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Synthesis, characterization and solution properties of some new organotellurium(IV) compounds derived from bis(2-phenylethyl)telluride

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Abstract

A new series of organotellurium(IV) compounds based on bis(2-phenylethyl)telluride ($(C_6H_5CH_2CH_2)_2Te(R)X$: R = X = I (**1**); R = X = Br (**2**); R = X = Cl (**3**); R = CN, X = Br (**4**); R = CH_3, X = I (**5**); R = CH_2CH_3, X = I (**6**); R = CH_2CH_3, X = Br (**7**); R = $CH_2CH{=}CH_2$, X = I (**8**); R = $CH_2CH{=}CH_2$, X = Br (**9**); R = $CH_2CH{=}CH_2$, X = Cl (**10**), R = $CH(CH_3)CH_3$, X = I (**11**)) have been prepared and characterized. ^1H NMR studies revealed that telluronium salts reductively eliminated the alkyl halide in $CHCl_3$ and in dimethyl sulfoxide (DMSO) solutions. Conductivity measurements in *N,N*-dimethylformamide (DMF) and DMSO indicate that all these solutes behave as weak electrolytes. The conductance data were analyzed by a minimization technique using the complete Fuoss–Hsia (F/H) equation. The effects of variation in the three parameters K_A, Λ_0 and $\underline{a}$ were fully investigated. IR and mass spectra of the new compounds are reported and discussed.

Introduction

Our recent works [1–4] on the synthesis, characterization and solution properties of cyclic telluronium salts, particularly the series $C_8H_8Te(R)X$, $C_4H_8OTe(R)X$ and 2-Me$C_4H_7Te(R)X$, suggested that these compounds are stable in $CHCl_3$, DMF and DMSO solutions towards reductive elimination and no reaction between solute and solvent was observed. These observations are inconsistent with telluronium salts derived from diphenyltelluride [5, 6] and phenoxatellurine [7]. Furthermore, our earlier works [1–4] demonstrated that in a solvent of low polarity, cyclic telluronium salts are associated to the dimer via a weak ionic interaction. Association also occurs in the gas phase as indicated by the mass spectra [1–4] and confirmed by crystallographic studies [8–12].

In the present work a new series of organotellurium(IV) compounds derived from bis(2-phenylethyl)telluride has been prepared in order to explore further some factors which affect the stability of telluronium salts in solution. Physical studies of the new compounds are reported and we particularly draw attention to the use of molar conductance as an investigative tool for the species formed in DMF and DMSO solutions, as it is well known [13] that the conductivity of the stable cyclic telluronium salts depends on the nature of the counter anion.

Experimental

Synthesis

Bis(2-phenylethyl)telluride

This compound was prepared by alkylation of Na_2Te with $C_6H_5CH_2CH_2Br$ as previously described by Gysling *et al.* [14].

Bis(2-phenylethyl)tellurium dibromide

A solution of bis(2-phenylethyl)telluride (3.38 g; 0.01 mol) in 50 ml of dry ether was treated dropwise with a solution of bromine (1.60 g; 0.01 mol) in 20 ml of ether. A pale yellow precipitate formed immediately; the solution was evaporated to dryness and the residue was recrystallized from ethanol, to give white microcrystals, melting point (m.p.) 80–81 °C.

Bis(2-phenylethyl)tellurium dichloride

Thionyl chloride (1.19 g; 0.01 mol) in ether (35 ml) was added slowly to a stirred solution of bis(2-phenylethyl)telluride (3.38 g; 0.01 mol) in the same solvent (45 ml) at room temperature. A pale yellow precipitate formed immediately. The solution was evaporated to dryness and the residue was recrys-

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tallized from ethanol to give white crystals, m.p. 76–77 °C.

