Diorganotellurium(IV) bis(fluorocarboxylates)

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Abstract

Diorganotellurium(IV) bis(fluorocarboxylates)[$R_2Te(OCOR')_2$] [R = Me, Ph, *p*-$MeOC_6H_4$ and *p*-$EtOC_6H_4$; R′ = CF_3, C_2F_5, C_3F_7] have been prepared by the interaction of $R_2Te(OMe)_2$ with fluorocarboxylic acids (R′COOH). Identical products were obtained by the metathetical reaction of R_2TeCl_2 with silver salts of the fluorocarboxylic acids in 1:2 molar ratios. However, when the reaction proceeded in a 1:1 molar ratio, the product was $R_2TeCl(OCOR')$. However, reaction of R_2TeO with CF_3COOH yielded $\{[(R_2TeOCOCF_3)_2O]_2 \cdot H_2O\}$ and $[(R_2TeOCOCF_3)_2O]$ species. The products are non-conducting and monomeric in solution. The mode of bonding of the fluorocarboxylate group and a possible geometry around the central tellurium atom are suggested on the basis of physicochemical and spectral (IR, mass, ^1H, ^{13}C, ^{19}F and ^{125}Te NMR) studies.

Introduction

The use of alkyltellurium carboxylates as polymer-stabilising agents has been reported [1]. Radiolabelled tellurium compounds with fatty acids of biological interest have also been synthesised and evaluated for their potential use in nuclear medicine [2]. In view of the above and our interest in the studies of the chemistry of organotellurium compounds [3–5], we report herein the synthesis and spectroscopic properties of some organotellurium(IV) fluorocarboxylates.

Results and discussion

The formation of organotellurium(IV) bis(fluorocarboxylates) may be represented as:

$$R_2Te(OMe)_2 + 2R'COOH \longrightarrow R_2Te(OCOR')_2 + 2MeOH$$

They are also prepared by simple metathetical reactions between the appropriate diorganotellurium(IV) halides and silver salts of fluorocarboxylic acids in 1:2 molar ratios in anhydrous benzene:

$$R_2TeCl_2 + 2R'OCOAg \longrightarrow R_2Te(OCOR')_2 + 2AgCl$$

However, when a 1:1 molar ratio is used the reaction proceeds as follows:

$$R_2TeCl_2 + R'OCOAg \longrightarrow R_2Te(Cl)(OCOR') + AgCl$$

(R = Me, Ph, *p*-$MeOC_6H_4$ and *p*-$EtOC_6H_4$; R′ = CF_3, C_2F_5 and C_3F_7)

The newly synthesised compounds are white crystalline solids with sharp melting points. They are highly soluble in common organic solvents, being monomeric in benzene and exhibiting non-electrolytic behaviour in C_6H_6, $CHCl_3$ or CH_3OH. They are stable towards atmospheric oxygen and moisture. The identity of $R_2TeCl(OCOCF_3)$ (R = Ph, *p*-$MeOC_6H_4$ or *p*-$EtOC_6H_4$) was ascertained by thin layer chromatography which rules out the possibility of a mixture of R_2TeCl_2 and $R_2Te(OCOCF_3)_2$.

The interaction of R_2TeO with CF_3COOH in benzene or methanol proceeds as follows:

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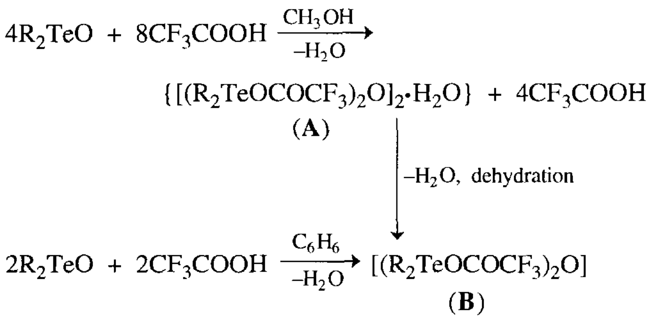

$$\begin{tikzcd}[column sep=small] 4R_2TeO + 8CF_3COOH \xrightarrow[-H_2O]{CH_3OH} & \{[(R_2TeOCOCF_3)_2O]_2\cdot H_2O\} + 4CF_3COOH \\ & (\mathbf{A}) \arrow[d, "-H_2O,\ dehydration"] \\ 2R_2TeO + 2CF_3COOH \xrightarrow[-H_2O]{C_6H_6} & [(R_2TeOCOCF_3)_2O] \\ & (\mathbf{B}) \end{tikzcd}$$

