H); 7.48 (d, J 9 Hz, 4H)	1646s; 1660s [c]
$Ph_2Te(OCOCH_2Ph)_2$	3.48 (s, 4H); 7.13 (s, 10H); 7.23–7.78 (m, 10H)	1630s(br) [c]
$(CH_3Ph)_2Te(OCOCHPh_2)_2$	2.4 (s, 6H); 4.91 (s, 2H); {7.06 (d); 7.2 (s): 24H [a]; 7.43 (d, J 9 Hz, 4H)	1620s; 1655s [c]
$(CH_3OPh)_2Te(OCOCHPh_2)_2$	3.75 (s, 6H); 4.91 (s, 2H); 6.76 (d, J 9 Hz, 4H); 7.16 (s, 20H); 7.43 (d, J 9 Hz, 4H)	1635s, 1660s [b]
$Ph_2Te(OCOCHPh_2)_2$	4.96 (s, 2H); 7.18 (s, 20H); 7.3–7.68 (m, 10H)	1625s; 1640s [b]
$(CH_3Ph)_2Te(OC)$	2.4 (s, 6H); 6.28 (d, J 16 Hz, 2H); 7.05–7.65 (m, 16H); 7.8 (d, J 9 Hz, 4H)	1627s; 1644s [b]
$(CH_3OPh)_2Te(OCOCH{=}CHPh)_2$	3.83 (s, 6H); 6.43 (d, J 16 Hz, 2H); 7.05 (d, J 9 Hz, 4H); 7.76 (m, 12H); 7.93 (d, J 9 Hz, 4H)	1630s; 1640s [b]
$Ph_2Te(OCOCH{=}CHPh)_2$	6.41 (d, J 16 Hz, 2H); 7.15–8.15 (m, 22H)	1640s [b]
$(CH_3Ph)_2Te(OCOCH_3)_2$	1.95 (s, 6H); 2.4 (s, 6H); 7.26 (d, J 9 Hz, 4H); 7.7 (d, J 9 Hz, 4H)	1640s; 1620(sh) [b]
$(CH_3OPh)_2Te(OCOCH_3)_2$	1.98 (s, 6H); 3.86 (s, 6H); 7.0 (d, J 9 Hz, 4H); 7.8 (d, J 9 Hz, 4H)	1648s; 1627s [b]
$Ph_2Te(OCOCH_3)_2$	1.96 (s, 6H); 7.26–7.96 (m, 10H)	1640s; 1625(sh) [b]
$(CH_3Ph)_2Te(OCOCH_2CH_3)_2$	1.0 (t, J 7 Hz, 6H); 2.2 (q, J 7 Hz, 4H); 2.41 (s, 6H); 7.26 (d, J 9 Hz, 4H); 7.71 (d, J 9 Hz, 4H)	1625–1640s [b]
$(CH_3OPh_2Te(OCOCH_2CH_3)_2$	1.03 (t, J 7 Hz, 6H); 2.23 (q, J 7 Hz, 4H); 2.83 (s, 6H); 6.98 (d, J 9 Hz, 4H); 7.76 (d, J 9 Hz, 4H)	1640s; 1630(sh) [b]
$Ph_2Te(OCOCH_2CH_3)_2$	1.06 (t, J 7 Hz, 6H); 2.25 (q, J 7 Hz, 4H); 6.25–7.9 (m, 10H)	1635s(br) [c]
$(CH_3Ph)_2Te(OCOCH(CH_3)_2)_2$	1.05 (d, J 7 Hz, 12H); 2.1–2.8 (m, 2H); 7.2–7.98 (m, 10H)	1620s; 1635s [b]
$(CH_3OPh)_2Te(OCOCH(CH_3)_2)_2$	1.06 (d, J 7 Hz, 12H); 2.1–2.8 (m, 2H); 2.83 (s, 6H); 7.0 (d, J 9 Hz, 4H); 7.76 (d, J 9 Hz, 4H)	1620s; 1630s [b]
$Ph_2Te(OCOCH(CH_3)_2)_2$	1.05 (d, J 7 Hz, 12H); 2.1–2.8 (m, 2H); 7.2–7.98 (m, 10H)	1620s; 1644s [c]
$(CH_3Ph)_2Te(OCOC(CH_3)_3)_2$	1.03 (s, 18H); 2.41 (s, 6H); 7.2 (d, J 9 Hz, 4H); 7.66 (d, J 9 Hz, 4H)	1646s [c]
$CH_3OPh)_2Te(OCOC(CH_3)_3)_2$	1.1 (s, 18H); 3.85 (s, 6H); 6.96 (d, J 9 Hz, 4H): 7.73 (d, J 9 Hz, 4H)	1615s; 1628s [c]
$Ph_2Te(OCOC(CH_3)_3)_2$	1.08 (s, 18H); 7.26–7.96 (m, 10H)	1633s; 1641s [c]

[a] The two signals are partially superimposed. [b] In Nujol. [c] In KBr.

$$Ar_2TeO + 2\ RCO_2H \rightarrow Ar_2Te(O_2CR)_2 + H_2O \qquad (4)$$

The observation in separate experiments, ($Ar = p\text{-}CH_3Ph$; $R = Ph$) that the conversion of a carboxylic acid into its silver salt by Ag_2O in boiling benzene (reaction 1) is much faster than the conversion of the dichloride to the telluroxide by the same reagent (reaction 3) supports the first mechanism.

