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I. SYNTHESIS, REACTIONS AND SPECTRAL CHARACTERISTICS OF DIARYLTELLURIUM DIACETATES

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Summary

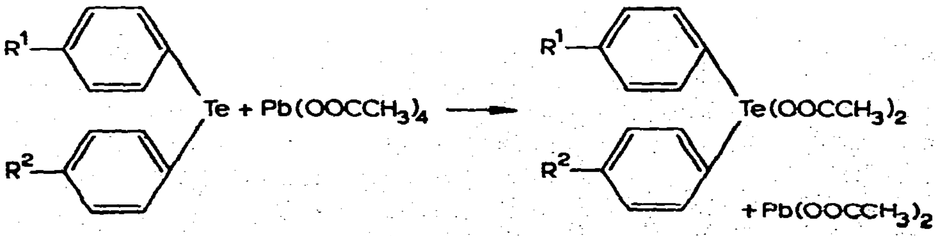
Diaryltellurium diacetates have been prepared in excellent yields by the oxidation of diaryltellurides with lead tetraacetate and also by the reaction of diaryltellurium dichlorides with silver acetate. Hydrolysis, reduction and exchange reactions of these derivatives and their spectral data are described.

Introduction

Whereas the syntheses and reactions of diaryltellurium dihalides have been studied in detail [1 - 3], relatively little is known about the chemistry of corresponding dicarboxylates. Although there are two reports which mention the preparation of these derivatives [4, 5], no systematic investigation has previously been undertaken. This paper describes the syntheses, reactions and spectral data of some new diaryltellurium diacetates.

Results and discussion

The synthesis of diaryltellurium diacetates has been achieved by the oxidation of diaryl tellurides with lead tetraacetate in hydrocarbon solvents (benzene or toluene) (eqn. 1).



(1)

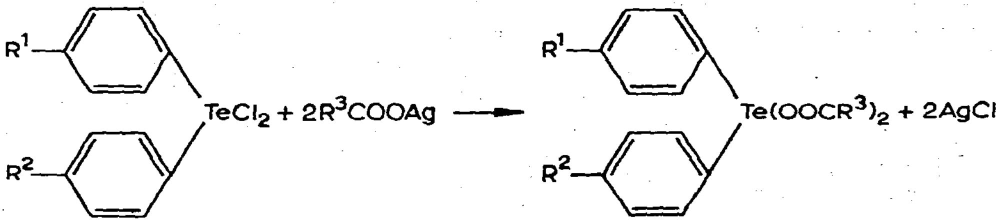
($R^1 = R^2 = H, CH_3O, C_2H_5O; R^1 = H, R^2 = C_2H_5O$)

TABLE 1
SYNTHESES, M.P.'S, YIELDS AND ANALYSES OF DIARYLTELLURIUM DICARBOXYLATES

Reactants	Organtellurium compound obtained	Yield (%)	M.p. (°C)	Analyses found (Calcd.)(%)	
				C	H
$(C_6H_5)_2Te + Pb(OOCCH_3)_4$	$(C_6H_5)_2Te(OOCH_3)_2$	98	139—141	48.19 (48.06)	4.02 (4.03)
$(C_6H_5)_2TeCl_2 + 2CH_3COOAg$		94		48.16	4.03
$(p\text{-}C_2H_5OC_6H_4)_2Te + Pb(OOCCH_3)_4$	$(p\text{-}C_2H_5OC_6H_4)_2Te(OOCCH_3)_2$	96	110—111	49.17 (49.22)	4.91 (4.96)
$p\text{-}C_2H_5OC_6H_4)_2TeCl_2 + 2\,CH_3COOAg$		89		49.29	4.89
$p\text{-}C_2H_5OC_6H_4(C_6H_5)Te + Pb(OOCCH_3)_4$	$p\text{-}C_2H_5OC_6H_4(C_6H_5)Te(OOCCH_3)_2$	97	114—116	48.65 (48.70)	4.51 (4.54)
$p\text{-}C_2H_5OC_6H_4(C_6H_5)TeCl_2 + 2CH_3COOAg$		90		48.64	4.56
$(p\text{-}CH_3OC_6H_4)_2Te + Pb(OOCCH_3)_4$	$(p\text{-}CH_3OC_6H_4)_2Te(OOCCH_3)_2$	89	135—137	46.96 (47.00)	4.37 (4.38)
$(p\text{-}CH_3C_6H_4)_2TeCl_2 + 2CH_3COOAg$	$(p\text{-}CH_3C_6H_4)_2Te(OOCCH_3)_2$	90	178—180	50.59 (50.52)	4.80 (4.71)
$(C_6H_5)_2TeCl + 2C_6H_5COOAg$	$(C_6H_5)_2Te(OOCC_6H_5)_2$	92	159—161	59.56 (59.59)	3.81 (3.85)

The reaction goes to completion at room temperature giving diaryltellurium diacetates in excellent yields. The isolation of the products presents no problem because of their solubility in the solvent used for the reaction, from which lead diacetate precipitates.

