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NEW ORGANYLTELLURIUM(IV) CARBOXYLATES, MALEATES, β-MERCAPTOPROPIONATES AND RELATED COMPOUNDS

SERA S. ABED-ALI and WILLIAM R. McWHINNIE

Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET (Great Britain)

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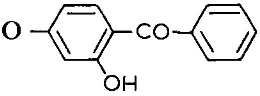
Summary

The synthesis of a range of tellurium(IV) carboxylates is reported: $R_2Te(OOC.CH{=}CHCOO)$ (R = Ph, cetyl), $R_2Te(OOC.CH{=}CH.COOBu^n)_2$ (R = Ph, $(CH_2)_4{}^-$,), $R_2Te(S.CH_2.CH_2COO)$ (R = Ph, p-$EtOC_6H_4$), $R_2Te(SCH_2COOCH_2$-CH_2O  $)_2$ (R = Ph, p-$EtOC_6H_4$), $(cetyl)_2Te(OOCCH_3)_2$.

The compounds are characterized by IR, ^1H NMR and mass spectra. The maleates and β-mercaptopropionates, are dimeric, but there was evidence of dissociation in some solvents; this was most marked for $(cetyl)_2Te(OOC.CH{=}CHCOO)$. The other compounds are similar to other well-known examples of diorganyltellurium bis(monocarboxylates). During an attempted preparation of n-hexyl and n-octyl derivatives, a material formulated as $[NEt_4][TeBr_3]$ was isolated, evidence is presented to suggest that the compound does indeed contain the tribromotellurate(II) anion.

Introduction

The organyltellurium carboxylates have recently become of interest in organyltellurium chemistry. Quite recently, McWhinnie et al. [1] have reported that phenylmethyltellurium(IV) phthalate is monomeric in chloroform solution and is thus similar to the diaryltellurium phthalate reported by Tamagaki et al. [2]. Diphenyltellurium phthalate has also been formulated as a dimeric [3,4]. It seems likely that there are monomeric and dimeric forms of some of these materials. It is convenient to regard the structure of an organyltellurium compound R_2TeX_2 (X is an electronegative group) as ψ-trigonal-bipyramidal, however, both crystallography [5] and ^{125}Te Mössbauer spectroscopy [6] indicate that the Te–C bonds have high tellurium

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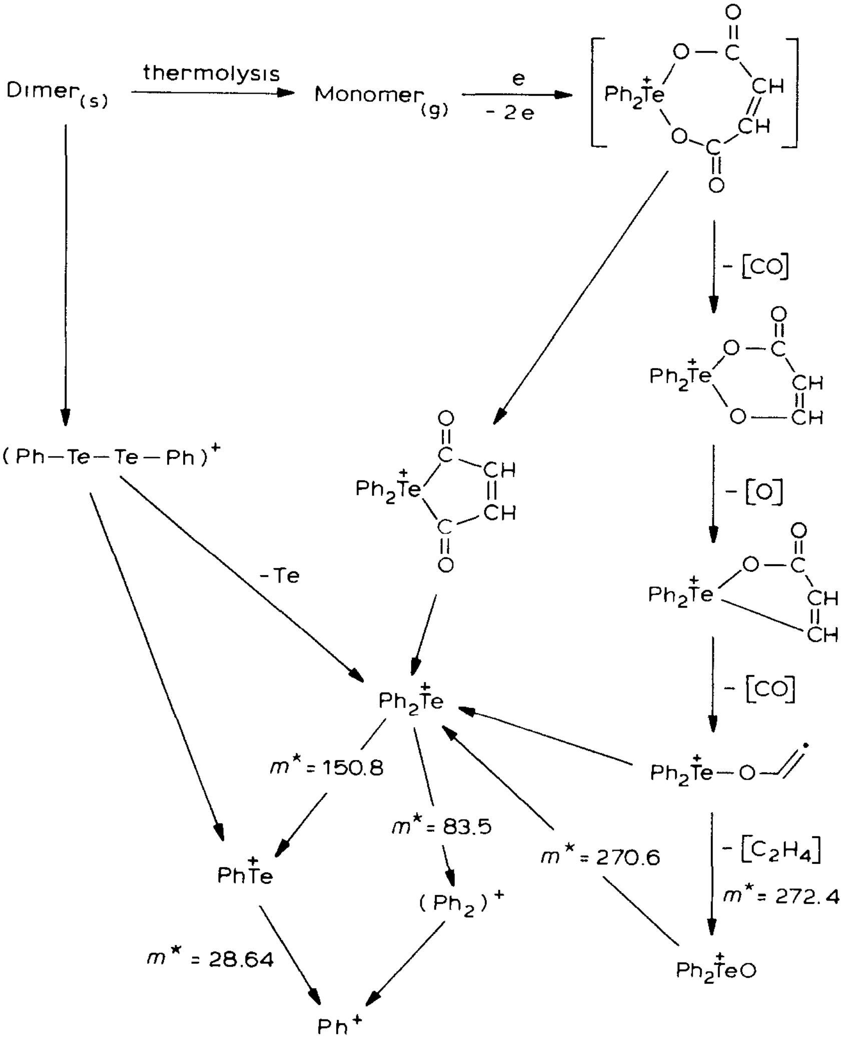
p-character, although the XTeX angle is generally close to 180°. Reduction of the XTeX angle, which would presumably be necessary on steric grounds in the case of monomeric $Ph(CH_3)Te(C_8H_4O_4)$, is likely to increase the *s*-character of the Te–C bond [7]. McWhinnie et al. [1] showed that the Te–C bonds in the R_2TeX_2 and $Ph(CH_3)Te(C_8H_4O_4)$ have similar *s*- and *p*-character. Evidence gained from Dreiding models supports McWhinnie's suggestion that the Te–O bond in a ψ-trigonal-bipyramidal monomer must be strained and off the Te–O axis. In this paper we report the synthesis of new organyltellurium compounds which we wished to study as stabilisers for polymers [8].