However the best method for the preparation of the dicarboxylates consists in the treatment of the corresponding dichloride with a basic anionic resin in which the OH^- was previously exchanged with the carboxylate anion.

$$Res^+\}OH^- + RCOOH \xrightarrow{EtOH} Res^+\}RCO_2^-$$

$$2\ Res^+\}RCO_2^- + Ar_2TeCl_2 \xrightarrow[1\ :\ 1]{THF/EtOH} Ar_2Te(O_2CR)_2 + 2\ Res^+\}Cl^-$$

Weak basic resins such as Amberlite IR 45$\}OH^-$ (or Merck "Ionenaustauscher II") were employed as the normal exchange reagent, although strong basic resins such as Amberlite IR $400^+\}OH^-$ (or Merck "Ionenaustauscher III") were also tested with good results. The carboxylate resin can also be prepared by conversion of anionic chloride resin (e.g. Amberlite IRA 400$\}Cl^-$) with an aqueous solution of the sodium carboxylate. The first procedure is, however, more practical since it avoids the preparation of the salt solutions.

A treatment of the dichlorides in THF/EtOH with an excess of this resin promotes their complete conversion to the carboxylates. These are the only soluble components in the solution and can be isolated easily in high yield and purity by evaporation of the solvent. A simple recrystallization (benzene/pet. ether) provides analytical samples of the carboxylates.

Tables 1 and 2 summarize m.p., yields and analytical data as well as IR and PMR data. For most C=O stretching frequencies a splitting of the band is observed, in accordance with reported data [8].

Two of the diaryltellurium dichlorides used in our work were prepared by the reaction of $TeCl_4$ with two equivalents of the corresponding arylmercuric chlorides in boiling dioxane:

$$TeCl_4 + 2\ ArHgCl \xrightarrow{diox.} Ar_2TeCl_2 + 2\ HgCl_2 \cdot diox.$$

$Ar = Ph, p\text{-}CH_3Ph$

This method, still unpublished, in an extension of older methods for preparing trichlorides [9] and dichlorides [10] starting respectively, from tellurium tetrachloride or aryltellurium trichlorides and the mercury reagent.

$$TeCl_4 + 2\ ArHgCl \xrightarrow{diox.} Ar_2TeCl_2 + HgCl_2 \cdot diox.$$

$$ArTeCl_3 + ArHgCl \xrightarrow{diox.} ArTeCl_2Ar' + HgCl_2 \cdot diox.$$

Experimental

The melting points were determined on a Kofler Hotstage apparatus and are uncorrected. The IR spectra were recorded on a Perkin—Elmer-337 spectrophotometer. PMR spectra were recorded on a Varian T 60 spectrometer using $CDCl_3$ as solvent and TMS as an internal reference. Di-*p*-methoxyphenyltellurium dichloride was prepared from $TeCl_4$ and anisole [11].

Diphenyl and di-p-tolyltellurium dichlorides

Tellurium tetrachloride, (10.8, 0.04 mol) and 0.08 mol of the ArHgCl derivative were heated at reflux in 100 ml anhydrous dioxane for 2 h. The solution then was cooled at 10° C and the $HgCl_2 \cdot$ diox. precipitate filtered and washed with 15 ml of cold dioxane. The filtrate was poured with stirring in 400 ml of ice-cold 1% HCl. The dichlorides precipitated as crystalline solids. Yields were greater than 90%. Recrystallization was effected from benzene/pet. ether. $(C_6H_5)_2TeCl_2$, m.p. 160—162°C in accordance with the literature [12]. $(p\text{-}CH_3C_6H_4)_2TeCl_2$ m.p. 165—166°C, in accordance with the literature [12].

Di-p-tolyltellurium dicarboxylates

(a) Reaction between di-tolyltellurium dichlorides and carboxylic acid in the presence of Ag_2O. Di-*p*-tolyltellurium dichloride (0.76 g, 0.002 mol), carboxylic acid (0.004 mol) and Ag_2O (0.47 g, 0.002 mol) were refluxed in 30 ml of benzene for 4 h. During this time, a progressive disappearance of the heavy black Ag_2O and formation of colloidal white AgCl was observed. The mixture was filtered and the solution evaporated, to give the crude dicarboxylate. The yields were always higher than 90%.

	M.p. (°C)	Recrystallized from:
Di-*p*-tolyltellurium dibenzoate [1]	230-234	benzene/pet. ether
Di-*p*-tolyltellurium dibutyrate [1]	125-127	pet. ether
Di-*p*-tolyltellurium dicaprilate [1]	84-86	methanol
Di-*p*-tolyltellurium dilaurate [1]	67-68	ethanol

(b) Reaction between diaryltellurium dichlorides and $Resin^+\}RCO_2^-$. A 4% ethanolic solution of the carboxylic acid was passed slowly through a column (about 10 mm inner diameter) charged with Amberlite IR 45 resin (OH^-) * until complete conversion was achieved (theoretical exchange capacity: 0.002 equiv./ per ml of dry resin). The resin was washed with EtOH to remove the excess of carboxylic acid and dried in a dry nitrogen stream.

A solution of diaryltellurium dichloride (0.001 mol) in 20 ml of 1 : 1 THF/ EtOH was passed slowly over 5 g of the IR 45 carboxylate resin described above. The resin was rinsed with 50 ml of the same solvent mixture, and the solution evaporated using a rotatory evaporator. The crude dicarboxylates (quantitative yields) were recrystallized from benzene/pet. ether.

The same results were obtained if the carboxylate resin was prepared by exchange of an IRA $400\}Cl^-$ resin with 4% aqueous sodium carboxylates (prepared by neutralization of carboxylic acid with NaOH in water).

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* No precautions were taken to exclude moisture.

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