Compound **A** is converted to **B** by dehydration over P_2O_5 under vacuum at 50 °C. Alkaline hydrolysis of $R_2Te(OCOR')_2$ yields R_2TeO. The relevant analytical data are given in Table 1.

IR spectra

The IR spectra of the compounds studied in the present investigation show bands associated with $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ at 1690 ± 10 and 1400 ± 10 cm^{-1}, respectively, their separation values (290 ± 10 cm^{-1}) indicating the presence of unidentate fluorocarboxylate groups [6–8]. A weak to medium intensity band at 300 ± 10 cm^{-1} was assigned tentatively to ν(Te–O) [9].

In the spectra of $\{[(R_2TeOCOCF_3)_2O]_2\cdot H_2O\}$ and $[R_2Te(OCOCF_3)]_2O$, in addition to the $\nu(C{=}O)$ and $\nu(C-O)$ bands new peaks appearing at 605 ± 5(s) and $500 \pm$(s) may be attributed to ν_{asym} and ν_{sym} of the Te–O–Te bridge and assigned by comparison with other μ-oxo derivatives [10]. The appearance of absorptions at 3590 cm^{-1} for ν(OH) and at 1660 cm^{-1} for $\delta(H_2O)$ in $[(R_2TeOCOCF_3)_2O\cdot H_2O)$ indicate the presence of a coordinated water molecule [11]. The absorptions associated with ν(OCO) are broad and split in the solid state but sharp and strong in solution. The 1300–1000 cm^{-1} region is characteristic of the usual absorptions associated with fluorocarboxylate groups.

^1H NMR spectra

^1H NMR spectra of a number of the compounds were recorded in $CDCl_3$ and the results are summarised in Table 2.

TABLE 1. Characterization data for $R_2Te(OCOR')_2$ and $R_2Te(Cl)(OCOR')$

Compound	M.p. (°C)	Yield (%)	Elemental analysis [Found (calc.) (%)]		
			Te	C	H
$Me_2Te(OCOCF_3)_2$ (**1**)	126	86	33.17 (33.26)	18.55 (18.76)	1.41 (1.56)
$Ph_2Te(OCOCF_3)_2$ (**2**)	102	85	25.06 (25.23)	37.74 (37.82)	1.86 (1.97)
(p-$MeOC_6H_4)_2Te(OCOCF_3)_2$ (**3**)	116	80	22.40 (22.48)	37.82 (38.05)	2.55 (2.46)
$Ph_2Te(Cl)(OCOCF_3)$ (**4**)	161	76	29.56 (29.66)	38.97 (39.06)	2.14 (2.32)
(p-$MeOC_6H_4)_2Te(Cl)(OCOCF_3)$ (**5**)	174	70	25.86 (26.03)	39.03 (39.17)	2.63 (2.85)
$Ph_2Te(OCOC_2F_5)_2$ (**6**)	127	80	20.88 (21.00)	35.37 (35.54)	1.47 (1.64)
(p-$MeOC_6H_4)_2Te(OCOC_2F_5)_2$ (**7**)	147	82	19.04 (19.11)	35.67 (35.94)	2.01 (2.10)
$Ph_2Te(OCOC_3F_7)_2$ (**8**)	136	80	18.01 (18.03)	33.83 (33.91)	1.37 (1.41)
(p-$MeOC_6H_4)_2Te(OCO_3F_7)_2$ (**9**)	155	76	16.50 (16.62)	34.31 (34.39)	1.79 (1.82)
(p-$EtOC_6H_4)Te(OCOCF_3)_2$ (**10**)	133	75	21.30 (21.42)	40.22 (40.29)	2.86 (3.02)
(p-$EtOC_6H_4)_2Te(Cl)(OCOCF_3)$ (**11**)	117	80	24.44 (24.62)	41.56 (41.69)	3.39 (3.47)
$[\{(Ph_2Te(OCOCF_3)\}_2O]$ (**12**)	195	80	31.54 (31.69)	41.44 (41.72)	2.41 (2.48)
$[\{(p$-$MeOC_6H_4)_2Te(OCOCF_3)\}_2O]$ (**13**)	200	86	27.26 (27.58)	41.70 (41.50)	2.86 (3.02)