Diaryltellurium dicarboxylates were also synthesized by the reaction of diaryltellurium dichlorides with silver carboxylates in boiling benzene or dioxane (eqn. 2). In view of the cost of silver salts and of the lower yields, this method seems to be less attractive than that using lead tetraacetate.



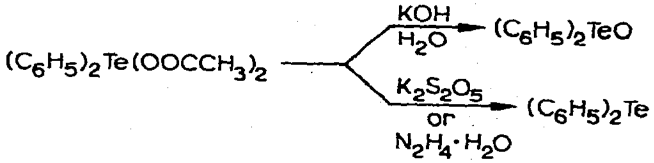
(2)

($R^1 = R^2 = H, C_2H_5O, CH_3, R^3 = CH_3; R^1 = H, R^2 = C_2H_5O, R^3 = CH_3; R^1 = R^2 = H,\ R^3 = C_6H_5$)

Various reactions, m.p.'s, yields and analytical data are summarized in Table 1.

Diaryltellurium diacetates are colourless, crystalline solids soluble in benzene, toluene, acetone, methanol and carbon tetrachloride. They can be stored over long periods without hydrolysis or decomposition.

Like diaryltellurium dihalides [6, 7], the diacetates could be hydrolyzed or reduced according to the reactions shown in eqn. (3). The diacetates also undergo "acetoxy group exchange" reactions of the type shown in eqns. (4) and (5).



$$(C_6H_5)_2Te(OOCCH_3)_2 \xrightarrow[H_2O]{KOH} (C_6H_5)_2TeO$$

$$(C_6H_5)_2Te(OOCCH_3)_2 \xrightarrow[\text{or } N_2H_4\cdot H_2O]{K_2S_2O_5} (C_6H_5)_2Te \qquad (3)$$

$$(C_6H_5)_2Te(OOCCH_3)_2 + 2KI \xrightarrow{(CH_3)_2CO} (C_6H_5)_2TeI_2 + 2CH_3COOK \qquad (4)$$

$$(C_6H_5)_2Te(OOCCH_3)_2 + 2(CH_3)_3SiCl \longrightarrow (C_6H_5)_2TeCl_2 + 2(CH_3)_3SiOOCCH_3 \qquad (5)$$

From infrared data, the structures of $(C_6H_5)_2Te(OOCCH_3)_2$, $(C_6H_5)_2Te(OOCC_6H_5)_2$ and $(p\text{-}C_2H_5OC_6H_4)_2(OOCCH_3)_2$ 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 solution for $(C_6H_5)_2Te(OOCC_6H_5)_2$ and for $(p\text{-}C_2H_5OC_6H_4)_2Te(OOCCH_3)_2$. The carboxylate groups are "ester-like" as in related organotin compounds (for details regarding structural considerations of

TABLE 2
SPECTRAL DATA FOR DIARYLTELLURIUM DIACETATES

Compound	IR[a] (cm^{-1})		PMR[b]		
	ν_{as}(OCO)	ν_s(OCO)	τ(ppm)	Multiplicity	Assignment
$(C_6H_5)_2(OOCCH_3)_2$	1641	1280	2.00—2.70	Complex	Phenyl ring protons
(I)			8.10	Singlet	$OOCCH_3$
(p-$CH_3OC_6H_4)_2Te(OOCCH_3)_2$	1650	1280	2.32	Doublet	Phenyl ring
(II)			3.10	Doublet	protons
			6.25	Singlet	OCH_3
			8.10	Singlet	$OOCCH_3$
(p-$CH_3CH_2OC_6H_4)_2Te(OOCCH_3)_2$	1654	1280	2.20	Doublet	Phenyl ring
(III)			3.02	Doublet	protons
			5.92	Quartet	$CH_3\underline{H}_2$
			8.10	Singlet	$OOCCH_3$
			8.55	Triplet	$C\underline{H}_3CH_2$
(p-$CH_3CH_2C_6H_4)Te(C_6H_5)(OOCCH_3)_2$	1650	1280	2.20—3.20	Complex	Phenyl ring protons
(IV)			5.95	Quartet	$CH_3C\underline{H}_2$
			8.15	Singlet	$OOCCH_3$
			8.57	Triplet	$C\underline{H}_3CH_2$
(p-$CH_3C_6H_4)_2Te(OOCCH_3)_2$	1652	1281	2.15	Doublet	Phenyl ring
(V)			3.07	Doublet	protons
			8.00	Singlet	CH_3
			8.20	Singlet	$OOCCH_3$

