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Synthesis and Study on Telluronium Salts Based on 1-Oxa-4-organo-4-telluracyclohexane Cation

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Abstract

A new series of heterocyclic telluronium salts (C_4H_8OTeRX: $R = CH_3CH_2$, $CH_2{=}CHCH_2$, CH_3, C_4H_9, $X = I$; $R = CH_2{=}CHCH_2$, $X = Br$; $R = CH_3$, $X = ClO_4$; $R = CH_3$, CH_3CH_2, C_6H_5, $X = BPh_4$) have been prepared. Conductivity measurements in dimethylsulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) have shown that there is an ion pair interaction between the anion and the tellurium cation.

^{1}H NMR studies showed that there is no reaction between the solute and the solvent. All compounds are stable in solution in DMSO. Infra-red spectra are reported and discussed.

Introduction

Recently we have been directing our interests toward the synthesis, characterization and solution properties of some cyclic telluronium salts derived from telluracyclopentane [1–4]. In particular we observed that the compounds C_8H_8TeRX and C_4H_8TeRX are stable in $CHCl_3$, DMF and DMSO solution toward reductive elimination. These observations are inconsistent with telluronium salts derived from diaryltelluride [5, 6] or phenoxatellurine [7].

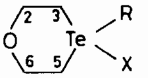
The present work reports the synthesis, solution properties and some spectroscopic data for a new series of cyclic telluronium salts (**I**–**VI**) of 1-oxa-4-organo-4-halo-4-telluracyclohexane. This series has been chosen since it might undergo a solute–solvent reaction analogous with 10-methylphenoxatelluronium iodide [7]. Furthermore, attempts were made to obtain more information about the structure of these species in solution.

Experimental

(a) Synthesis

1-Oxa-4-telluracyclohexane-4,4-diiodide

The following new method was used to prepare this compound. A stirred mixture of bis(β-chloroethyl)ether (5.72 g; 0.04 mol), tellurium powder (5.1 g; 0.04 mol) and sodium iodide (23.9 g; 0.16 mol) in 2-butoxyethanol (~120 ml) was heated gently for 3 h, cooled and then deionized water was added. The precipitate was filtered off, washed with water, rinsed with acetone and air dried. Recrystallization from ethanol gave orange–red crystals. Melting point (m.p.) 152 °C (literature value [8] 155 °C). *Anal.* Found: C, 10.7; H, 1.70; Te, 27.3. Calc. for $C_4H_8OTeI_2$: C, 10.6; H, 1.77; Te, 28.1%.



I–**VI**

Ia: $R = CH_3CH_2$, $X = I$
Ib: $R = CH_3CH_2$, $X = BPh_4$
IIa: $R = CH_2{=}CHCH_2$, $X = I$
IIb: $R = CH{=}CHCH_2$, $X = Br$
IIIa: $R = CH_3$, $X = ClO_4$
IIIb: $R = CH_3$, $X = I$
IIIc: $R = CH_3$, $X = BPh_4$
IV: $R = CH_3CH_2CH_2CH_2$, $X = I$
V: $R = C_6H_5$, $X = BPh_4$
VI: $R = I$, $X = I$

1-Oxa-4-telluracyclohexane

The above compound (3.2 g) was dissolved in hot methanol (50 ml) and heated under reflux. A solution of hydrazine hydrate (0.05 g) in methanol (30 ml) was added slowly to the refluxing solution. The solution was filtered, then added to one liter of water. Extraction with ether left 1-oxa-4-telluracyclohexane as a yellow oil with a persistent odor. This was purified by distillation. Boiling point (b.p.) 92 °C/21 mm Hg (literature value [8] 91 °C/21 mm Hg.

*1-Oxa-4-ethyl-4-iodo-4-telluracyclohexane (**Ia**)*

An excess of freshly distilled iodoethane was placed with 1-oxa-4-telluracyclohexane (2.0 g; 0.01 mol) in a flask flushed with dry nitrogen. An exothermic reaction took place giving pale yellow crystals which, on crystallization from ethanol, gave bright white crystals which melted at 168–170 °C.