TABLE 2. ^{1}H, ^{19}F and ^{125}Te spectral data[a] for $R_2Te(OCOR')_2$ and $R_2Te(Cl)(OCOR')$

Compound no.[b]	^{1}H NMR (ppm) (in $CDCl_3$)		^{19}F NMR (ppm) (in $CDCl_3$)
	(R = Me, Ph or p-$MeOC_6H_4$)	OCH_3	
1	–	–	−74.10; −74.70
2	7.8–7.3 (m, 10H)		−74.21; −74.64
3	7.73 (d, 4H, *m*-protons); 7.70 (d, 4H, *o*-protons)	3.87 (s, 6H, OMe)	−74.19; −74.94(0.05 g ml^{-1}) −73.55; −74.13(0.15 g ml^{-1}) −73.61; −73.32(0.3 g ml^{-1}) −71.64; −71.93(0.6 g ml^{-1})
4	7.76–7.28 (m, 10H)		−74.17; −74.57
5	7.76 (d, 4H, *m*-protons) 7.14 (d, 4H, *o*-protons)	3.89 (s, 6H, OMe)	−74.24; −74.55
6	7.76–7.24 (m, 10H)		−81.74 (s, CF_3); −119.87 (s, CF_2)
7	7.7 (d, 4H, *m*-protons); 7.06 (d, 4H, *o*-protons)	3.87 (s, 6H, OMe)	−81.83 (s, CF_3); −119.95(s, CF_2)
8	7.79–7.28 (m, 10H)		−78; −87 (s, CF_3); −117.47 (s, CF_2); −125.80 (s, CF_2CO)
9	7.65 (d, 4H, *m*-protons); 7.01 (d, 4H, *o*-protons)	3.82 (s, 6H, OMe)	−79.98 (s, CF_3); −117.51 (s, CF_2); −125.91 (s, CF_2CO)
10	7.81 (d, 4H, *m*-protons); 7.2 (d, 4H, *o*-protons)	1.43 (t, 6H, Me); 4.10 (q, 4H, OCH_2)	−74.20; −74.76
11	7.87 (d, 4H, *m*-protons); 7.31 (d, 4H, *o*-protons)	1.46 (t, 6H, OMe); 4.08 (q, 4H, OCH_2)	−74.14; −74.67
12	7.81 (d, 8H, *m*-protons); 6.92 (d, 8H, *o*-protons)	3.69 (s, 12H, OMe)	–

[a] ^{125}Te NMR signals for various compounds: **2**, 1107.44; **3**, 1119.65; **6**, 1096.84; **8**, 1102.01; **10**, 1104.03 ppm.
[b] The numbers correspond to the compounds listed in Table 1.

^{13}C NMR spectra

^{13}C NMR spectra of two representative compounds were recorded in CCl_4 and are listed in Table 3.

^{19}F NMR spectra

^{19}F NMR spectra of the compounds were recorded in $CDCl_3$. The values are listed in Table 2. The unidentate and bidentate CF_3COO- groups usually resonate at δ 74 ppm and δ 70 ppm, respectively [12–14]. In the present investigation, the ^{19}F signals fall mainly in the unidentate region. In a representative compound $(p\text{-}MeOC_6H_4)_2Te(OCOCF_3)_2$ (**7**), the ^{19}F NMR signals in $CDCl_3$ (0.6 g ml^{-1}) corresponded to two sets at δ −71.93 and −71.64 ppm, respectively. On dilution, the two signals gradually shifted and appeared at δ −74.19 and −74.94 ppm. The change in chemical shift may be due to the change in bonding of fluorocarboxylate groups from bi- to uni-dentate character. There is also the possibility of strong secondary interaction between the non-bonded oxygen of the fluorocarboxylate groups and tellurium in the solid as well as in concentrated solution that becomes weak or negligible on dilution.