[a] As Nujol mull; [b] 60 MHz; tetramethylsilane as the internal standard; solvents used are as follows: (I), (III) and (IV) in CCl_4; (II) in $CDCl_3$ and (V) in C_6D_6.

diaryltellurium dicarboxylates see ref. 8). Some IR and ^{1}H NMR data for diaryltellurium diacetates are given in Table 2.

The reaction of diphenyl ditelluride with lead tetraacetate in benzene at room temperature affords a solution of phenyltellurium triacetate as shown by ^{1}H NMR spectroscopy [9]. Attempts to isolate the product yielded a white crystalline material of indefinite composition. Infrared analysis revealed the presence of two types of acetate groups together with free acetic acid. Other experiments involving the reaction of *p*-ethoxyphenyltellurium trichloride (1 mole) with silver acetate (3 moles) also gave a white solid of variable carbon content. Infrared analysis of this material gave definite evidence of the presence of a quantity of the anhydride, $[(p\text{-}C_2H_5OC_6H_4)TeO]_2O$. Thus it is likely that rapid hydrolysis of initially formed triacetate led to the formation of a mixture of the anhydride with $[(p\text{-}C_2H_5OC_6H_4)Te(O)(OOCCH_3)]$.

Experimental

All the reactions were carried out under dry nitrogen. The solvent used for the reaction (benzene, toluene or dioxane) was refluxed over sodium for 4h and fractionated. Tellurium tetrachloride (BDH) was used without further purification. Diaryltellurium dichlorides were synthesized by a recently reported method [10]. Infrared spectra were recorded for Nujol mulls with caesium iodide plates on a Perkin - Elmer 225 or 457 instrument. ^{1}H NMR spectra were recorded with a Perkin - Elmer R10 instrument. As similar experimental procedures were followed for all the reactions, only typical examples are described.

Reaction between diphenyl telluride and lead tetraacetate

A solution of diphenyl telluride (5.04 g in 25 ml of benzene) was added to a well stirred solution of lead tetraacetate (7.92 g) in benzene (50 ml) during 25 min at room temperature. A white precipitate appeared after the addition of first few drops. The mixture was stirred for an additional 4 h. Filtration followed by evaporation of benzene gave the crude material, which was recrystallised from a mixture of benzene/hexane (1/9) to give pure diphenyltellurium diacetate.

Reaction between diphenyltellurium dichloride and silver benzoate

Silver benzoate (5.0 g) was added in small portions to a stirred solution of diphenyltellurium dichloride (3.5 g) in dioxane (50 ml) at room temperature. An exothermic reaction occurred with the formation of a white precipitate. The mixture was refluxed for 4 h. Filtration followed by evaporation of dioxane from the filtrate and recrystallization of the crude product gave white crystals of diphenyltellurium dibenzoate.

Reaction between diphenyltellurium diacetate and potassium hydroxide

An aqueous solution of potassium hydroxide (1 g) was added to a solution of diphenyltellurium diacetate (1.2 g in 20 ml of ethanol). The mixture was stirred at room temperature for 1 h. Evaporation of ethanol/water gave a white solid which was recrystallized from benzene/hexane (1/4) to give diphenyltellurium oxide (m.p. 185 - 187°); lit. [11] 185°).

Reaction between diphenyltellurium diacetate and trimethylchlorosilane

Diphenyltellurium diacetate (2 g) was refluxed with an excess of trimethylchlorosilane (10 ml) for 1 h. Removal of the excess of trimethylchlorosilane and trimethylacetoxysilane (separated from trimethylchlorosilane by fractionation and identified by its PMR spectra) gave diphenyltellurium dichloride (m.p. 160°, lit. [2] 160°).

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