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SYNTHESIS AND PROPERTIES OF TELLURIUM(II) COMPOUNDS: DIARYLTELLUROESTERS, ArCOTeAr'

SYLVIA A. GARDNER and HENRY J. GYSLING

Research Laboratories, Eastman Kodak Company, Rochester, New York
14650 (U.S.A.)

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Summary

A series of organotellurium(II) derivatives of the general formula ArCOTeAr' (Ar,Ar' = phenyl, p-tolyl, p-anisyl, p-bromophenyl, p-trifluoromethylphenyl, 1-naphthyl) have been prepared and characterized chemically and spectroscopically. Various chemical reactions of this class of compounds have been investigated, and the reaction of these compounds with $(PhCN)_2PdCl_2$ to give the polymeric $(Pd(TeAr')_2)_n$ derivatives suggests that these organotellurium reagents may be useful precursors of $TeAr'^-$ ligands in reactions with transition-metal substrates.

Introduction

A recent paper on the ^{13}C NMR spectroscopy of several telluroesters* [1] has prompted us to report our results in this area. Previous workers have described the synthesis and IR spectra of several such compounds [2]; however, the utility of these compounds as precursors to tellurium-containing transition-

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*Compounds of the general formula ArCOTeAr' have been referred to as telluroesters in the literature [1,2]. Barton, however, has recently prepared the first telluroester derivative of the type RCTeOR [3].

metal complexes has not been reported to date. We now describe the synthesis and characterization of a series of diaryltelluroesters and discuss their use as precursors to transition-metal compounds containing an aryltelluro ligand.

Experimental

Microanalyses were done by the Analytical Sciences Division of the Kodak Research Laboratories. Infrared spectra were recorded on a Perkin-Elmer model 567 infrared spectrometer and calibrated with a polystyrene film. The mass spectra were recorded with a Du Pont 21-110B instrument using temperature programming in the direct inlet probe (70 eV). DSC and TGA scans of the compounds were recorded with a Du Pont 990 and a Du Pont 900 thermal analyzer, respectively. ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer.

The diaryl ditellurides [4] and $(PhCN)_2PdCl_2$ [5] were prepared as previously described. Sodium borohydride and Te powder were purchased from Alfa Products, Inc. All other compounds and solvents were obtained from Eastman Organic Chemicals.

Synthesis of ArCOTeAr' derivatives

These derivatives were all prepared by the reaction of a benzoyl chloride with NaTeAr' [2]. The general synthesis is illustrated by the following example.

Synthesis of $C_6H_5COTeC_6H_5$. A solution of diphenyl ditelluride (5.12 g, 12.5 mmol) in 5 ml of benzene and 15 ml of ethanol was heated to reflux. To this solution was added dropwise a solution of sodium borohydride (0.75 g, 20 mmol) in 17 ml of 1 N NaOH. The reaction mixture evolved hydrogen during the addition and was colorless at the end of the addition. Benzoyl chloride (4.22 g, 30 mmol) was then added rapidly, and the warm mixture was stirred for 5 min, poured into 100 ml of water, and extracted with ether

(2 x 100 ml). The ether extract was dried over anhydrous magnesium sulfate, filtered, and reduced to dryness. One recrystallization from hexane gave a yellow solid (5.4 g, 70%), m.p. 70-72°C.

The other derivatives (along with analytical data and melting points) prepared by this general route are listed in Table 1.