^{125}Te NMR spectra

^{125}Te NMR spectra for compounds **2**, **3**, **6**, **8** and **10** have been recorded in chloroform and exhibit a single signal only (see footnote a to Table 2).

TABLE 3. ^{13}C NMR data (δ, ppm) for representative compounds

Compound	Phenyl carbon	$OCOCF_3$ carbon
$Ph_2Te(OCOCF_3)_2$ (**2**)	137.63 (C_1); 144.40 (C_2); 129.61 (C_3); 131.31 (C_4)	161.64 (OCO); 121.13 (CF_3)
$(p\text{-}MeOC_6H_4)_2Te(OCOCF_3)_2$ (**7**)	122.7 (C_1); 134.89 (C_2); 116.04 (C_3); 162.90 (C_4); 55.41 (OCH_3)	160.52 (OCO); 120.64 (CF_3)

Mass spectra

The mass spectra for $Ph_2Te(OCOR')_2$ ($R' = C_2F_5$ and C_3F_7) and $(p\text{-}MeOC_6H_4)_2Te(OCOR')_2$ ($R' = CF_3$ and C_3F_7) were examined. The parent ions were not observed in all cases. Loss of one fluorocarboxylate group always occurred from the parent ion and the resulting ion generally showed loss of the second fluorocarboxylate group as part of its fragmentation pattern. Thus we have found that replacement of chloride by fluorocarboxylate group, e.g. in Ar_2TeCl_2 (AR = Ph or p-$MeOC_6H_4$), does not change the general pattern of fragmentation and the spectra are consistent with the reported spectra for Ar_2TeCl_2 [15] and other organotellurium(IV) species [16]. A typical mass spectrum for $Ph_2Te(OCOC_2F_5)_2$ (**6**) is given in Fig. 1.

The molecular weights of the bis(fluorocarboxylates) as saturated solutions in $CHCl_3$ or C_6H_6, determined by vapour phase osmometry, demonstrate the monomeric nature of the species. The change in ^{19}F chemical shifts with a change in the concentration suggest the possibility of a significant interaction between tellurium and the non-bonded oxygen of the $-OCOCF_3$ group, which may be strong in the solid state. When the fluorocarboxylate group is C_2F_5 or C_3F_7, a change in the ^{19}F shift on dilution was not observed, which may be attributed to the decreased inductive effect of that group. Similar results in the solid state and solution have been reported by other workers in this field [17]. Furthermore, a comparison of the ^{125}Te NMR chemical shifts for $R_2Te(OCOR')_2$ with those for other organotellurium(IV) molecules is of interest. The diaryltellurium dihalides and tellurium(IV) halides (having a trigonal bipyramidal arrangement around tellurium) generally have shifts ranging from 800 to 1200 ppm [18, 19]. Because of the similarity to the chemical shifts for other organotellurium(IV) species and in anticipation of other physicochemical studies, a similar geometry around the tellurium atom is proposed.

Thus, from the data, it is likely that $R_2Te(OCOR')_2$ and $R_2Te(Cl)(OCOR')$ contain four-coordinate tellurium atoms with a trigonal bipyramidal coordination. In four-coordinate tellurium(IV) complexes, the lone pair usually occupies an equatorial position in a trigonal bipyramidal arrangement. The other equatorial positions are presumably occupied by the two stronger Te^{IV} to ligand bonds [20, 21].

