

## Synthesis and Characterization of New Cyclic Organo-Tellurium Dialkoxides

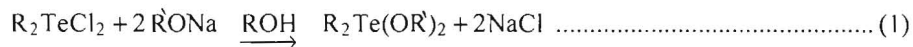
Ibrahim S. Al-Naimi<sup>1</sup>, Hatif A. Alshirayda<sup>2</sup> and Khalid G. Aladely<sup>2</sup>

<sup>1</sup>Chemistry Department, College of Science, University of Qatar, Doha,  
P.O.Box 2713, Qatar

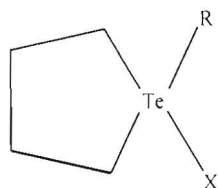
<sup>2</sup>Chemistry Department, College of Science, University of Basrah, Basrah, Iraq

ABSTRACT. A new series of heterocyclic tellurium dialkoxides ( $C_nH_{2n}Te(OR)_2$ ;  $n = 4, 5$ ,  $R = CH_3, CH_2CH_3, CH_2CH_2CH_3$ , and n-But.) have been prepared by the reaction of sodium alkoxides with the corresponding cyclic tellurium diiodide. These compounds were characterized on the basis of their IR, <sup>1</sup>H NMR and Mass spectral data. Conductivity measurements in DMSO and DMF have shown a considerable ionic behaviour.

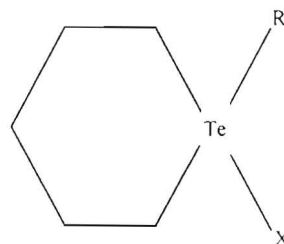
The synthesis and chemistry of structurally related cyclic tellurium dihalides  $C_nH_{2n}TeX_2$ ; ( $X = I, Br$  and  $Cl$ ) are well investigated (Farrer and Gulland 1945, Ziolo and Guenther 1978, and Zumbulyadis and Gysling 1980). The use of these tellurium dihalides as a tool for the synthesis of corresponding dialky and diaryl derivatives is well established (Drew 1929 and Campos *et al.* 1964). A previous paper (Wieber and Kaunzinger 1977) has reported on the preparation of a series of an open chain tellurium dialkoxide  $R_2Te(OR)_2$  via the interaction between sodium alkoxides and the desired dihalide, (eq. 1).



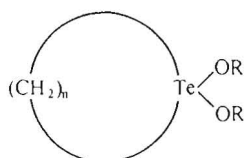
Recent studies by our group and others on the synthesis and characterization of telluronium salts derived from telluracyclopentane and telluracyclohexane (I, II), prompted the preparation of a series of the corresponding cyclic dialkoxides (Al-Rubaie *et al.* 1985, 1987 and Alshirayda *et al.* 1992). This paper describes the synthesis, properties in solution and some spectral data on the previously unreported cyclic tellurium dialkoxides (III<sub>a</sub> - III<sub>g</sub>).



(I)



(II)



n = 4,5

(III)

n = 4; (IIIa): R = Me

(IIIc): R = n-Pr

n = 5; (IIIe): R = Me

(IIIg): R = n-Pr

(IIIb): R = Et

(IIId): R = n-But

(IIIf): R = Et

## Experimental

### a) Synthesis

#### *Preparation of initial diiodides; 1,1-Diiodo-1-telluracyclopentane and 1,1-Diiodo-1-telluracyclohexane*

The initial diiodides 1,1-diiodo-1-telluracyclopentane and 1,1-diiodo-1-telluracyclohexane were prepared as previously reported (Al-Rubaie *et al.* 1987 and Alshirayda *et al.* 1992). Telluracyclopentane diiodide obtained as orange-red crystals, m.p. 151°C, Lit. (Morgan and Burstall 1931), 149-150°C. The 1,1-diiodo-1-telluracyclohexane was obtained as violet-brown crystals, m.p. 133-134°C, Lit. (Morgan and Burstall 1931), 135-136°C.