Bis(2-phenylethyl)tellurium bromide cyanide

Cyanogen bromide (1.06 g; 0.01 mol) in ether (30 ml) was added to a stirred solution of $(C_6H_5CH_2CH_2)_2Te$ (3.38 g; 0.01 mol) in ether (25 ml) at room temperature. The white crystals which formed immediately in quantitative yield, were filtered off, washed with ether and recrystallized from ethanol to give white crystals, m.p. 173–174 °C.

Bis(2-phenylethyl)tellurium diiodide

This compound was prepared as previously described by Gysling *et al.* [14].

Bis(2-phenylethyl)methyltelluronium iodide

Excess of freshly distilled iodomethane (14.2 g; 0.1 mol) was added to a solution of bis(2-phenylethyl)telluride (3.38 g; 0.01 mol) in 50 ml of ether. An exothermic reaction took place giving pale yellow crystals; the excess of iodomethane was allowed to evaporate. Recrystallization from methanol gave bright white crystals which melted at 88–89 °C.

The new telluronium salts (along with their melting points and elemental analyses), which were prepared by the above general routes, are listed in Table 1.

Physical measurements

Infrared spectra were recorded as KBr pellets in the range of 4000–200 cm^{-1} using a Pye-Unicam SP3-300s infrared spectrophotometer. ^1H NMR data were obtained with Brucker WH-90DS spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectral data were determined at 70 eV with a Finnigan mass spectrometer MAT 1125, (Universität Konstanz, F.R.G.). Analyses for carbon and hydrogen were carried out by an Heraeus instrument. Tellurium analysis was carried out as described by Thavornyutikarn [15] by use of a Pye-Unicam Spy flameless atomic absorption spectrometer. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Conductivity measurements were made with a Wayne-Kerr autoblance precision bridge model B331.

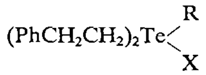


TABLE 1. Analytical[a] and physical data for the new organotellurium(IV) compounds, $(PhCH_2CH_2)_2Te\langle^{R}_{X}$

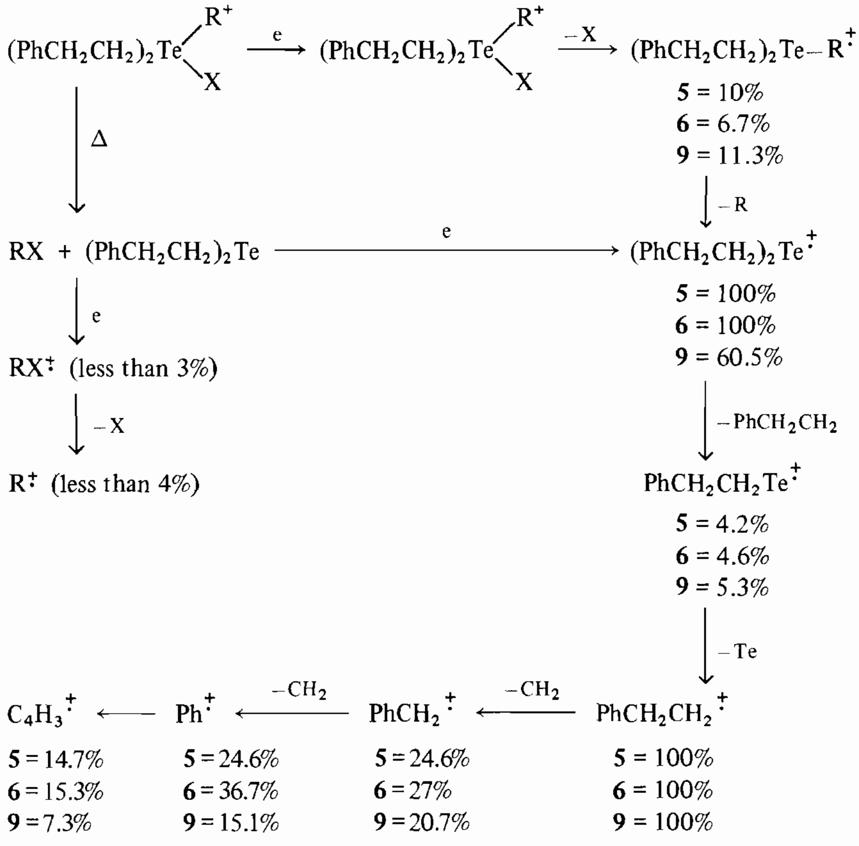
Compound	R	X	Melting point (°C)	C (%)	H (%)	Te (%)
1	I	I	103	32.35 (32.47)	3.20 (3.06)	
2	Br	Br	80–81	38.98 (38.91)	3.67 (3.64)	
3	Cl	Cl	76–77	47.22 (47.00)	4.42 (4.43)	
4	CN[b]	Br	173–174	45.21 (46.00)	4.22 (4.08)	28.17 (28.75)
5	CH_3	I	88–89	41.21 (42.55)	4.29 (4.41)	
6	C_2H_5	I	122	44.21 (43.77)	4.77 (4.69)	
7	C_2H_5	Br	111	47.60 (48.36)	4.93 (5.18)	28.13 (28.55)
8	C_3H_5	I	98	44.90 (45.11)	4.44 (4.58)	24.98 (25.22)
9	C_3H_5	Br	176	49.20 (49.73)	4.85 (5.05)	27.33 (27.80)
10	C_3H_5	Cl	164	54.73 (55.06)	5.59 (5.05)	30.33 (30.78)
11	C_3H_7	I	208–210	44.52 (44.93)	4.80 (4.96)	