Experimental

All manipulations were carried out under dry nitrogen atmospheres. Solvents (BDH) (A.R. grade) were dried by standard procedures. Trifluoroacetic acid (Koch–Light), pentafluoropropionic acid and heptafluorobutyric acid (Fluka) were distilled over silver oxide before use. Me_2TeI_2 [22], Ph_2TeCl_2 [23], $(p\text{-}MeOC_6H_4)_2TeCl_2$ [24] and $(p\text{-}EtOC_6H_4)_2TeCl_2$ [25] were prepared and crystallised according to literature procedures. $R_2Te(OMe)_2$ compounds were prepared by treating NaOMe with R_2TeCl_2 in anhydrous benzene. NMR spectra were recorded on a JEOL Fx 90Q FT NMR spectrometer. ^1H NMR and ^{19}F NMR spectra of the compounds were recorded in $CDCl_3$ using Me_4Si and C_6F_6 as internal and external references, respectively. ^{13}C NMR spectra were measured at 22.49 MHz and referenced against internal Me_4Si. ^{125}Te NMR were recorded at 28.25 MHz with an external D_2O capillary lock and referenced against neat Me_2Te. The values reported exhibit positive upfield shifts. Mass spectra were recorded on a VG Mass Lab 12-250 spectrometer at 70 eV. Measurements were carried out on the ^{130}Te isotope which is that of highest mass number and relative abundance. Other physicochemical studies were made as described earlier [4, 5]. Some representative reactions are given below.

(a) Reaction of $R_2Te(OMe)_2$ and fluorocaboxylic acids

$Ph_2Te(OMe)_2$ (1.72 g, 5 mmol) in benzene (30 ml) was added to C_2F_5COOH (1.64 g, 10 mmol) in the same solvent (10 ml). The reaction mixture was refluxed.

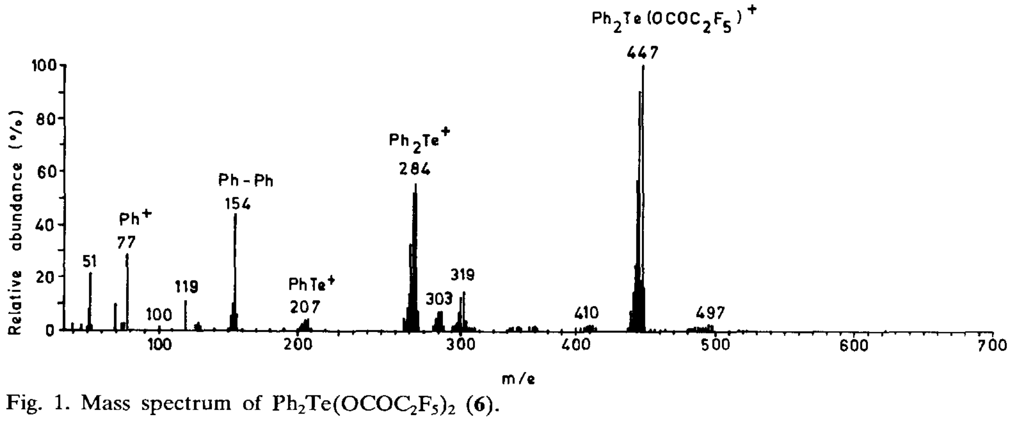

Fig. 1. Mass spectrum of $Ph_2Te(OCOC_2F_5)_2$ (**6**).

Excess solvent was distilled off and the product placed in a freezer to allow crystallisation. After removal of the crystalline product, the mother liquor yielded an additional crop on precipitation with solvent ether. Identical products were obtained by the reaction of R_2TeCl_2 and $AgOCOC_2F_5$ in refluxing anhydrous benzene.

(b) Preparation of $R_2TeCl(OCOCF_3)$

$AgOCOCF_3$ (2.21 g, 5 mmol) in anhydrous benzene (20 ml) was added to a solution of Ph_2TeCl_2 (1.76 g, 5 mmol) in the same solvent (20 ml). The reaction flask was wrapped in black paper to avoid exposing the contents to light and the latter were refluxed for a few hours. Filtration followed by evaporation of the solvent under reduced pressure gave a white mass which was recrystallised from CH_2Cl_2 and petroleum ether (40–60 °C) (1:5 mixture).