(Species in square brackets not observed)

SCHEME 1. Diphenyltellurium maleate

Experimental

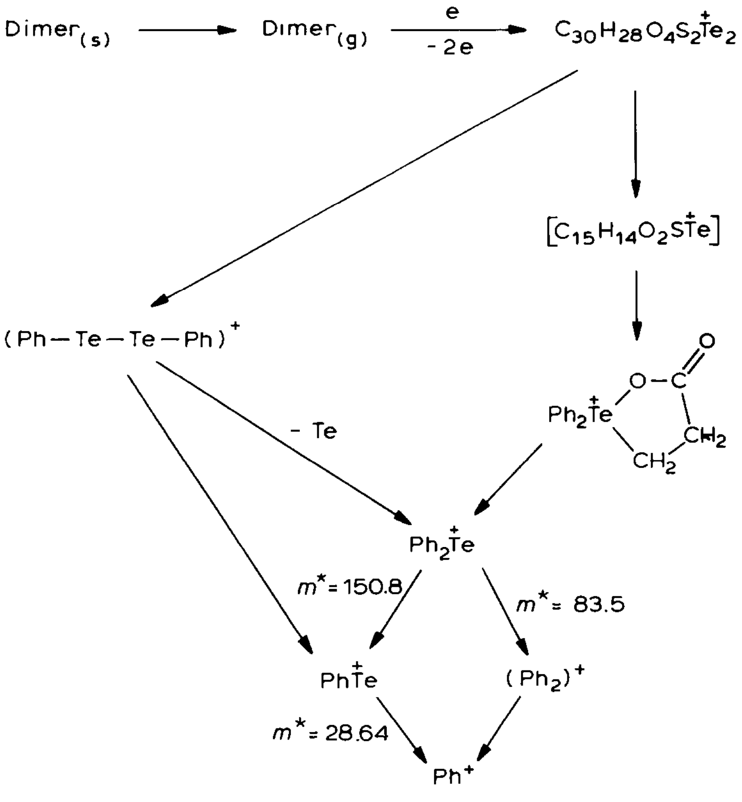
Syntheses

Diphenyltellurium maleate

Diphenyltelluroxide (0.01 mol) was allowed to react with an equimolar amount of maleic anhydride (0.01 mol) in dry chloroform from which ethanol had been removed. The reaction was carried out under dinitrogen with stirring for 1 h at room temperature, followed by evaporation of the solvent. The crude product was recrystallised from chloroform and hexane to give diphenyltellurium maleate as a white solid, m.p. 115–117°C. (Found: C, 48,0; H, 3.20. $C_{16}H_{12}O_4Te$ calcd.: C, 48.6; H, 3.03%).

Diaryltellurium β-mercaptopropionate (aryl = Ph or p-EtOC$_6$H$_4$)

Diaryltelluroxide (0.05 mol) was dissolved in anhydrous toluene (50 cm^3) in a 250 cm^3 round-bottomed flask and β-mercaptopropionic acid (0.05 mol) added. The mixture was stirred under reflux for 3 h to complete the reaction. Water was removed by continuous azeotropic distillation and collected in a Dean-Stark's trap.