[a]Calculated values are given in parentheses. [b]N: found 2.92; calc., 3.15%.

TABLE 2. Infrared data for the organotellurium(IV) compounds (cm^{-1})[a]

Compound	$\nu(Te\text{–}C_{CH_2})$	$\nu(Te\text{–}C_{alkyl})$	Other selected bands
1	470w		3060w, 3020w, 2920w, 1590m, 1490w, 1450w, 1390w, 1025m, 750s, 698s.
2	480w		3060w, 3020w, 2920w, 1595m, 1490m, 1450w, 1390w, 1023m, 750s, 693s.
3	480w	350s[b]	3060w, 3020w, 2925w, 1595m, 1490m, 1450w, 1390w, 1025m, 753s, 694s.
4	480w	2030m[c]	3060w, 3020w, 2925m, 1598w, 1490m, 1450w, 1328w, 1028m, 750s, 696s.
5	480w	521w	3060w, 3020w, 2925w, 1598m, 1490m, 1450m, 1390w, 1025m, 750s, 700s.
6	480w	521w	3060w, 3020w, 2920w, 1600m, 1490w, 1450w, 1390w, 1028w, 745s, 700s.
7	475w	520w	3060w, 3020w, 2920w, 1595m, 1490w, 1450w, 1390w, 1025w, 750s, 695s.
8	470w	520w	3060w, 3020w, 2920w, 1595w, 1490w, 1450w, 1390w, 1025m, 750s, 698s.
9	478w	520w	3060w, 3020w, 2920w, 1595w, 1490w, 1450w, 1385w, 1023w, 750s, 695s.
10	480w	520w	3060w, 3020w, 2925w, 1595w, 1484w, 1445m, 1390w, 1023w, 750s, 700s.
11	480w	520w	3060w, 3020w, 2920w, 1595m, 1490m, 1450w, 1390w, 1028w, 750s, 694s.

[a]Following the notation of Ellestad *et al.* [19]. [b]For ν(Te–Cl). [c]For ν(CN).



Scheme 1.

The bridge was calibrated against a standard low inductance resistance box; its sensitivity and reproducibility were found to be better than +0.01% over the range 10^3–10^6 ohms. The temperature of the oil-filled thermostat used in the conductivity measurements was maintained at 25.00±0.01 °C and was monitored by a Hewlett Packard quartz thermometer.

The conductance cell and method used for measuring conductance have been described previously [13, 16]. The cell constant was found to be 0.17667±0.0001.

