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SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF 1-ORGANO-1-HALO-1-TELLURACYCLOPENTANE

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Summary

A new class of cyclic telluronium salts has been prepared. All the salts are stable in solution in $CHCl_3$ or dimethylsulphoxide (DMSO). Conductivity measurements in DMSO and dimethylformamide (DMF) have shown that considerable ion pairing occurs in solution. Infrared, ^1H, ^{13}C, ^{125}Te NMR, and mass spectra are reported and discussed.

Introduction

We described recently the synthesis, spectroscopic properties and the solution behaviour of a series of cyclic telluronium salts of 1-organo-3,4-benzo-1-telluracyclopentane [1]. The earlier work demonstrated that in solvents of low polarity these compounds are associated to dimers via a weak ionic interaction. Association also occurs in the gas phase as indicated by the mass spectra. The compounds were stable toward reductive elimination [1,2,3]. These association was confirmed by X-ray and other structural studies [4].

In the present work a series of new cyclic telluronium salts (I–VI) has been prepared. During the course of this work, McWhinnie reported the preparation of some structurally related compounds through the reaction of 1,4-dibromobutane with RTeNa (R = p-$EtOC_6H_4$ or Ph) [5].

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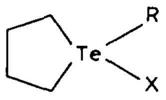


(I- VI)

(Ia : R = CH_3CH_2, X = I^- ;
Ib : R = CH_3CH_2, X = Br^- ;
IIa : R = $PhCH_2$, X = Br^- ;
IIb : R = $PhCH_2$, X = Cl^- ;
IIIa : R = $CH_2{=}CHCH_2$, X = I^- ;
IIIb : R = $CH_2{=}CHCH_2$, X = Br^- ;
IIIc : R = $CH_2{=}CHCH_2$, X = Cl^- ;
IVa : R = $PhCOCH_2$, X = Br^- ;
IVb : R = p-$BrPhCOCH_2$, X = Br^- ;
V : R = CH_3, X = I^- ;
VI : R = Ph , X = BPh_4^- ;
VII : R = I^-, X = I^-)

Results and discussion

The molar conductivities of the telluronium salts in 10^{-3} M of DMF and DMSO were determined; the values shown in Table 1 approach those expected for 1/1 electrolytes in both solvents. Plots of molar conductance (ΛM) against (concentration)$^{1/2}$ are typical of weak electrolytes. The molar conductance of compounds I–VI is in good agreement with previously reported data for telluronium salts [1–3,5–6]. It appears that there is an ion-pair interaction between the anion and the tellurium cation.

TABLE 1

IR AND CONDUCTIVITY DATA FOR A RANGE OF 1-ORGANO-1-TELLURACYCLOPENTANETELLURONIUM SALTS C_4H_8TeRX

Compound	Λ_M(DMSO) [a] (ohm^{-1} cm^2 mol^{-1})	Λ_M(DMF) [a] (ohm^{-1} cm^2 mol^{-1})	ν(Te–R) (cm^{-1})
Ia	36.8	75.9	530
Ib	37.2	76.8	535
IIa	32.0	46.3	530
IIb		45.2	530
IIIa	31.6	48.8	538
IIIb	33.5	62.6	536
IIIc	32.6	48.4	540
IVa	29.7	43.5	532
IVb	31.2	46.6	540
V	29.8	46.6	530
VI	25.7	45.7	

[a] 10^{-3} M solutions: Et_4NCl Λ_M(DMSO) 30; Λ_M(DMF) 80 ohm^{-1} cm^2 mol^{-1}.

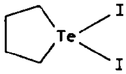
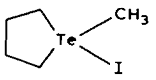
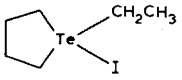
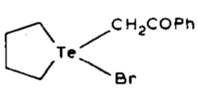
The infrared spectra (KBr disc) of compounds I–V show the ν(Te–C_{alkyl}) bands between 530–540 cm^{-1} as can be seen from Table 1. The spectra of IVa as solid and in chloroform solution showed a ν(C=O) band at 1658 cm^{-1}. The slight lowering of the ν(C=O) frequency compared with that in acetophenone (1668 cm^{-1}) may be due to the coordination of carbonyl oxygen to the tellurium atom, in which the phenacyl group acts as an unsymmetrical bidentate ligand. The infrared spectra of IVa in chloroform solution remained unchanged with time providing good evidence for the non-occurrence of reductive elimination.