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Anal. Found: C, 20.6; H, 3.10; Te, 34.9. Calc. for $C_6H_{13}OTeI$: C, 20.3; H, 3.68; Te, 33.9%.

The following compounds were then prepared by oxidative addition of the appropriate organyl halide using the previous conditions.

1-Oxa-4-allyl-4-iodo-4-telluracyclohexane (IIa)

White crystals, m.p. 113–115 °C. *Anal.* Found: C, 23.1; H, 3.74; Te, 33.9. Calc. for $C_7H_{13}OTeI$: C, 22.9; H, 3.56; Te, 34.8%.

1-Oxa-4-allyl-4-bromo-4-telluracyclohexane (IIb)

White precipitate formed after 4–6 h, m.p. 193–195 °C. *Anal.* Found: C, 25.8; H, 4.35; Te, 39.7. Calc. for $C_7H_{13}OTeBr$: C, 26.3; H, 4.09; Te, 39.9%.

1-Oxa-4-methyl-4-iodo-4-telluracyclohexane (IIIb)

This compound was prepared according to the method reported by Farrar and Mulland [8]; m.p. 199–200 °C (literature value [8] 199 °C). *Anal.* Found: C, 17.6; H, 2.90; Te, 36.8. Calc. for $C_5H_{11}OTeI$: C, 17.6; H, 3.20; Te, 37.4%.

1-Oxa-4-butyl-4-iodo-4-telluracyclohexane (IV)

White precipitate formed after 4 days, m.p. 172–174 °C (dec.). *Anal.* Found: C, 25.00; H, 4.50. Calc. for $C_8H_{17}OTeI$: C, 25.04; H, 4.47%.

1-Oxa-4-methyl-4-telluracyclohexane perchlorate (IIIa)

An ethanolic solution of 1-oxa-4-methyl-4-iodo-4-telluracyclohexane (3.4 g; 0.01 mol) was added to an aqueous solution of silver perchlorate (2.0 g; 0.01 mol). The solution was stirred for 2 h, heated under reflux for 2 h, and then filtered hot to remove silver iodide. The filtrate was allowed to evaporate at room temperature and a white precipitate deposited. Recrystallization from ethanol–water (3:1) gave white needles, m.p. 182 °C (dec.). *Anal.* Found: C, 19.5; H, 3.44; Te, 39.9. Calc. for $C_5H_{11}O_5TeCl$: C, 19.1; H, 3.53; Te, 40.6%.

1-Oxa-4-ethyl-4-telluracyclohexane tetraphenylborate (Ib) and 1-oxa-4-methyl-4-telluracyclopentane tetraphenylborate (IIIc)

Compounds **Ib** and **IIIc** were prepared by the following method. A hot solution of 1-oxa-4-organo-4-iodo-4-telluracyclohexane (0.01 mol) was treated with an ethanolic solution of sodium tetraphenylborate (3.4 g; 0.01 mol) to give a voluminous white precipitate. The mixture was stirred for 2 h and then heated under reflux for 2 h. On colling to room temperature, a white solid was separated, washed with water and ethanol and dried over P_4O_{10}. Recrystallization from DMF/water gave white crystals.

Ib: m.p. 210–212 °C. *Anal.* Found: C, 65.45; H, 6.25; Te, 22.2; Calc. for $C_{30}H_{33}OTeB$: C, 65.45; H, 6.41; Te, 23.2%.

IIIc: m.p. 210–212 °C. *Anal.* Found: C, 64.85; H, 5.76; Te, 22.9. Calc. for $C_{29}H_{31}OTeB$: C, 64.98; H, 6.06; Te, 23.8%.

1-Oxa-4-phenyl-4-telluracyclohexane tetraphenylborate (V)

This compound was prepared by the following variation of the method reported in the literature [1, 2]. To a solution of 1-oxa-4-telluracyclohexane-4,4-diiodide (3.26 g; 0.01 mol) in 50 ml of ethanol was added a solution of sodium tetraphenylborate (6.84 g; 0.02 mol) in 50 ml of ethanol. The resulting solution was refluxed for 2 h. The hot solution was filtered, white crystals of compound **V** collected and washed with water and ethanol. Recrystallization from DMF/water gave white crystals, m.p. 218–220 °C. *Anal.* Found: C, 68.95; H, 5.33. Calc. for $C_{34}H_{33}OTeB$: C, 68.51; H, 5.58%.