#### *Preparation of tellurium dialkoxides, III<sub>a</sub> - III<sub>g</sub>*

The compounds III<sub>a</sub> - III<sub>g</sub> were prepared according to the method described in the Lit. for the open chain derivatives (Wieber and Kaunzinger 1977). A typical procedure was as follows: (0.01 mol.) of the 1,1-diiodide was dissolved in 50 ml. of hot alcohol. Freshly prepared sodium alkoxide (0.02 mol.) was added to the mixture and stirred under reflux

for 1h. The precipitate was filtered off, washed with water, rinsed with acetone and air-dried. Recrystallization from the alcohol used in the reaction, or, in some cases, benzene gave light-yellow precipitate or crystals. Yield and physical properties of the products are listed in Table I.

**Table I.** Analytical and Physical Properties of Compounds III<sub>a</sub>-III<sub>g</sub>

Comp.	Yield %	Colour and Solid State	m.p.°C	Found (Calcd.) %	
				H	C
IIIa	85	Colourless Crystals	182-183	5.62 (5.74)	29.25 (29.32)
IIIb	87	Colourless Crystals	170-172	6.39 (6.62)	35.34 (35.90)
IIIc	78	Colourless Crystals	191-192	7.16 (7.34)	39.26 (39.78)
IIId	81	Light Yellow Crystals	211-213	8.01 (7.94)	43.26 (43.68)
IIIe	76	Colourless Crystals	178-179	6.48 (6.18)	32.42 (32.43)
IIIf	78	Colourless Crystals	186-188	6.55 (6.96)	37.46 (37.63)
IIIg	72	Light Yellow Crystals	196-198	7.22 (7.62)	41.54 (41.90)

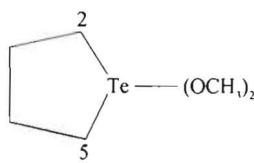
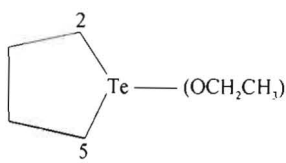
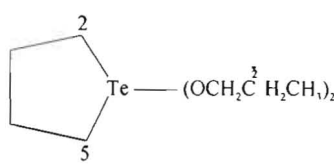
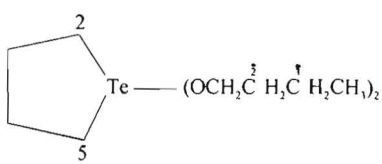
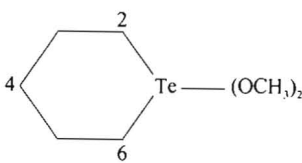
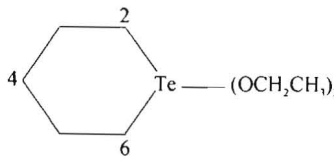
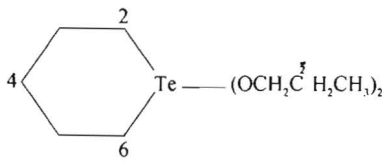
### b) Physical Measurements

Infrared spectra were obtained as KBr pellets in the range 4000 - 200 cm<sup>-1</sup> using a Beckman TM spectrophotometer. <sup>1</sup>H NMR data were obtained with a Bruker WH 90 DC spectrophotometer, using TMS as internal reference. Solution conductivities were measured with a WTW conductivity meter LBR, using a standard conductivity cell with a cell constant of 0.0577. Mass spectra were obtained at 70 eV with an AEI MS9 instrument.

## Results and Discussion

In the present work compounds III<sub>a</sub> - III<sub>g</sub> were prepared in 72-87% yield, under the conditions cited, by reacting the appropriate sodium alkoxide with the cyclic tellurium diiodide. The <sup>1</sup>H NMR spectral data in DMSO-d<sub>6</sub> solution of compounds III<sub>a</sub> - III<sub>g</sub>, (Table 2), shows two sets of aliphatic resonances, one due to the alkoxy-protons and the other due to the methylene ring protons. Peak assignments were based on intensity, multiplicity and comparison of chemical shift data with previous literature values. For the five member ring series (n = 4), compound III<sub>a</sub> showed three well separated signals of (3: 2: 2) ratio, sharp singlet at δ 3.02 ppm for the methoxy protons, triplet, J = 6H<sub>2</sub>, at δ 2.80 ppm for the (2, 5-CH<sub>2</sub>) and complex overlap at δ 2.41-2.69 ppm for the (3, 4-CH<sub>2</sub>). The <sup>1</sup>H NMR spectrum of all other compounds are helpful in showing the correct ratio of alkoxy protons to the ring protons and hence supporting the stoichiometry of the materials.