The ^1H NMR spectra in $CDCl_3$ and DMSO (Table 2) show two sets of aliphatic resonances, one due to the alkyl group attached to tellurium and the other due to the methylene ring protons. The initial spectrum of V in $CDCl_3$ showed a singlet for methyl protons at δ 2.51 ppm with satellites corresponding to $^1H-^{125}Te$ coupling (J 25.2 Hz) and complex broad signals at 2.60–2.80 and 3.10–3.40 ppm from the methylene protons for H(3,4) and H(2,5), respectively. The position of the methyl signal was unchanged after 24 h, indicating the resistance of this compound to reductive elimination behaviour consistent with that of salts derived from 1,3-dihydro-2-telluraindene [1,7].

The spectrum of V in DMSO was similarly recorded. The slight upfield shift of methyl protons arises from the superior solvating power of DMSO compared with $CDCl_3$. The positions of the alkyl resonances did not vary with time for the telluronium salts I–V.

TABLE 2

^1H NMR DATA FOR TELLURACYCLOPENTANE DERIVATIVES

Compound	Solvent	Chemical shifts TMS 0 ppm	$J(^1H-^{125}Te)$ (Hz)
	$CDCl_3$	H(2,5): 3.02 (s); H(3,4): 2.02 (s).	
	$CDCl_3$	H(2,5): 3.2 (s); H(3,4): 2.23 (s).	
	$CDCl_3$	CH_3: 2.51(s); H(2,5): 3.1–3.4 [a]; H(3,4): 2.6–2.8 [a].	25.2
	DMSO-d_6	CH_3: 2.1(s); H(2,5): 2.8–3.1 [a]; H(3,4): 2.2–2.5 [a].	25.0
	DMSO-d_6	CH_3: 1.5(t); CH_2: 2.3(q); H(2,5): 2.9–3.2 [a]; H(3,4): 2.5–2.7 [a].	21.2
	DMSO-d_6	CH_2: 4.3(s); H(2,5): 2.8–3.4 [a]; H(3,4): 2.0–2.5 [a]; Ar–H: 7.3–8.2 (m).	22.0

[a] H(2,5) and H(3,4) gave a complex overlapping signal in all cases.

The ^{13}C NMR data were obtained in $CDCl_3$ and/or in DMSO (Table 3). The $^{13}C-^{125}Te$ coupling was detectable in the ^{13}C spectra. Chadha and Miller [8] argue that the chemical shifts of carbon atoms bound to tellurium should be sensitive to the polarity of the Te–C bond, and so the $\delta(C(2))$ and δ(C-alkyl) values in $CDCl_3$ and DMSO indicate the tellurium atom is more positive in $CDCl_3$ than in DMSO solution.

The ^{125}Te NMR data (Table 3) give useful information. The existence of a $^1J(^{13}C-^{125}Te)$ coupling constant indicates that the alkyl chain is covalently bonded to the tellurium atom. The ^{125}Te chemical shifts are insensitive to the nature of the anion. No correlation between the anion electronegativities and the chemical shifts is observed. The ^{125}Te chemical shifts for each group in compounds Ia, Ib or IIa, IIb or IIIa, IIIb, IIIc in $CDCl_3$ are identical. As is well known the change of halogen covalently bonded to the tellurium atom leads to a large variation of the chemical shifts [1,9], and so we interpret this result as a proof of the ionic nature of the halogen–tellurium bond.

For derivatives IIb, IIIa, IIIb and IVa, there is a large tellurium chemical shift difference, of about 30–40 ppm, between DMSO and $CDCl_3$ solutions. Similarly, there is a chemical shift difference of several ppm for the ^{13}C signals in $CDCl_3$ and in DMSO for compounds IIIa and IIIb. Such large effects confirm that the solvent has a major influence. There is no chemical reaction between the solute and the solvent such as was recently demonstrated for other telluronium salts [10]; in our case the ^1J(C–Te) coupling constant is always observed between tellurium and the acyclic component, and if a reaction did occur, there would be observed a tellurium resonance at lower frequency, since the species formed would be a telluracyclopentane [9].