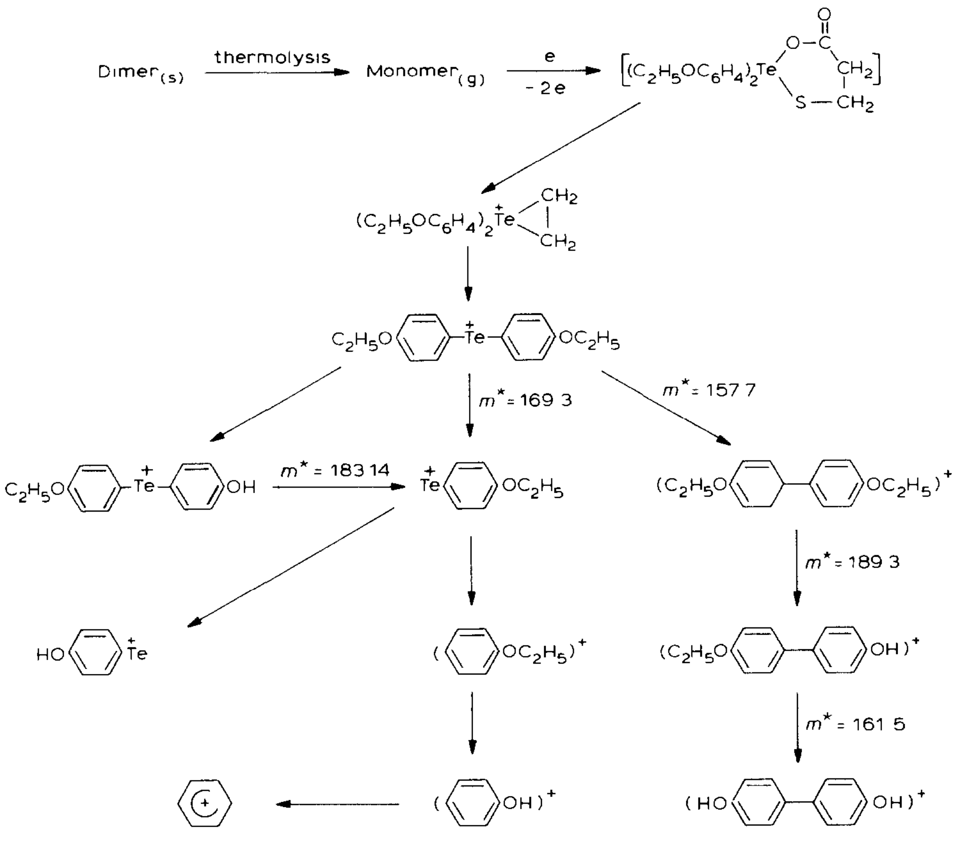
(Species in square brackets not observed)

SCHEME 2. Diphenyltellurium β-mercaptopropionate

Toluene was removed by evaporation. The diphenyltellurium β-mercaptopropionate was purified by preparative thin layer chromatography and column chromatography, using toluene. The product is a yellow viscous fluid. (Found: C, 46.5; H, 3.80; S, 8.40. $C_{15}H_{14}O_2STe$ calcd.: C, 46.7; H, 3.63; S, 8.31%). The di-*p*-ethoxyphenyltellurium β-mercaptopropionate was recrystallised from benzene and hexane to give a yellowish solid, m.p. 85–87°C (Found: C, 47.5; H, 4.70; S, 7.00. $C_{19}H_{22}O_4STe$ calcd.: C, 48.2; H, 4.65; S, 6.76%).

Diorganyltellurium bis(monobutylmaleate) (R = cyclopentane or Ph)

Silver 3-butoxycarbonyl-2-propenoate (0.02 mol), prepared by the reaction of silver nitrate with 2-butoxycarbonyl-2-propenoic acid [9] in an ammonia solution was added in small portion to a continuously stirred dry dioxane (50 cm^3) solution of the diorganyltellurium dihalide (0.01 mol) (telluracyclopentane-1,1-diiodide or diphenyltellurium dichloride), at room temperature. The reaction was carried out under dinitrogen. After 5 h of reflux with stirring, the reaction mixture was filtered and the solvent evaporated. The crude material was purified by preparative thin



(Species in square brackets not observed)