**Table 2.**  $^1\text{H}$  NMR Data for 1, 1-Dialkoxy Telluracyclopentane and Telluracyclohexane Derivatives III<sub>b</sub> - III<sub>e</sub> in DMSO- $d_6$ .

Compound	Chemical shift (ppm); TMS = 0 ppm.
	OCH <sub>3</sub> : 3.02(s); H(2,5): 2.80(t); H(3,4): 2.41-2.69 (m*)
	CCH <sub>3</sub> : 1.34(t); OCH <sub>2</sub> : 3.12(q); H(2,5): 2.78(t); H(3,4): 2.44-2.62 (m*)
	CCH <sub>3</sub> : 1.04(t); H( $\bar{2}$ ): 1.46(h); OCH <sub>2</sub> : 3.1(t); H(2,5): 2.69(t); H(3,4): 2.23-2.45 (m*)
	CCH <sub>3</sub> : 0.94(t); H( $\bar{3}$ ): 1.50(h); H( $\bar{2}$ ): 1.58(q); OCH <sub>2</sub> : 3.01(t); H(2,5): 2.71(t); H(3,4): 2.2-2.36 (m*)
	OCH <sub>3</sub> : 3.23(s); H(2,6): 3.01(t); H(3,5): 2.01-2.10 (m*); H(4): 1.8-1.92 (m*)
	CCH <sub>3</sub> : 1.39(t); OCH <sub>2</sub> : 3.04(q); H(2,6): 3.5(t); H(3,5): 2.2-2.36 (m*); H(4): 1.94-2.01 (m*)
	CCH <sub>3</sub> : 0.92(t); CH <sub>2</sub> ( $\bar{2}$ ): 1.44(h); O-CH <sub>2</sub> : 2.93(t); H(2,6): 3.3(t); H(3,5): 2.3-2.4 (m*); H(4): 1.87-1.98 (m*)

A starred item; H(3,4), H(3,5) and H(4) gave a complex overlapping in all cases.



The molar conductivities ( $\Lambda_m$ ) for the prepared compounds are measured in DMSO and DMF solutions. Single concentration data ( $10^{-3}$ M) are presented in Table 3. The data obtained from the plots between  $\Lambda_m$  against (concentration)<sup>1/2</sup> showed that these compounds are weak electrolytes in both solvents, but in DMSO at least, the values of  $\Lambda_m$  reach those expected for 1:1 electrolytes (Musa and McWhinnie 1987). This observation is consistent with that previously reported (Gilbert and Lowry 1928), for the ionic characteristics of dialkyl-tellurium dihydroxide  $[R_2Te(OH)]^+[OH]^-$ . It is also noted that the values of  $\Lambda_m$  for the dialkoxides III<sub>a</sub> - III<sub>g</sub> are considerably larger than those of corresponding dihalide compounds which shows low conductance that may be due to the possible association of these compounds via weak ionic bonds in both solvents (Hope *et al.* 1973).