TABLE 1

Ar'TeCOAr DERIVATIVES

		Analysis found (calc.)						
Ar'	Ar	%C	%H	%Br	%Te	m.p.* (°C)	Recryst. solvent	Yield(%)
C_6H_5	C_6H_5	50.5	3.2		41.5	70-72	pet ether	70
		(50.40)	(3.25)		(41.18)	(66-70[2])		
C_6H_5	p-$CH_3C_6H_4$	51.9	3.8		40.0	69-71	pet ether	54
		(51.92)	(3.74)		(39.40)			
C_6H_5	p-$CH_3OC_6H_4$	49.1	3.7		37.7	103-105	benzene/ pet ether	35
		(49.48)	(3.56)		(37.55)	(100-103[2])		
C_6H_5	p-BrC_6H_4	40.0	2.4		32.4	77-79	benzene/ pet ether	48
		(40.17)	(2.33)		(32.83)			
C_6H_5	p-$CF_3C_6H_4$	44.9	2.4		34.1	70-72	hexane	56
		(44.51)	(2.40)		(33.77)			
p-$CH_3C_6H_4$	C_6H_5	51.9	3.9		39.1	65-67	pet ether	54
		(51.92)	(3.74)		(39.40)	(65[1])		
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	53.3	4.2		38.2	72-74	pet ether	45
		(53.32)	(4.18)		(37.77)			
p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$	50.6	4.0		36.2	73-75	ether/ hexane	71
		(50.91)	(3.99)		(36.06)	(75[1])		
p-$CH_3C_6H_4$	p-BrC_6H_4	40.7	2.6		32.7	111-113	ether/ hexane	50
		(41.75)	(2.75)		(31.68)			
p-$CH_3C_6H_4$	p-$CF_3C_6H_4$	45.9	2.7		33.0	115-117	hexane	52
		(45.98)	(2.83)		(32.56)			

TABLE 1 (continued)

p-$\mathrm{BrC_6H_4}$	$\mathrm{C_6H_5}$	40.2	2.0	20.5	33.4	56-58	hexane	46
		(40.17)	(2.33)	(20.56)	(32.83)			
p-$\mathrm{BrC_6H_4}$	p-$\mathrm{CH_3C_6H_4}$	42.2	2.7	18.8	32.5	77-79	hexane	60
		(41.75)	(2.75)	(19.84)	(31.68)			
p-$\mathrm{BrC_6H_4}$	p-$\mathrm{CH_3OC_6H_4}$	40.5	2.6	19.1	31.8	83-85	benzene/	59
		(40.16)	(2.65)	(19.08)	(30.47)		hexane	
p-$\mathrm{BrC_6H_4}$	p-$\mathrm{BrC_6H_4}$	33.4	1.7	35.0	28.5	88-90	benzene/	21
		(33.39)	(1.72)	(34.18)	(27.29)		hexane	
p-$\mathrm{BrC_6H_4}$	p-$\mathrm{CF_3C_6H_4}$	37.0	1.6	16.8	28.9	93-95	hexane	45
		(36.82)	(1.77)	(17.50)	(27.94)			
p-$\mathrm{BrC_6H_4}$	1-naphthyl	46.8	2.5		30.3	87-89	benzene/	24
		(46.53)	(2.53)		(29.08)		hexane	
p-$\mathrm{CH_3OC_6H_4}$	p-$\mathrm{CH_3C_6H_4}$	44.1	2.6		31.3	84-86	hexane	20
		(44.17)	(2.72)		(31.29)			
1-naphthyl	p-$\mathrm{CH_3C_6H_4}$	50.3	2.5		29.5	93-95	hexane	34
		(50.53)	(2.59)		(29.82)			

*Literature values are given in parentheses for those compounds which are known.

Synthesis of $(\mathrm{Pd(TeC_6H_5)_2})_n$

$\mathrm{(PhCN)_2PdCl_2}$ (0.96 g, 2.5 mmol) and $\mathrm{C_6H_5COTeC_6H_5}$ (1.55 g, 5 mmol) were mixed in 75 ml of chloroform. The reaction mixture was stirred at room temperature for 24 h. The deep red-brown precipitate was filtered, washed with ether, and vacuum dried to yield 1.2 g (92%) of $(\mathrm{Pd(TeC_6H_5)_2})_n$, m.p. 157-159°C.

The other palladium compounds prepared by this general method are listed in Table 2.

TABLE 2

$(Pd(TeAr')_2)_n$ DERIVATIVES

	Analysis found (calc.)					
Ar'	%C	%H	%Pd	%Te	m.p.(°C)	Yield(%)
C_6H_5	27.8 (27.94)	2.0 (1.95)	21.3 (20.63)	49.2 (49.48)	157-159	92
p-$CH_3C_6H_4$	30.7 (30.92)	2.6 (2.59)	20.0 (19.56)	46.3 (46.92)	161-163 dec	65
p-$CH_3OC_6H_4$	28.8 (29.20)	2.1 (2.45)	18.2 (18.48)	44.5 (44.32)	141-143 dec	30
p-BrC_6H_4	21.3 (21.40)	1.2 (1.20)	16.1 (15.80)	36.5 (37.89)	168-170 dec	92
1-naphthyl	39.5 (39.00)	2.5 (2.29)	16.9 (17.27)	40.8 (41.43)	169-171 dec	85

Results and Discussion

The classical preparation of an ester, by reaction between an acid chloride and an alcohol or a phenol in the presence of an organic base, is a general one and can also be used for the preparation of thioesters and selenoesters, giving products in excellent yields in a short time [6].