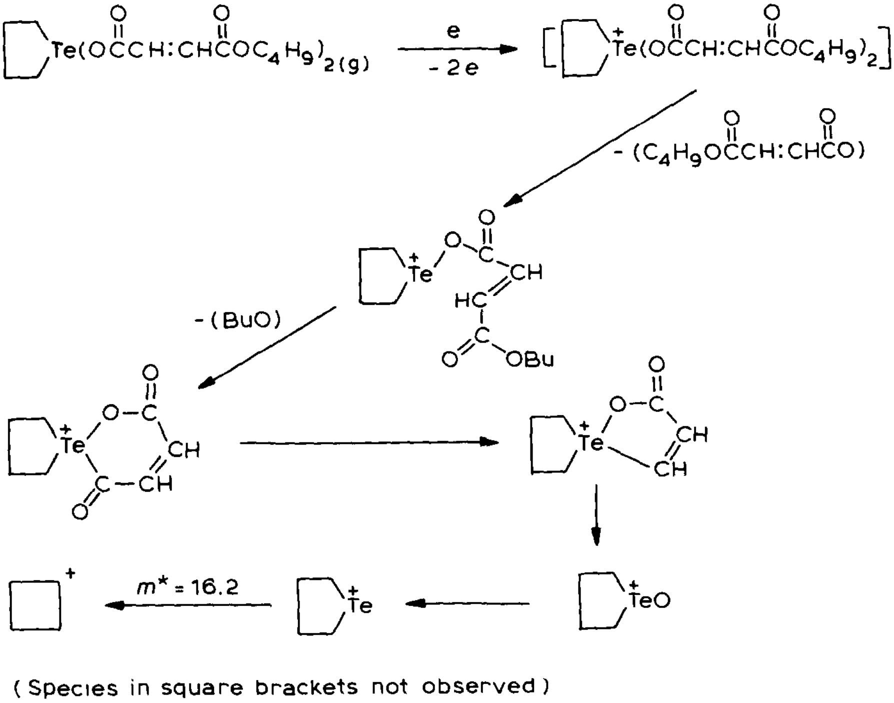
SCHEME 3. Di-*p*-ethoxyphenyltellurium β-mercaptopropionate layer chromatography and column chromatography, to give pure telluracyclopentane-1,1'-bis(monobutylmaleate) which is a yellow oil with a strong odour. (Found: C, 44.9; H, 6.10. $C_{20}H_{30}O_8Te$ calcd.: C, 45.7; H, 5.80%). Diphenyltellurium bis(monobutylmaleate) is a colourless oil (Found: C, 52.5; H, 5.10. $C_{28}H_{32}O_8Te$ calcd.: C, 53.9; H, 5.13%).

Diaryltellurium di(4-ethoxythioglycolate-2-hydroxybenzophenone) (aryl = Ph or p-EtOC$_6$H$_4$)

This compound was prepared in the same way as diaryltellurium β-mercaptopropionate from 4-ethoxythioglycolate-2-hydroxybenzophenone [10] (0.02 mol) and diaryltelluroxide (0.01 mol). The crude product was purified by preparative thin layer and column chromatography, using toluene. The product was collected as a viscous brown oil. Diphenyltellurium di(4-ethoxythioglycolate-2-hydroxybenzophenone) (Found: C, 59.3; H, 4.10; S, 6.80. $C_{46}H_{40}O_{10}S_2Te$ calcd.: C, 58.4; H, 4.24; S, 6.78%). Di-*p*-ethoxyphenyltellurium di(4-ethoxythioglycolate-2-hydroxybenzophenone) (Found: C, 57.9; H, 4.90; S, 5.70. $C_{50}H_{50}O_{12}S_2Te$ calcd.: C, 58.2; H, 4.65; S, 6.20%).

Dicetyltelluride [11]

This compound was prepared by a new method involving the reaction of a mixture of cetyl chloride (0.08 mol), tellurium powder (0.04 mol) and sodium or potassium iodide (0.16 mol) in *N,N*-dimethylformamide (30 cm^3). The mixture was stirred and heated gently under reflux for 2 h. After the reaction was completed the



(Species in square brackets not observed)

SCHEME 4. Telluracyclopentane bis(monobutylmaleate) solution was filtered. The filtrate was poured into distilled water (500 cm^3) and extracted with diethyl ether. The combined diethyl ether extracts were dried over calcium chloride. The diethyl ether was evaporated to give a red-brown oil. Aqueous sodium sulphide was added to the red-brown oil. The mixture was heated at 80°C for approximately 1 h until the red-brown colour disappeared. The solution was poured into distilled water (500 cm^3) and extracted with diethyl ether. The diethyl ether was washed several times with water. The combined diethyl ether extracts were dried over calcium chloride and concentrated to dryness on a rotary evaporator.

The crude product was treated with activated copper powder in dry dioxane under dinitrogen for 6 h. The hot solution was filtered and the filtrate was evaporated to dryness. The crude product was recrystallised from acetone after treatment with charcoal to give very pale pink dicetyltelluride, m.p. 42–43°C (lit. 43–44°C) (Found: C, 64.9; H, 11.5; Te, 21.0. $C_{32}H_{66}Te$ calcd.: C, 66.5; H, 11.4; Te, 22.0%).

Dicetyltellurium dichloride

To a solution of dicetyltelluride (0.01 mol) in diethyl ether (20 cm^3) thionyl chloride (0.03 mol) was added dropwise with stirring. The mixture was stirred for 4 h in an ice bath, after which the diethyl ether was evaporated. The crude product was recrystallised from acetone to give dicetyltellurium dichloride. Dicetyltellurium dichloride was treated with tetraethylammonium bromide (to remove any trichloride impurities as Et_4N^+ $[cetylTeCl_3Br]^-$) in chloroform. The mixture was shaken at room temperature for 2 h after which the solution was filtered and the chloroform was evaporated. The crude product was recrystallised from acetone to give dicetyltellurium dichloride, a white solid, m.p. 34°C (Found: C, 61.0; H, 11.2; Cl, 10.2; Te, 18.5. $C_{32}H_{66}Cl_2Te$ calcd.: C, 59.4; H, 10.2; Cl, 10.8; Te, 19.3%).