All experiments were carried out under a dry, oxygen-free, nitrogen atmosphere. DMSO and DMF were purified and dried as described in the literature [17, 18].

All solvent mixtures and stock solutions (for conductivity measurements) were prepared by weight, and all measurements were made by the weight

TABLE 3. Some ^1H NMR data for bis(2-phenylethyl)telluride derivatives in $CDCl_3$

Compound	Chemical shifts (ppm); TMS = 0 ppm
$(PhCh_2CH_2)_2Te\begin{smallmatrix}I\\I\end{smallmatrix}$	H(1): 3.27(t); H(2); 3.73(t); H-Ar: 7.32(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}Br\\Br\end{smallmatrix}$	H(1): 3.44(t); H(2): 3.99(t); H-Ar: 7.32(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$	H(1): 3.45(t); H(2): 3.79(t); H-Ar: 7.32(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}CH3\\I\end{smallmatrix}$	CH_3: 2.24(s); H(1): 3.16(m); H(2): 3.55(m); H-Ar: 7.22(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}CH2CH3\\I\end{smallmatrix}$	CH_3: 1.39(t); CH_2: 2.34(q); H(1): 2.96(m); H(2): 3.15(m); H-Ar: 7.27(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}CH2CH3\\Br\end{smallmatrix}$	CH_3: 11.38(t); CH_2: 2.48(q); H(1): 2.95(m); H(2): 3.14(m); H-Ar: 7.25(s).
$(PhCH_2CH_2)_2Te\begin{smallmatrix}CH2CH{=}CH2\\I\end{smallmatrix}$	Te-CH_2: 2.45(d); H(1)+H(2): 3.69–3.99(m); =CH_2: 4.89(d); -CH: 6.11(p); H-Ar: 7.26(s).

dilution technique. The solvent properties were taken from the literature [17, 18].

Results and discussion

Bis(2-phenylethyl)telluride can be readily oxidized to the organotellurium(IV) derivatives in ether, with $SOCl_2$, Br_2, I_2 or alkyl halide as the oxidants. All compounds are white solids (except compound **1**) and mostly soluble in DMF and DMSO. Their physical properties and elemental analysis are listed in Table 1.

The IR spectra of compounds **1–11** displayed common features in certain regions and characteristic bands in the finger-print and other regions. They are described briefly in Table 2. The IR spectra show the $\nu(\mathrm{Te–C_{alkyl}})$ bands at 513–570 cm^{-1} while $\nu(\mathrm{Te–CH_2})$ occurs in the range 470–480 cm^{-1}.

The mass spectra of the three compounds **5**, **6** and **9** were analyzed and the probable fragmentation pattern is portrayed in Scheme 1. The absence of molecular ions, for compounds **5**, **6** and **9**, can be attributed either to pyrolytic decomposition, in direct inlet, under the high temperature which was used, or to electron impact. The fragments corresponding to high *m/e* values can be regarded as direct fragments of the molecular ions (Scheme 1).

The spectra are in general closely related to those of cyclic [1–4] and acyclic [5, 6] telluronium salts. Unfortunately there was no evidence from metastable ions to support all the steps in Scheme 1.

^1H NMR data in $CDCl_3$ are presented in Table 3. The methylene protons (Te–CH_2 and –CH_2Ph) give two separate triplets for compounds **1**, **2** and **3**. However, formation of the telluronium salts change the methylene spectrum to multiplet complex signals (Table 3).

The ^1H NMR spectrum of compounds **5**, in $CDCl_3$, shows two separate singlets at 2.24 and 3.04 ppm due to the methyl resonance of Te–CH_3 and CH_3I, respectively [5, 6]. The sum of the intensities of the singlets corresponded to the three protons when compared with the intensities of the ten protons in the aromatic region. As time passes (3 h), the methyl resonance of Te–CH_3 diminishes slowly while the resonance of CH_3I grows slowly reaching equilibrium after 180 min. This could be attributed to the reductive elimination [5, 6] of these compounds in $CHCl_3$ solution. The initial ^1H NMR spectrum of compound **5**, in DMSO, also shows two singlets at 2.41 and 2.11 ppm. The signal observed at 2.11 ppm could be attributed to the formation of $[(CD_3)_2SO....CH_3]^+I^-$ which indicates the reaction between the solute and the solvent as recently demonstrated for other telluronium salts [7].