(c) Reaction of R_2TeO and CF_3COOH

Ph_2TeO (0.769 g, 2.5 mmol) was added to CF_3COOH (0.855 g, 15 mmol) in anhydrous methanol (20 ml). The mixture was filtered and allowed to crystallise slowly at room temperature yielding $\{[(Ph_2TeOCOCF_3)_2O]_2 \cdot H_2O\}$ which on dehydration over P_2O_5 under vacuum with slight heating (for 12–16 h) gave the anhydrous products, i.e. $[(R_2TeOCOCF_3)_2O]$. This was also formed when the above reaction was carried out in anhydrous benzene and the resultant water removed azeotropically.

(d) Hydrolysis reaction

$R_2Te(OCOR')_2$ (0.5 g) was refluxed with a hot solution of 10%–20% aqueous NaOH solution (10 ml) for 2 h. The precipitated mixture was identified as R_2TeO. Ph_2TeO; m.p. 180 °C (lit. value [24], 185 °C (decomp.). Analysis: Found (calc.) (%): Te, 41.62 (41.48). (p-$MeOC_6H_4)_2TeO$; m.p. 187 °C (lit. value [24], 188 °C). Analysis: Found (calc.)%: Te, 35.57 (35.68).

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References

1 S.S. Abed Ali and W.R. McWhinnie, *J. Organomet. Chem., 277* (1984) 365.
2 F.F. Knapp, Jr., K.R. Ambrose and A.P. Callahan, *J. Nucl. Med., 21* (1980) 251, 258.
3 T.N. Srivastava and J.D. Singh, *Indian J. Chem., 26A* (1987) 260, and references cited therein.
4 T.N. Srivastava, J.D. Singh and S.K. Srivastava, *Polyhedron, 9* (1990) 943.
5 T.N. Srivastava, J.D. Singh and S.K. Srivastava, *Phosphorus Sulfur, 55* (1990) 117.
6 C.D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem., 17* (1975) 1.
7 G.B. Deacon and R.J. Philips, *Coord. Chem. Rev., 33* (1980) 227.
8 C. Oldham, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Pergamon, London, 1987, Vol. 2, p. 435.
9 B.C. Pant, W.R. McWhinnie and N.S. Dance, *J. Organomet. Chem., 63* (1975) 305.
10 N.W. Alcock and W.D. Harrison, *J. Chem. Soc., Dalton Trans.,* (1982) 1421.
11 A.J. Blake and G.P. McQuillan, *J. Chem. Soc., Dalton Trans.,* (1984) 1849.
12 A. Dobson, D.S. Moore, S. Robinson, A.M.R. Galas and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* (1985) 611.
13 K. Teramato, Y. Sasaki, K. Migita, M.I. Waizumi and K. Saito, *Bull. Chem. Soc. Jpn., 52* (1979) 440.
14 C.M. Mitchell and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.,* (1972) 102.
15 M. Albeck and S. Shaik, *J. Organomet. Chem., 91* (1975) 307.
16 G.T. Sturgeon and M.L. Gross, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds,* Wiley, New York, 1986, Vol. 1, p. 243.
17 D. Dakternieks, R.D. Giacomo, R.W. Gable and B.F. Hoskins, *J. Am. Chem. Soc., 110* (1988) 6541, 6753, 6762.
18 C.H.W. Jones and R.D. Sharma, *J. Organomet. Chem., 332* (1987) 115.
19 D.H. O'Brien, K.J. Irgolic and C.K. Huang, in F. J. Berry and W.R. McWhinnie (eds.), *Proc. 4th Int. Conf. Org. Chem. Sellenium and Tellurium,* University of Aston, Birmingham, UK, 1983, p. 468.
20 S. Husebye, Ref. 19, p. 363.
21 I. Hargittai and B. Rozsondai, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds,* Wiley, New York, 1986, Vol. 1, p. 125.
22 R.H. Vernon, *J. Chem. Soc.,* (1920) 86.
23 R.C. Paul, K.K. Bhasin and R.K. Chadha, *J. Inorg. Nucl. Chem., 37* (1975) 2337.
24 G.T. Morgan and R.E. Kellet, *J. Chem. Soc.,* (1926) 1080.
25 G.T. Morgan and F.H. Burstall, *J. Chem. Soc.,* (1930) 2599.