**Table 3.** Conductivity Data ( $10^{-3}$  M Solutions) for a Series of 1,1-Dialkoxy-1-Telluracyclopentane  $C_4H_8Te(OR)_2$ , -1-Telluracyclohexane  $C_5H_{10}Te(OR)_2$  and their Diiodides

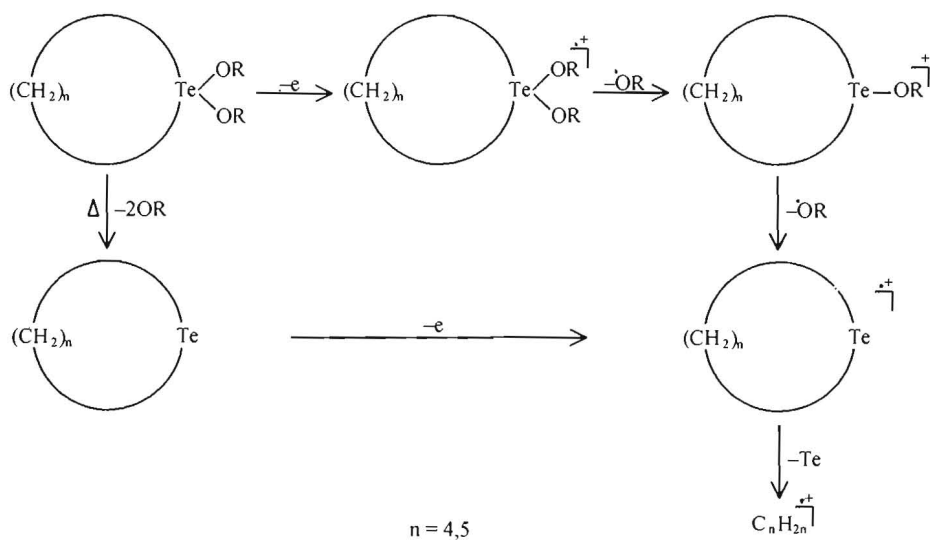
Compound	Conductivity ( $\Lambda_m$ ) $ohm^{-1} cm^2 mol^{-1}$	
	DMSO	DMF
$C_4H_8Te(OMe)_2$	26.15	42.34
$C_4H_8Te(OEt)_2$	25.96	41.66
$C_4H_8Te(OPr)_2$	21.75	43.50
$C_4H_8Te(OBut)_2$	21.66	40.80
$C_5H_{10}Te(OMe)_2$	25.20	41.50
$C_5H_{10}Te(OEt)_2$	23.55	38.10
$C_5H_{10}Te(OPr)_2$	21.88	37.67
$C_4H_8TeI_2$	16.20	18.00
$C_5H_{10}TeI_2$	15.00	17.00

\* Molar conductivities were measured for  $10^{-3}$  M solution of the compound  $(C_2H_5)_4 N^+ Cl^-$ ;  $\Lambda_m$ : 30 (DMSO); 80 (DMF)  $ohm^{-1} cm^2 mol^{-1}$ .

The mass spectral data of IIIa, IIIb, and IIIe (Table 4) show certain common features. The parent ion  $C_nH_{2n}Te(OR)_2^+$  [ $n = (4,5)$ ], has not been observed in any case. The fragmentation involved successive losses of the dialkoxy group forming the corresponding cyclic telluride cation  $C_nH_{2n}Te^+$ , followed by the loss of tellurium to give the cyclobutane and cyclopentane cation  $C_nH_{2n}^+$ . Other fragments such as  $Te-CH_2^+$  and  $Te-CH_2CH_2^+$  were observed only at low intensities in all cases. Therefore it is likely that fragmentation of the compounds proceed by the same route as previously reported for other tellurium compounds (Zumbulyadis and Gysling 1980, De Silva *et al.* 1983, and Singh and McWhinnie 1984). The spectra showed no ions appearing at higher mass charge ratio than that corresponding to the monomer ions, while association to dimers was observed previously for analogous tellurium compounds (Hope *et al.* 1973, McCullough 1975, Ziolo and Extine 1980, and DeSilva *et al.* 1983). A proposed fragmentation pattern is represented in Scheme 1.