Dicetyltellurium diacetate

A solution of dicetyltelluride (0.01 mol) in dry benzene was added slowly to a stirred solution of freshly prepared lead tetraacetate (0.01 mol) in the same solvent (50 cm^3). The mixture was stirred at room temperature for 5 h under dinitrogen. Filtration followed by evaporation of benzene gave the crude material, which was recrystallised from diethyl ether to give dicetyltellurium diacetate, a white solid, m.p. 56–57°C (Found: C, 61.1; H, 10.6. $C_{36}H_{72}O_2Te$ calcd.: C, 62.2; H, 10.4%).

An alternative synthesis was from dicetyltellurium dichloride (0.01 mol) and silver acetate (0.02 mol).

Dicetyltellurium maleate

Freshly prepared silver maleate (0.01 mol) was added in small portions to a stirred solution of dicetyltellurium dichloride (0.01 mol) in dry chloroform at room temperature. The mixture was shaken for 24 h. Filtration followed by evaporation of chloroform from the filtrate and recrystallisation of the crude product from petroleum ether gave dicetyltellurium maleate, a white solid, m.p. 92–93°C (Found: C, 61.6; H, 10.1. $C_{36}H_{68}O_4Te$ calcd.: C, 62.2; H, 10.4%).

Tetraethylammonium tribromotellurate(II) and tetraethylammonium pentabromotellurate(IV)

A mixture of tellurium powder (0.02 mol), 1-bromooctane (0.04 mol) and tetraethylammonium bromide (0.08 mol) in 2-methoxyethanol (50 cm^3) was refluxed for

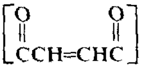
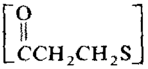
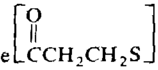
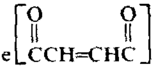
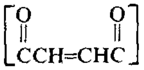
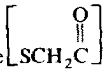
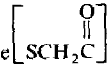
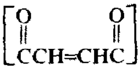
(Continued on p. 373)

TABLE 1

INFRA-RED DATA FOR NEW ORGANYLTELLURIUM COMPOUNDS

Compound		ν(cm^{-1})	Assignment	
Diphenyltellurium maleate	**(1)**	1665s	*as*[COO]	
		1625s		
		1315s	*s*[COO]	
		1235s		
		1720s	*as*	bridge carboxylate
		1175s	*s*	
Diphenyltellurium β-mercaptopropionate	**(2)**	1650s	*as*[COO]	
		1255s	*s*[COO]	
		1725s	*as*	bridge carboxylate
		1190s	*s*	
		265s	[Te–S]	
Di-*p*-ethoxyphenyltellurium β-mercaptopropionate	**(3)**	1645s	*as*[COO]	
		1240s	*s*[COO]	
		1720m	*as*	bridge carboxylate
		1170s	*s*	
		220w	[Te–S]	
Telluracylopentane bis(monobutylmaleate)	**(4)**	1670s	*as*[COO]	
		1620s		
		1210s	*s*[COO]	
		1170s		
		1730s	[C=O] ester	
		540w	[Te–C]	
Diphenyltellurium bis(monobutylmaleate)	**(5)**	1660s	*as*[COO]	
		1615s		
		1215s	*s*[COO]	
		1170s		
		1730s	[C=O] ester	
Diphenyltellurium di(4-ethoxythioglycolate-2-hydroxybenzophenone)	**(6)**	3350br	[OH]	
		1740s	[C=O] ester	
		265m	[Te–S]	
Di-*p*-ethoxyphenyltellurium di(4-ethoxythioglycolate-2-hydroxybenzophenone)	**(7)**	3350br	[OH]	
		1740s	[C=O] ester	
		225s	[Te–S]	
Dicetyltelluride	**(8)**	2960s	[C–H] stretching	
		1470s	[C–H] deformation	
		490 ($\frac{1}{4}$-multiplier with 5-expansion)	[Te–C]	
Dicetyltellurium dichloride	**(9)**	490 ($\frac{1}{4}$-multiplier with 5-expansion)	[Te–C]	
		255m	[Te–Cl]	
Dicetyltellurium diacetate	**(10)**	1640s	*as*[COO]	
		1290s	*s*[COO]	
Dicetyltellurium maleate	**(11)**	1645s	*as*[COO]	
		1610s		
		1315s	*s*[COO]	
		1250s		
		1670m	*as*	bridge carboxylate
		1150m	*s*	