Unfortunately, the analogous reaction in organotellurium chemistry is not applicable, owing to the extreme instability of tellurophenol-type compounds [7]. A modification of the general procedure has therefore been used,[2] and the mixed aryl derivatives, ArCOTeAr', have been prepared (Table 1) by the reaction sequence in eq. 1.

$$Ar'_2Te_2 \xrightarrow[NaBH_4]{NaOH} \{Ar'TeNa\} \xrightarrow{ArCOCl} ArCOTeAr' \qquad (1)$$

The final step is accompanied by several secondary reactions, primarily re-formation of the diaryl ditelluride; however, a 10-20% excess of the aromatic acid chloride is generally sufficient to retard these unwanted processes. The telluroesters formed by this method (Table 1) are stable in the reaction medium and can be easily isolated in pure form after only one recrystallization from an organic solvent.

TABLE 3

THERMAL MEASUREMENTS, Ar'TeCOAr DERIVATIVES

			Gross	% Residue
Ar'	Ar	Tm(°C)	dec. temp.(°C)	(T,°C)
C_6H_5	C_6H_5	75	194	2(485)
C_6H_5	p-$CH_3C_6H_4$	74	221	1(419)
C_6H_5	p-$CH_3OC_6H_4$	107	207	1(426)
C_6H_5	p-BrC_6H_4	81	218	1(485)
C_6H_5	p-$CF_3C_6H_4$	75	181	0(239)
p-$CH_3C_6H_4$	C_6H_5	69	177	0(239)
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	76	218	6(400)
p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$	75	221	3.5(485)
p-$CH_3C_6H_4$	p-BrC_6H_4	112	227	5(427)
p-$CH_3C_6H_4$	p-$CF_3C_6H_4$	124	174	3(288)
p-BrC_6H_4	C_6H_5	69	209	10.5(422)
p-BrC_6H_4	p-$CH_3C_6H_4$	77	222	14(428)
p-BrC_6H_4	p-$CH_3OC_6H_4$	89	217	4(438)
p-BrC_6H_4	p-BrC_6H_4	101	221	5(408)
p-BrC_6H_4	p-$CF_3C_6H_4$	102	188	6(485)
p-BrC_6H_4	1-naphthyl	98	220	18(485)
p-$CH_3OC_6H_4$	p-$CF_3C_6H_4$	89	169	3(329)
1-naphthyl	p-$CF_3C_6H_4$	101	194	17(414)

These diorganotellurium(II) derivatives, in contrast to the dialkyl analogues R_2Te [8,9] and the mixed alkyl aryl derivatives RTeAr [10-12], which are both liquids, are isolated as stable crystalline solids [2]. They are relatively low melting and soluble in a variety of organic solvents (e.g. acetone, DMF, acetonitrile, benzene, and chloroform).

Thermal analytical data have been obtained on this series of compounds (Table 3). The organotellurium materials are quite stable at the melting point, with gross decomposition occurring over 165°C. The percentage residue remaining after heating these compounds at elevated temperatures (TGA) is very low, indicating that most of the tellurium present in the molecule is being carried off in volatile decomposition products.

The electron-impact mass spectrum of one of the derivatives, PhCOTePh, has been recorded. As with diaryltellurides and diaryl ditellurides [13], the molecular ion (M+) is present in the spectrum. Other ions visible in the spectrum are $Ph_2Te_2^+$, $PhTe_2^+$, $PhTe^+$, Ph_2^+, $PhCO^+$, and Ph^+.

Infrared spectra for each of the organotellurium compounds in CCl_4 solution and for several in Nujol mulls have been recorded. Frequencies for the C=O stretching mode are given in Table 4.

^{13}C NMR spectra for several of the telluroesters have been determined in an attempt to correlate the chemical shift of the carbonyl carbon with the various substituents on the phenyl rings. The chemical shift data (Table 5) show no correlation between the Hammett σ values of the various substituents and the position of the carbonyl carbon.