**Table 4.** Mass spectral Data of Compounds III<sub>a</sub>, III<sub>b</sub>, and III<sub>c</sub> (Relative to C<sup>12</sup>, H<sup>1</sup>, O<sup>16</sup> and Te<sup>130</sup>)

Compound	Possible ion of major fragment
III <sub>a</sub>	m/e = 217 (C <sub>5</sub> H <sub>11</sub> OTe <sup>+</sup> ), 37%; 186(C <sub>4</sub> H <sub>8</sub> Te <sup>+</sup> ), 55%; 56(C <sub>4</sub> H <sub>8</sub> <sup>+</sup> ), 21%
III <sub>b</sub>	m/e = 231 (C <sub>6</sub> H <sub>13</sub> OTe <sup>+</sup> ), 43%; 186(C <sub>4</sub> H <sub>8</sub> Te <sup>+</sup> ), 53%; 130(Te <sup>+</sup> ), 12%; 45(C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> ), 77%
III <sub>c</sub>	m/e = 231 (C <sub>6</sub> H <sub>11</sub> OTe <sup>+</sup> ), 32%; 200(C <sub>5</sub> H <sub>10</sub> Te <sup>+</sup> ), 66%; 70(C <sub>5</sub> H <sub>10</sub> <sup>+</sup> ), 19%; 31(CH <sub>3</sub> O <sup>+</sup> ), 44%; 130(Te <sup>+</sup> ), 14%

**Scheme 1**

The infrared spectra of compounds III<sub>a</sub> - III<sub>g</sub>, (KBr pellets) show common features in certain regions. All compounds show  $\nu(\text{Te-C})$  between 475-500  $\text{cm}^{-1}$  and characteristic broad bands at 360-375  $\text{cm}^{-1}$  and 605-620  $\text{cm}^{-1}$  assigned for the  $\nu(\text{Te-O})$ . These values are in good agreement with those previously reported (Al-Rubaie *et al.* 1988), and Alshirayda *et al.* 1992). Relevant IR data are presented in Table 5.

Table 5. IR Data of 1,1-Dialkoxy-1-Telluracyclopentane and Telluracyclohexane.  $\nu_{\text{cm}^{-1}}$ 

III <sub>a</sub>	III <sub>b</sub>	III <sub>d</sub>	III <sub>e</sub>	III <sub>f</sub>	Assignment
2855m	2870w	2865m	2850m	2855m	C-H stretching
1450m	1455m	1450m	1460m	1455m	C-H bending
485w	480m	475w	500w	500w	Te-C stretching
360wb	365wb	360wb	370wb	375wb	Te-O stretching
610sb	605sb	615sb	620sb	615sb	

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## تحضير ودراسة خواص بعض المركبات الحلقية للتلوريوم ثنائية الالكوكسيد

إبراهيم صالح النعيمي<sup>١</sup> و هاتف عبدالرزاق الشريدة<sup>٢</sup>  
و خالد جواد العادلي<sup>٢</sup>

<sup>١</sup> قسم الكيمياء - كلية العلوم - جامعة قطر - ص.ب. ٢٧١٣ - الدوحة - قطر  
<sup>٢</sup> قسم الكيمياء - كلية العلوم - جامعة البصرة - العراق

يتضمن البحث تحضير ودراسة طيفية لبعض مركبات التلوريوم الحلقية من  
نوع ١,١ - ثنائي الكوكسي - ١ - تيلورا البنتان الحلقي وتيلورا الهكسان  
الحلقي:  $C_nH_{2n}Te(OR)_2$  حيث  $n=4,5$   $R = Me, Et, n-Pr, n-Bu$ .

وقد أظهرت نتائج الرنين النووي المغناطيسي لذرة الهيدروجين لهذه  
المركبات والتوصيلات المولارية لها في محلولي ثنائي ميثيل سلفوكسيد وثنائي  
ميثيل فورماميد أن المركبات المحضرة لها بعض الصفات الأيونية، كما أنها تمتلك  
قيم  $\Delta m$  أعلى من مثيلاتها من نوع ١,١ - ثنائي هاليد - ١ - تيلورا البنتان  
الحلقي وتيلورا الهكسان الحلقي.

كما يشتمل البحث على دراسة مختصرة لطيف الكتلة وطيف الأشعة تحت  
الحمراء لهذه المركبات.