TABLE 2. ^{1}H NMR DATA FOR NEW ORGANYLTELLURIUM COMPOUNDS

Compound	Solvent	Chemical shifts δ (ppm) vs. TMS		Assignment
1	$CDCl_3$	7.2–7.9	(m)	Aromatic
		5.96–6.2	(m)	Alkene  $\left[\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}\right]$
2	$CDCl_3$	2.7	(q)	Methylene  $\left[\overset{O}{\overset{\|}{C}}CH_2CH_2S\right]$
		7.2–7.9	(m)	Aromatic
3	$CDCl_3$	1.39	(t)	Methyl
		4.00	(q)	Methylene
		2.7	(q)	Methylene  $\left[\overset{O}{\overset{\|}{C}}CH_2CH_2S\right]$
		6.6–7.8	(m)	Aromatic
4	DMSO	0.9 (a)	(t)	Aliphatic $[\underset{d}{OCH_2}\underset{c}{CH_2}\underset{b}{CH_2}\underset{a}{CH_2}]$
		1.45 (b)	(m)	
		3.55 (c)	(m)	
		4.1(d)	(t)	
		2.4	(s)	C_8H_4Te
		3.15	(s)	
		6.01–6.12	(d)	Alkene  $\left[\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}\right]$
		6.31–6.42	(d)	
5	$CDCl_3$	0.9 (a)	(t)	Aliphatic $\underset{d}{OCH_2}\underset{c}{CH_2}\underset{b}{CH_2}\underset{a}{CH_3}$
		1.5 (b)	(m)	
		3.95 (d)	(t)	
		3.55 (c)	(m)	
		5.8–6.0	(d)	Alkene  $\left[\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}\right]$
		6.1–6.3	(d)	
		7.3–7.8	(m)	Aromatic
6	$CDCl_3$	6.2–7.7	(m)	Aromatic
		4.15	(s)	Methylene $[OCH_2CH_2O]$
		4.4	(s)	
		2.25	(s)	Methylene  $\left[SCH_2\overset{O}{\overset{\|}{C}}\right]$
7	$CDCl_3$	1.3	(t)	Methyl
		3.7–4.1	(q)	Methylene
		6.3–7.8	(m)	Aromatic
		4.2	(s)	Methylene $[OCH_2CH_2O]$
		4.4	(s)	
		2.3	(s)	Methylene  $\left[SCH_2\overset{O}{\overset{\|}{C}}\right]$
8	$CDCl_3$	0.9–1.6	(m)	Aliphatic
9	$CDCl_3$	0.9–1.6	(m)	Aliphatic
10	$CDCl_3$	0.9–1.6	(m)	Aliphatic
		2.1	(s)	Acetate
11	$CDCl_3$	0.9–1.6	(m)	Aliphatic
		6.25	(s)	Alkene  $\left[\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}\right]$

24 h. The solution changed from colourless to a red-brown colour. The hot solution was filtered and the precipitate collected. The solid was recrystallysed from 2-methoxyethanol to give a greenish solid which, on drying, melted with decomposition at 270°C (Found: C, 20.0; H, 4.20; N, 2.90. $C_8H_{20}Br_3NTe$ calcd.: C, 19.3; H, 4.04; N, 2.81%). The use of 1-bromohexane instead of 1-bromooctane afforded the same product.

A solution of bromine in chloroform was slowly added, dropwise to a solution of Et_4NTeBr_3 in chloroform and was stirred for 2 h resulting in a yellow-orange precipitate. The precipitate was dried which melted with decomposition at 320°C (Found: C, 14.8; H, 3.00; N, 2.30. $C_8H_{20}Br_5NTe$ calcd.: C, 14.6; H, 3.00; N, 2.13%).

Physical measurements

Analysis for C, H, N, Cl and S was by the Analytical Services Unit, University of Aston; tellurium was determined volumetrically [12]. Infra-red measurements were carried out using KBr discs, CsI discs and Nujol mulls between two polyethylene plates with a Perkin–Elmer 599 instrument. Mass spectra were determined at 70 and 15 eV with an AEI MS9 instrument. ^1H NMR spectra were determined with a Perkin–Elmer R14 instrument using $SiMe_4$ as an internal standard. Molecular weights were determined by freezing point depression in appropriate solvents.

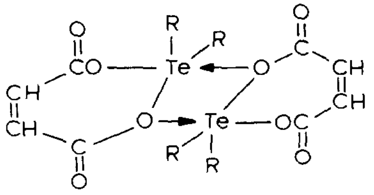
Results and discussion

The compounds considered in this paper gave satisfactory elemental analyses, IR data (Table 1) and ^1H NMR data (Table 2). In particular, correct ratios of aromatic to aliphatic protons were noted in the ^1H NMR spectra. The major features of the mass spectra are presented in Table 3. The molecular weights were determined by freezing point depression in solvents such as nitrobenzene and benzene and the results are tabulated in Table 4.