The measured molar conductances (Λ_{exp}) and the corresponding concentrations (mol dm^{-3}) were analyzed by means of the complete Fuoss–Hsia equation

TABLE 4. The best fit parameters Λ_0, K_A and $\underline{a}$ together with the standard deviations (σ) for the new organotellurium(IV) compounds

Compound	R	X	DMF				DMSO			
			$\underline{a}$ (Å)	Λ_0 (ohm^{-1} cm^2 mol^{-1})	K_A (l mol^{-1})	σ	$\underline{a}$ (Å)	Λ_0 (ohm^{-1} cm^2 mol^{-1})	K_A (l mol^{-1})	σ
1	I	I	3	56.29	7550	2.05	3	69.56	256	0.834
2	Br	Br	3	45.00	8000	1.01	3	64.60	2210	1.11
3	Cl	Cl	3	24.05	9060	2.05	3	42.01	2800	1.24
4	CN	Br	3	72.85	4450	0.872	3	27.96	164	0.31
5	CH_3	I	3	73.00	18.8	0.311	3	31.13	35.8	0.121
6	C_2H_5	I	3	78.54	54.3	0.044	3	34.75	19	0.123
7	C_2H_5	Br	3	78.30	403	0.134	3	34.50	20	0.043
8	C_3H_5	I	3	106.80	2312	1.123	3	41.5	27.3	0.451
9	C_3H_5	Br	3	40.50	2350	1.210	3	29.50	218.8	0.351
10	C_3H_5	Cl	3	14.60	3510	0.091	3	14.10	1180	0.056

[20]. For the interpretation of the characteristic parameters of an electrolyte solution from conductance data, a minimization technique was used [21] in terms of K_A, Λ_0 and $\underline{a}$. The results are given in Table 4 together with the corresponding values of the standard deviation σ, given by:

$$\sigma = (S^2/N)^{1/2}$$

where S^2 is obtained by:

$$S^2 = \sum_{j=1}^{N} (\Lambda_{calc} - \Lambda_j)^2$$

The K_A values (Table 4) for compounds **1**, **2** and **3** indicate that these compounds are weak electrolytes and undergo more ion-pair formation than other compounds. The Λ_0 values increase as the halogen size increases (Table 4).

Plots of Λ against (concentration)$^{1/2}$ for compounds **5**–**10** show a maximum Λ at an approximate concentration range of 1.5×10^{-4} to 5×10^{-4} M), as can be seen in Figs. 1 and 2. Such behaviour has been noted in solvents of high dielectric constant [22]. This phenomenon could be attributed to the reaction between solute and solvent [7] or to the reductive