(b) Physical Measurements

Infrared spectra were obtained as KBr pellets or Nujol mulls in the range 4000–200 cm^{-1} using a Beckman Acculab TM spectrophotometer. ^1H NMR data were obtained with a Brucker WH 90DC spectrometer using TMS as internal reference. The sample temperature was 34.5 °C. Solution conductivities were measured with a WTW conductivity meter LBR, using a standard conductivity cell with a cell constant of 0.0577. Microanalysis for carbon and hydrogen were carried out by the Micro Analytical Laboratories of the Chemistry Department of College of Science, University of Mousul. Tellurium analysis was carried out by the method of Thavornyutikarn [9] using a Pye Unicam (Philips) Spy Flameless Atomic Absorption spectrophotometer. The melting points of all solid compounds were determined by a Frost melting point apparatus which was heated electrically and are uncorrected.

Results and Discussion

We have found that 1-oxa-4-telluracyclohexane-4,4-diiodide (**VI**) can be easily prepared in moderate yields by modification of the method described earlier [1–4]. This synthesis of compound **VI** using 2-butoxyethanol as a solvent and excess of sodium iodide avoids the use of a sealed-tube reaction as previously reported for compound **VI** and other dialkyltellurium diiodides [8].

We reduced the diiodide (**VI**) with N_2H_4 in ethanol, forming 1-oxa-4-telluracyclohexane. This compound can be easily oxidized to the corresponding telluronium salts with the appropriate organyl halide.

The conductivity of each compound was obtained in both DMSO and DMF solution. Single concentration data (10^{-3} M) are presented in Table I. Each

TABLE I. Conductivity Data (10^{-3} M solutions) for a series of 1-Oxa-4-organo-4-telluracyclohexane Telluronium Salts, C_4H_8OTeRX

R	X	Molar conductance (Λ_M) (ohm^{-1} cm^2 mol^{-1})	
		DMSO[a]	DMF[a]
CH_3	BPh_4	14.6	32.5
CH_3	I	28.3	50.8
CH_3	ClO_4	25.7	49.6
C_2H_5	I	29.1	52.5
C_2H_5	Br	30.0	51.2
C_2H_5	BPh_4	17.6	38.7
C_3H_5	I	31.2	57.9
C_3H_5	Br	28.9	56.4
C_4H_9	I	27.8	50.2
C_6H_5	BPh_4	15.9	38.7
I	I	19.6	22.5

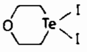
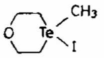
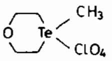
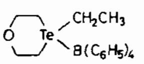
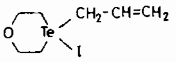
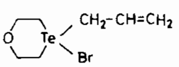
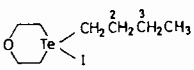
[a] $[(C_2H_5)_4N]Cl$: Λ_M 30(DMSO); 80(DMF) ohm^{-1} cm^2 mol^{-1}

compound was examined over a range of concentrations. In each case non-linear plots of molar conductivity (Λ_M) against (concentration)$^{1/2}$ were obtained indicating some degree of ion pairing in both solvents. These observations agree well with previous work [1, 2, 5, 6].

Compounds **Ib**, **IIIc** and **IV** give a surprisingly low conductivity in DMSO and DMF (Table I). This may be attributed to the close contact between a tellurium atom and one phenyl ring of the BPh_4^- ion as observed by X-ray and molecular structure studies on analogous compounds [10]. The low conductivity of the diiodide (**VI**) may be due to its existence as a dimer [11].

Infrared spectra of telluronium salts (**I–V**) displayed common features in certain regions and characteristic bands in the finger-print and other regions. Relevant IR data are presented in Table II. The IR spectra show the ν(Te–C_{alkyl}) bands between 485–530 cm^{-1} while the ν(Te–$C^{3,5}$) occurs between 465–500 cm^{-1}.