We can consider two possible explanations of this solvent effect. First a solvent molecule may be bonded to the compound, and in that case DMSO would interact

TABLE 3

^{125}Te AND ^{13}C NMR DATA FOR TELLURACYCLOPENTANE DERIVATIVES

Compounds	Solvent	$\delta(^{125}Te)$ [a] (ppm)	$\delta(^{13}C)$ [b]			$^1J(^{13}C-^{125}Te)$ (Hz)	
			C(2)	C(3)	Other [c]	C-cyclic	C-alkyl
Ia	DMSO-d_6	699.6	30.2	31.5	18.2, 10.8	141	145.5
Ib	DMSO-d_6	692.5	30.4	31.5	18.8, 10.8	138	142.5
IIa	$CDCl_3$	696.1	31.1	32.6	32.9, 133.9, 129.9, 128.8, 127.8	150.5	156
IIb	DMSO-d_6	725.6	31.8	30.8	29.7, 135.1, 129.8, 128.8, 127.1	147	153
	$CDCl_3$	696.5					
IIIa	DMSO-d_6	704.5	30.5	31.3	27.1, 130.6, 120.5	144	150
	$CDCl_3$	661.3	32.0	33.0	32.0, 130.3, 121.3	144	150
IIIb	DMSO-d_6	700.0	30.9	31.2	30.5, 130.8, 120.2	148	148
	$CDCl_3$	663.3	32.0	32.9	31.2, 130.4, 121.1	144	150
IIIc	$CDCl_3$	663.2	33.0	32.0	30.2, 130.4, 120.8	144	150
IVa	DMSO-d_6	692.2	31.5	31.5	47.4, 135.5, 128.8, 128.8, 134.0	130	150
	$CDCl_3$	658.2			195.8 (CO)		
V	DMSO-d_6	634.4	31.2	31.2	5.1	136.5	136.4
VI	DMSO-d_6	772.7	35.1	31.5	?, 133.3, 129.7, 130,7, [163.1, 135.6, 125.4, 121.4 (bounded to B)]		
VII	DMSO-d_6	929.2	42.9	32.8		138.0	

[a] Referred to neat $(CH_3)_2$ Te. [b] Referred to internal TMS in ppm. [c] Chemical shifts are given in increasing order C(1′), C(2′) etc.

more strongly through its oxygen than chloroform through its chlorines, and this could account for the greater deshielding arising with DMSO than with chloroform. Second, some dimerisation might occur (see the discussion of the mass spectra below), to give an equilibrium between the monomer and the dimer, which would vary in position with the concentration or the nature of the solvent, we cannot decide between the two possibilities and we are making a detached study of the effect of change of concentration, solvent, and temperature.

The mass spectra of compounds Ia, IIa, IIIb, IVa and V were recorded at 70 eV. The spectra are in general closely related to those of cyclic telluronium salts [1,5]. The fragmentation of these materials is similar to that described in ref. 1. Unfortunately there was no evidence from metastable ions to support all the steps in the scheme. The mass spectra of IIa, IIIb and IVa gave ions at higher mass charge ratio than that corresponding to the monomer telluronium salts, indicating that IIa, IIIb and IVa are associated in the gas phase, and that the ordinary species must be at least a dimer. This conclusion is supported by the literature [1,5]. The fragments lost from the supposed dimer are consistent with ethyltellurium iodide, allyltellurium bromide, and phenacyltellurium bromide.

Experimental

(a) Synthesis

1,1-Diiodo-1-telluracyclopentane. A variation of the method reported by Ziolo et al. was used [11]. A stirred mixture of 1-bromo-4-chlorobutane (6.78 g, 0.04 mol), tellurium powder (5.1 g, 0.04 g-atom) and sodium iodide (23.9 g, 0.16 mol) in 2-butoxyethanol (100 ml) was heated gently in an open beaker for 1 hour then cooled, and water was added. The precipitate was filtered off, washed with water, rinsed with acetone, and air dried. Recrystallization from DMF gave orange-red crystals, m.p. 153°C (Lit. 149–150°C [12], 152°C [7]). Found: C, 22.5; H, 3.70. $C_4H_8I_2$ calcd.: C, 22.2; H, 3.70%.

Telluracyclopentane. Sodium borohydride was added to a boiling methanolic solution of 1,1-diiodo-1-telluracyclopentane until the orange colour disappeared. The solution was filtered, then added to one litre of water. Extraction with ether followed by drying ($CaCl_2$) and evaporation of the extract left telluracyclopentane, as a heavy yellow oil with a persistent odour. This was purified by distillation b.p. 165–167°C (760 torr) (Lit. 166–167°C (760 torr) [12a], 105–106°C (122 torr) [12b]).

1-Ethyl-1-iodo-1-telluracyclopentane (Ia). An excess of freshly distilled iodoethane was placed with telluracyclopentane (1.84 g, 0.01 mol) in a flask flushed with dry nitrogen. A white precipitate formed after 3 h. Recrystallization from ethanol/water (3/1) gave white crystals of m.p. 210°C (vap.). Found: C, 21.7; H, 3.70; I, 36.8; Te, 36.8. $C_6H_{13}ITe$calcd.: C, 21.2; H, 3.83; I, 37.4; Te, 37.6%. [Tellurium was analysed by the method of Suttle (14)].