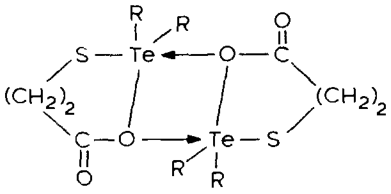
Infra-red data

Included in Table 1 are assignments of vibrations from the carboxylate groups of the ligands. A comparison of data for compounds **1**–**5** is useful. Thus, whereas there are many points of similarity, compounds **4** and **5** which are unlikely to contain bridging carboxylate groups, fail to show the medium to strong band at 1720–1725 cm^{-1} which is observed for **1**–**3**. It is, therefore, suggested that compounds **1**–**3** contain a structural feature which is absent for **4** and **5**. This may well correlate with the fact (Table 4) that **1**–**3** are dimers. Interestingly, compound **11** also shows extra bands (1670, 1150 cm^{-1}) although the former has shifted to lower wave number, perhaps suggesting a weaker bridging group and hence correlating with the fact that this compound exists in solution as an equilibrium of monomer and dimer (Table 4).

On the basis of the above evidence, a structure for the dimer which would allow ready dissociation to the monomer is sought. Also in the case of the β-mercaptopropionate compounds (**2**,**3**) bridging carboxylates rather than bridging sulphur would be indicated for a self consistent interpretation of the above data. The suggestion of Dance and McWhinnie [3] for the structure of diorganyltellurium orthophthalates now seem less attractive and we speculate that structures Ia and Ib may be more realistic:



(Ia)



(Ib)

TABLE 3A

MASS SPECTRAL DATA FOR DIPHENYLTELLURIUM MALEATE RELATIVE TO ^{130}Te, ^{16}O, ^{12}C, ^{1}H

Species	*m/e*	*R.I.* (%)
$C_{12}H_{10}\overset{+}{Te}_2$	414	7
$C_{15}H_{12}O_3\overset{+}{Te}$	370	50
$C_{16}H_{12}O_2\overset{+}{Te}$	366	35
$C_{15}H_{12}O_2\overset{+}{Te}$	354	20
$C_{14}H_{12}O\overset{+}{Te}$	326	15
$C_{12}H_{10}O\overset{+}{Te}$	298	25
$C_{12}H_{10}\overset{+}{Te}$	284	100
$C_{12}H_{10}^{+}$	154	100
$C_6H_5\overset{+}{Te}$	207	100
$C_6H_5^{+}$	77	100
$\overset{+}{Te}{=}C{=}O$	158	100
$C_4H_3O_4^{+}$	115	35
$C_2H_3^{+}$	27	50
CO_2^{+}	44	100

TABLE 3B

MASS SPECTRAL DATA FOR DIPHENYLTELLURIUM β-MERCAPTOPROPIONATE RELATIVE TO ^{130}Te, ^{32}S, ^{16}O, ^{12}C, ^{1}H (15 eV)

Species	*m/e*	*R.I.* (%)
$C_{30}H_{28}O_4S_2\overset{+}{Te}$	776	10
$C_{12}H_{10}\overset{+}{Te}_2$	414	40
$C_{15}H_{14}O_2\overset{+}{Te}$	356	25
$C_{12}H_{10}\overset{+}{Te}$	284	100
$C_6H_5\overset{+}{Te}$	207	100
$C_6H_5^{+}$	77	100
$C_3H_5O_2\overset{+}{S}$	105	50
$\overset{+}{Te}{=}C{=}O$	158	100
CO_2^{+}	44	100

TABLE 3C

MASS SPECTRAL DATA FOR DI-*p*-ETHOXYPHENYLTELLURIUM β-MERCAPTOPROPIONATE RELATIVE TO ^{130}Te, ^{32}S, ^{16}O, ^{12}C, ^{1}H

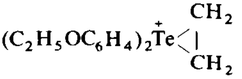
Species	*m/e*	*R.I.* (%)
 $(C_2H_5OC_6H_4)_2\overset{+}{Te}\begin{matrix}CH_2\\ \mid\\ CH_2\end{matrix}$	400	18
$(C_2H_5OC_6H_4)_2\overset{+}{Te}$	372	100
$C_2H_5OC_6H_4\overset{+}{Te}C_6H_4OH$	344	50
$C_2H_5OC_6H_4\overset{+}{Te}$	251	100
$(C_2H_5OC_6H_4\text{-}C_6H_4OC_2H_5\overset{+}{)}$	242	100
$(C_2H_5OC_6H_4\text{-}C_6H_4OH\overset{+}{)}$	214	100
$HOC_6H_4\overset{+}{Te}$	223	100
$(HOC_6H_4\text{-}C_6H_4OH\overset{+}{)}$	186	100
$(C_6H_5OH\overset{+}{)}$	93	100
$(C_6H_5OC_2H_5)^+$	121	100
(C_6H_5)	77	100
$C_3H_5O^+S$	105	100
$\overset{+}{Te}{=}C{=}O$	158	100