To evaluate their chemical properties, diaryltelluroesters were used in several reactions. In an attempt to prepare a tellurium-containing hydrazone, several telluroesters were treated with p-nitrophenylhydrazine or phenylhydrazine. With the former, no reaction was evident, and the reaction with phenylhydrazine yielded only the diaryl ditelluride. Thus, although the IR and ^{13}C NMR spectra indicate the presence of a "normal" carbonyl function in these derivatives, these two typical reactions of carbonyl groups are not observed, apparently because of the marked tendency to form the ditelluride under reducing conditions.

The potential use of telluroesters as ligands in transition-metal systems was also evaluated. Attempted reaction of

TABLE 4

INFRARED SPECTRA, Ar'TeCOAr DERIVATIVES

		$\nu_{C=O}(cm^{-1})$	
Ar'	Ar	Nujol	CCl_4
C_6H_5	C_6H_5	1670	1675
C_6H_5	*p*-$CH_3C_6H_4$	1685	1685
C_6H_5	*p*-$CH_3OC_6H_4$	1665	1682
C_6H_5	*p*-BrC_6H_4	1665	1678
C_6H_5	*p*-$CF_3C_6H_4$		1680
p-$CH_3C_6H_4$	C_6H_5		1672
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$		1683
p-$CH_3C_6H_4$	*p*-$CH_3OC_6H_4$		1675
p-$CH_3C_6H_4$	*p*-BrC_6H_4		
p-$CH_3C_6H_4$	*p*-$CF_3C_6H_4$		1679
p-BrC_6H_4	C_6H_5		1674
p-BrC_6H_4	*p*-$CH_3C_6H_4$		1683
p-BrC_6H_4	*p*-$CH_3OC_6H_4$		1679
p-BrC_6H_4	*p*-BrC_6H_4		1673
p-BrC_6H_4	*p*-$CF_3C_6H_4$		1682
p-BrC_6H_4	1-naphthyl		1689
p-$CH_3OC_6H_4$	*p*-$CF_3C_6H_4$		1679
1-naphthyl	*p*-$CF_3C_6H_4$		1680

TABLE 5

^{13}C NMR SPECTRA[a] of ArCOTeAr'

Ar	Ar'	σ[b]	Chemical shift[c] (C=O)ppm
C_6H_5	$p\text{-}CH_3C_6H_4$	0	196.20
$p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	−0.17	195.42
$p\text{-}CH_3OC_6H_4$	$p\text{-}CH_3C_6H_4$	−0.27	193.50
$p\text{-}BrC_6H_4$	$p\text{-}CH_3C_6H_4$	+0.23	195.24
$p\text{-}CF_3C_6H_4$	$p\text{-}CH_3C_6H_4$	+0.54	196.14

[a] Recorded in $CDCl_3$ with TMS as internal standard. [b] Hammett σ constant. [c] Chemical shifts recorded for benzophenone and acetophenone under similar conditions are 196.9 ppm and 195.2 ppm, respectively.

$p\text{-}CH_3C_6H_4COTeC_6H_5$ with CuCl in chloroform yielded no product, and the CuCl remained undissolved. Reaction of $C_6H_5COTeC_6H_5$ with $(PhCN)_2PdCl_2$ gave an extremely insoluble red-brown product which was identified as $(Pd(TePh)_2)_n$. Telluroesters, therefore, appear to react as analogous but less reactive reagents than $ArTeSn\phi_3$ [15,16,17] for the introduction of bridging $ArTe^-$ ligands (e.g., $CuCl + ArTeSn\phi_3 \xrightarrow{CH3CN} [CuTeAr]_n$ [16]). Other compounds isolated by this procedure are listed in Table 2. Benzoyl chloride was also isolated as a by-product. An attempted reaction of $(Pd(TePh)_2)_n$ with Ph_3P in $CHCl_3$ was unsuccessful. Compounds of the general formula $[(PPh_3)Pd(TeAr')_2]_2$ have been isolated from the reaction of $(PPh_3)_4Pd$ and Ar'_2Te_2 [14]. The exact mechanism of this type of reaction is undetermined, although it is likely that an unstable intermediate of the form $(ArCOTeAr')_2PdCl_2$ decomposes to $(Pd(TeAr')_2)_n$ and the chlorine-containing by-product. The utility of these reagents (i.e., XTeAr; X = COAr, MAr_3 (M = Ge, Sn, Pb) as aryl telluro ligand precursors is being further investigated.

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