TABLE III. Some ^{1}H NMR Data for 1-Oxa-4-telluracyclohexane Derivatives in DMSO-d_6[a]

Compound	Chemical shifts (ppm); TMS = 0 ppm
	H(3,5): 3.24(t); H(2,6): 4.42(t)
	CH_3: 2.47(s); H(3,5): 2.66–3.08(m*); H(2,6): 3.56–4.13(m*)
	CH_3: 2.15(s); H(3,5) 2.35–2.82(m*); H(2,6): 3.25–3.82(m*)
	CH_3: 1.41(t); CH_2: 2.59(q); H(3,5): 2.78–3.05(m*); H(2,6): 3.58–4.09(m*); H–Ar: 6.6–7.3(m*)
	Te–CH_2: 3.69(d); CH_2; 4.97–5.51(m*); CH: 5.84(Q); H(3,5): 2.29–2.99(m*); H(2,6): 3.68–4.00(m*)
	Te–CH_2: 3.63(d); CH_2: 5.07–5.51(m*); CH: 5.73(Q); H(3,5): 2.34–3.05(m*); H(2,6): 3.68–4.00(m*)
	CH_3: 0.91(t); CH_2(3): 1.41(h); CH_2(2): 1.68(Q); Te–CH_2: 2.68(t); H(3,5): 2.39–3.14(m*); H(2,6): 3.46–4.07(m*)

[a] Starred items: H(3,5) and H(2,6) gave a complex overlapping in all cases.

The IR spectrum of 1-oxa-4-methyl-4-telluracyclohexane perchlorate (**IIIa**) merits special mention. As a Nujol mull it shows the typical broad band of the ionic perchlorate group centered on 1080 cm^{-1} (ν_3) together with a sharper band at 622 cm^{-1} (ν_4). However, when pressed into a KBr pellet the ν_3 and ν_4 bands split ($\nu_3 \rightarrow$ 1148, 1112, 1090 cm^{-1}; $\nu_4 \rightarrow$ 636, 628 cm^{-1}). This implies that the perturbation has reduced the effective symmetry of the perchlorate group to C_{2v} [1, 12–15], possibly by weak interaction with the tellurium atom [1].

Some representative ^{1}H NMR data in DMSO are presented in Table III. The methylene protons

TABLE II. Some Representative IR Data (KBr disc) of Tellurenium Salts Derived from 1-Oxa-4-organo-4-telluracyclohexane[a]

Ia	Ib	IIa	IIb	IIIa	IIIb	IIIc	V	Assignments
	3075m					3060	3085	arom. C–H stretching
2865m	2885m	2895m	2895m	2870m	2875m	2870m		aliph. C–H stretching
1475m	1485m	1475m	1635m	1475m	1470m	1475m		aliph. C–H bending
1230m	1205m			1230m				symm. CH_3 vibration
1095s	1100s	1095s	1100s	1095s	1090s	1095s	1100s	C–O–C stretching
850m	850m			845m	850m	850m		CH_3 rocking
525w	485m	515w	515w	530w	525w	520w	255w[b]	ν(Te–C_{alkyl})
500w	465w-m	500w	500w	500w	495w	500w	500w	ν(Te–$C^{3,5}$)

[a] Following the notation of Ellestad *et al.* [16]. [b] For ν(Te–C_{phenyl}).

(3,5 and 2,6) give two separate triplets for compound **VI**. However, replacement of iodine by an alkyl group covalently attached to the tellurium atom showed a remarkable change in the methylene spectrum; it appeared as a multiplet complex signal (Table III).

In the ^{1}H NMR spectrum of compound **IIIb**, in DMSO, one singlet was observed at 2.47 ppm. The position of the methyl group did not change after 24 h, which may be attributed to the stability of this compound to reductive elimination [1, 2, 5, 6]. No signal was observed at 2.07 ppm (due to the formation of $(CH_3)_2SO\cdots CH_3^+$ [7]) indicating that there is no reaction between the solute and the solvent such as recently demonstrated for other telluronium salts derived from phenoxatellurine [7].

The spectra of **I**–**V** in DMSO were similarly recorded but none of the salts studied showed reductive elimination of alkylhalides or reaction with DMSO.

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