TABLE 3D

MASS SPECTRAL DATA FOR TELLURACYCLOPENTANE BIS(MONOBUTYLMALEATE) RELATIVE TO ^{130}Te, ^{16}O, ^{12}C, ^{1}H

Species	*m/e*	*R.I.* (%)
$C_{12}H_{18}O_4\overset{+}{Te}$	357	35
$C_8H_{10}O_3\overset{+}{Te}$	284	100
$C_7H_{10}O_2\overset{+}{Te}$	256	10
$C_4H_8O\overset{+}{Te}$	202	100
$C_4H_8\overset{+}{Te}$	186	100
$C_4H_7{}^+$	55	100
$\overset{+}{Te}{=}C{=}O$	158	100
$C_8H_{11}O_4{}^+$	171	100
$C_4H_9\overset{+}{O}$	73	100
$C\overset{+}{O}$	28	100

The square pyramidal structure is not unreasonable although "*cis*" and "*trans*" possibilities, in the sense identified by Harrison and Alcock [13] for $PhTeI_3$, must be allowed.

^1H NMR data

The spectrum of compound **1** (Table 2) show a singlet superimposed on a weak

TABLE 4

MOLECULAR WEIGHT OF NEW ORGANYLTELLURIUM COMPOUNDS

Compound No.	M (monomers)	M (dimer)	M (obs)	Exp Error
1	395	790	810 [a]	+20
2	385	770	800 [b]	+30
3	473	946	914 [b]	−32
8	580	–	560 [b]	−20
11	691	1382	950 [b]	
6	943	–	920 [a]	−23

[a] Nitrobenzene. [b] Benzene.

multiplet in the alkene proton region. This complexity might reflect some dissociation of the dimer in $CDCl_3$:

Dimer $\rightleftharpoons$ 2 Monomer

The singlet is assigned to the monomer, the multiplet to the dimer for which the alkene protons have become inequivalent.

The ^1H NMR data for compounds **2** and **3** shows a quartet in the CH_2 region which is attributed to overlap of triplets arising from the inequivalent methylene groups. The data for other compounds seem unremarkable and generally in accord with expectation. The singlet for the alkene protons of compound **11** is noted, this implies almost complete dissociation to monomer in $CDCl_3$. Compounds **4** and **5** show the expected *AB* spectrum for the alkene protons with J_{AB} 12 Hz.

Mass spectra

The mass spectrum of compound **1** contains, as the fragment of highest *m/e*, $Ph_2Te_2^+$. It has previously been pointed out that ditelluride ions appear characteristic mass spectral features of organyltellurium compounds which are dimeric or oligomeric [14]. Thus, this observation is in good accord with others which suggest diphenyltellurium maleate to be dimeric. Also, when recorded at 15 eV, the mass spectrum of diphenyltellurium β-mercaptopropionate gives clear support to the contention that the material may be dimeric, since in addition to $Ph_2Te_2^+$, an ion is observed at *m/e* 776 which corresponds to the parent ion of the dimer.

The fragmentation schemes contain additional features of interest, not least the suggestion that tetraorganyl fragments may exist within the mass spectrometer.

Conclusions

The balance of the evidence suggests that compounds **1**, **2** and **3** (Table 1) are dimeric in the solid state and in some solvents, although there is evidence that some dissociation can occur for **1** in media such as $CDCl_3$. Compound **11** is much more prone to dissociation in solution (MW and ^1H NMR) but is probably dimeric in the solid state. Compounds **4–7**, **9** and **10** are, on the basis of available data, straight forward diorganyltellurium(IV) species. A local ψ-trigonal-bipyramidal stereochemistry about tellurium is doubtless complicated by secondary bonding interactions in the crystals. Although dicetyl telluride may have been contaminated by ditelluride as initially prepared, the physical data on the purified specimin establishes its authenticity.

It thus seems clear that diorganyltellurium dicarboxylates can exist in monomeric and dimeric forms. Usually one form is favoured over the other but, sometimes, as with dicetyltellurium maleate, an equilibrium involving both forms is seen.

Trihalotellurate(II)

In experiments in which bromohexane and tetraethylammonium bromide were treated with tellurium, materials unstable with respect to elimination of tellurium were found which analysed as $[NEt_4][TeBr_3]$. The decomposition presumably involves disproportionation:

$$2\ TeBr_3^- \rightarrow Te + TeBr_6^{2-} \xrightarrow{H_2O} TeO_2$$

Evidence that the oxidation state of tellurium was indeed (II) was obtained from the reaction with bromine, when the familiar $[NEt_4][TeBr_5]$ was obtained. The mechanism of formation of $TeBr_3^-$ is not immediately obvious from the observations made.

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