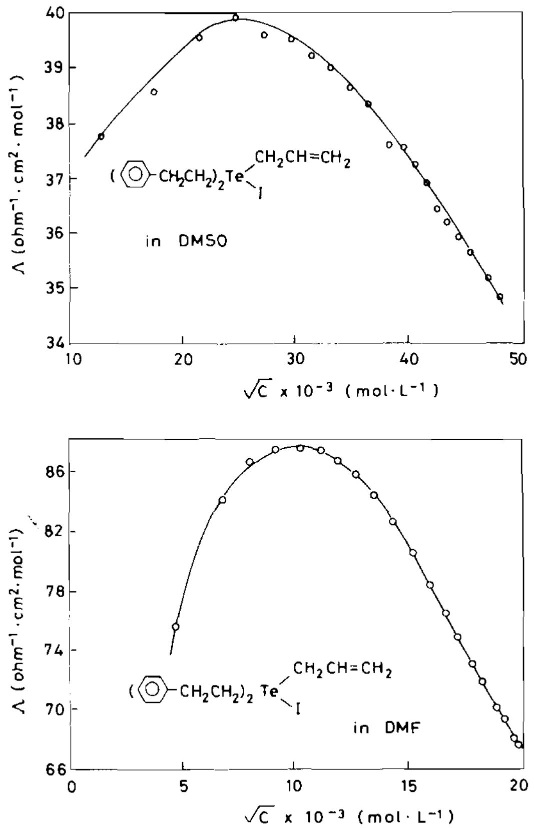


Fig. 1. Plots of experimental molar conductance against (concentration)$^{1/2}$ for compound **8** in DMSO and DMF at 25 °C.

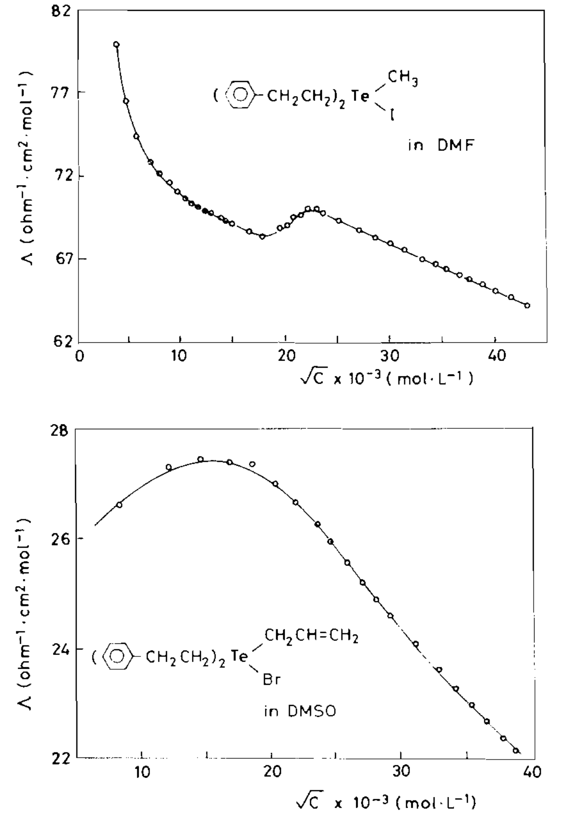


Fig. 2. Plots of experimental molar conductance against (concentration)$^{1/2}$ for compounds **5** and **9** in DMF and DMSO, respectively at 25 °C.

elimination [5, 6] (see NMR 'Discussion') which may lead to the formation of different ionic species in such a concentration range.

The conductivities of compounds **4**–**10** in DMF are greater than those in DMSO. Also, Λ_0 values are considerably lower than those expected for a 1:1 electrolyte indicating that these compounds are much more associated in DMF solution. By contrast, in DMSO, values of K_A are less than in DMF, indicating that these compounds are much more ionic in DMSO than in DMF. It appears that the size and the nature of the alkyl group seem to be effective for iodo derivatives (Table 4). Therefore, the order of increasing Λ_0 is as follows: **8**>**6**>**5**. Moreover, the conductivity of telluronium salts is inversely proportional to the size and electronegativity of the counter ions [6], as can be seen for compounds **8**, **9** and **10**.

The behaviour of compound **4** approaches that expected for a 1:1 electrolyte. Again, it has a maximium Λ in a more diluted concentration range.

In general, the parameter Λ_0 had the greatest effect on the values of S^2 during the variation of the three parameters K_A, Λ_0 and $\underline{a}$. This is to be expected in so far as Λ_0 is the leading term in the F/H equation [20]. However, Λ_0 was relatively insensitive to the values of K_A and $\underline{a}$ at the corresponding minima of S^2.

The $\underline{a}$ values obtained do not show any dependence upon the extent of iron–solvent interactions in solution; the ion–dipole forces are small.

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