Compounds Ib, IIa, IIIa, IIIb, IVa, IVb and V were prepared by similar procedures.

1-Ethyl-bromo-1-telluracyclopentane (Ib): white crystals vaporised at 233–235°C. Found: C, 25.0; H, 4.30; Br, 26.4; Te, 42.4. $C_6H_{13}BrTe$ calcd.: C, 24.6; H, 4.44; Br, 27.3; Te, 43.1%.

1-Benzyl-1-bromo-1-telluracyclopentane (IIb): white crystals, m.p. 170°C (dec.). Found: C, 37.1; H, 4.20; Br, 22.2; Te, 35.6. $C_{11}H_{15}BrTe$ calcd.: C, 37.3; H, 4.23; Br, 22.5; Te, 36.0%.

1-Allyl-1-iodo-1-telluracyclopentane (IIIa): the white crystals vaporised at 170°C. Found: C, 23.7; H, 3.70; I, 34.7; Te, 35.2. $C_7H_{13}ITe$ calcd.: C, 23.9; H, 3.70; I, 36.1; Te, 36.3%.

1-Allyl-1-bromo-1-telluracyclopentane (IIIb); the white crystals vaporised at 200–202°C. Found: C, 27.3; H, 4.40; Br, 25.4; Te, 40.2. $C_7H_{13}BrTe$ calcd.: C, 27.6; H, 4.27; Br, 26.2; Te, 41.9%.

1-Phenacyl-1-bromo-1-telluracyclopentane (IVa): the white solid decomposed at 145°C. Found: C, 42.7; H, 4.30; Te, 36.2. $C_{12}H_{15}BrOTe$ calcd.: C, 42.6; H, 4.44; Te, 37.7%.

1-(*p*-Bromophenacyl)-1-bromo-1-telluracyclopentane (IVb): the white solid decomposed at 133°C. Found: C, 31.5; H, 3.10; Te, 27.0. $C_{12}H_{14}Br_2OTe$ calcd.: C, 31.2; H, 3.03; Te, 27.7%.

Compounds IIb and IIIc were prepared by the following method:

An aqueous solution of silver chloride was added to an ethanolic solution of the appropriate 1-organo-1-iodo(or bromo)-1-telluracyclopentane. The mixture was heated under reflux for 3 h, then filtered hot and concentrated. The product was recrystallized from a mixture of ethanol and water to give white crystals.

1-Benzyl-1-bromo-1-telluracyclopentane (IIb): this compound melted with decomposition at 165–167°C. Found: C, 42.4; H, 4.60; Cl, 10.8; Te, 40.3. $C_{11}H_{15}ClTe$ calcd.: C, 42.6; H, 4.84; Cl, 11.4; Te, 41.1%.

1-Allyl-1-chloro-1-telluracyclopentane (IIIc): this compound vaporised at 186°C. Found: C, 32.6; H, 4.30; Cl, 12.3; Te, 47.8. C_7H_9ClTe calcd.: C, 32.6; H, 4.99; Cl, 13.6; Te, 49.0%.

Compound V was prepared according to the method reported by Morgan [12a]; m.p. 245°C (vap.) (Lit. vaporise > 240°C [12a]). Found: C, 18.5; H, 3.30; Te, 38.6. $C_5H_{11}Te$ calcd.: C, 18.5; H, 3.38; Te, 39.2%.

1-Phenyl-1-telluracyclopentane tetraphenylborate (VI). This compound was prepared by Al-Rubaie [7] by a variation of the method reported by Ziolo et al. [13]. A mixture of 1,1-diiodo-1-telluracyclopentane (4.37 g, 0.01 mol) with $NaBPh_4$ (6.84 g, 0.02 mol) in dry ethanol (100 ml) was stirred for 2 h under reflux. The solution was filtered hot and the white VI collected was washed with water and ethanol then recrystallized from water/DMF; m.p. 218°C (dec.) (Lit. m.p. 214°C [7]). Found: C, 70.2; H, 5.40; Te, 20.8. $C_{34}H_{33}TeBr$ calcd.: C, 70.4; H, 5.69; Te, 22.0%.

(b) Physical measurements

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 457 spectrometer. Conductivity measurements were carried out with a standard conductivity bridge.

^1H NMR spectra were recorded on Varian instrument using DMSO-d_6 or $CDCl_3$ as solvents relative to TMS as an internal standard. The ^{13}C and ^{125}Te NMR data were obtained as previously described [1,15].

Mass spectra were determined with an AEI MS9 spectrometer.

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