Arab Gulf J. Scient. Res., **10**(1), pp. 13-21 (1992)

Synthesis and Spectroscopic Investigation of Telluronium Salts Based Upon 1,1-Bis (Phenoxy Derivatives) of 1-Telluracyclopentane

**Hatif A. Alshirayda[1], Ibrahim S. Alnaimi[2]*, Ala'a Auoob[1]
and Khalid G. Aladely[1]**

[1]*Department of Chemistry, College of Science,
University of Basrah, Basrah, Iraq*
[2]*Department of Chemistry, College of Science,
University of Qatar, P.O. Box 2713, Doha, Qatar*

ABSTRACT. A new series of cyclic diphenoxytelluronium salts based on telluracyclopentane of the type $C_4H_8TeL_2$; where: L = C_6H_5O-; $p\text{-}CH_3C_6H_4O-$; $p\text{-}CH_3OC_6H_4O-$; $o\text{-}ClC_6H_4O-$; $o\text{-}NO_2C_6H_4O-$; $o,p\text{-}(NO_2)_2C_6H_3O-$; have been prepared. The ^1H NMR data and molar conductivities in dimethylsulphoxide (DMSO) revealed considerable ionic character, particularly in compounds with nitro-substituents. I.R. spectroscopic data are reported and briefly discussed.

Previously (Wieber, and Kaunzinger 1977), it has been demonstrated that dialkyl tellurium dihalogenides R_2TeX_2 could be reacted with sodium alkoxide derivatives yielding dialkoxytellurium salts of the type $R_2Te(OR)_2$. In continuation of previous work (Alrubaie *et al.* 1985, 1988), on the synthesis and spectroscopic investigation of heterocyclic telluronium salts derived from telluracyclopentane, we have examined the preparation of a new series of cyclic telluronium salts (I-VI) corresponding to 1,1-bis (phenoxy derivatives) of 1-telluracyclopentane by reacting 1,1-diiodo-1-telluracyclopentane $C_4H_8TeI_2$ with the corresponding sodium aryloxide.

---

* Author to whom all correspondence should be addressed.

The present work reports the synthesis, solution properties and some spectroscopic data of compounds (I-VI), in addition, attempts were made to obtain more information about the ionic properties of such salts in relation to variation of the counter ion inductive effect.

Experimental

A. Synthesis

1,1-Diiodo-1-telluracyclopentane

This compound was prepared by the method of Ziolo and Guenther 1978. A mixture of 1,4-dibromobutane (6.78g, 0.04 mole), finely powdered elemental tellurium (5.1g, 0.04g-atom) and sodium iodide (23.9g, 0.16 mole) in 2-butoxyethanol (100 ml) was stirred at the boiling point (1h.) in a beaker, cooled, and deionized water (200 ml) was added. The precipitate was collected, washed with water, then with acetone, and dried.

Recrystallization from dimethylformamide gave orange-red crystals (m.p. 153°C) (Lit. 149-150°C) (Morgan and Burstall 1931). (Found: C, 22.5; H, 3.70. Calc. for $C_4H_8I_2$: C, 22.2; H, 3.70%).

1,1-Bis (phenoxy)-1-telluracyclopentane (I):

To a hot ethanolic solution of 1,1-diiodo-1-telluracyclopentane (3.69g, 0.01 mol), was added with continuous stirring, the appropriate amount (1:2 ratio) of sodium phenoxide (prepared from the reaction of 20% sodium hydroxide solution with phenol) dissolved or suspended in the minimum volume of ethanol. The mixture was boiled under reflux (1h.). The solution was cooled and the precipitate was collected, washed with water, acetone and air dried. Recrystallization from ethanol gave white crystals, m.p. 189-191°C. (Found: C, 51.95; H, 4.90; Te, 34.49. Calc. for $C_{16}H_{18}O_2Te$: C,51.80; H, 4.72; Te, 34.33%). Tellurium was analyzed by the method of Thavornyutikarn (1973).

The following compounds were prepared by the same procedure.

1,1-Bis(p-methylphenoxy)-1-telluracyclopentane (II):

White crystals, m.p. 197-198°C, (Found: C, 54.32; H, 5.57; Te, 32.06. $C_{18}H_{22}O_2Te$ requires C, 54.08; H, 5.93; Te, 31.91%).

1,1-Bis(p-methoxyphenoxy)-1-telluracyclopentane (III):

Brown precipitate, m.p. 193-195°C. (Found: C, 50.28; H, 5.15; Te, 29.67. $C_{18}H_{22}O_4Te$ requires C, 49.66; H, 5.01; Te, 28.93%).

1,1-Bis(o-chlorophenoxy)-1-telluracyclopentane (IV):

Pale yellow precipitate, m.p. 194-198°C. (Found: C, 43.88; H, 3.68; Te, 29.13. $C_{16}H_{16}O_2TeCl_2$ requires C, 43.22; H, 3.52; Te, 28.56%).

1,1-Bis(o-nitrophenoxy)-1-telluracyclopentane (V):

Yellow-orange precipitate, m.p. 172-175°C. (Found: C, 41.78; H, 3.50; Te, 27.74. $C_{16}H_{16}O_6N_2Te$ requires C, 39.55; H, 3.41; Te, 26.98%).

1,1-Bis(o,p-dinitrophenoxy)-1-telluracyclopentane (VI):

Orange-red precipitate, m.p. 118-122°C. (Found: C, 34.94; H, 2.56; Te, 23.20, $C_{16}H_{14}O_{10}N_4Te$ requires C, 34.12; H, 2.21; Te, 22.82%).

B. Physical Measurements

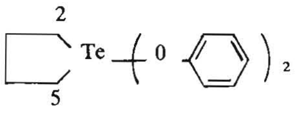
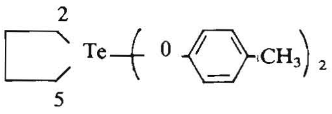
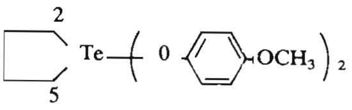
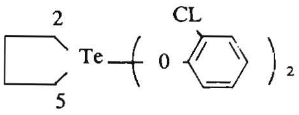
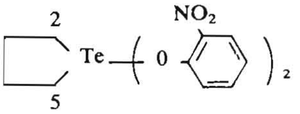
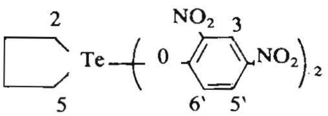
Infrared spectra were obtained (KBr disc) in the range 4000-200cm^{-1} using PYE-UNICAM 2000 spectrometer. Conductivities were measured in (DMSO). With a WTW conductivity meter LBR, using a standard conductivity cell with a cell constant of 0.8. The DMSO was dried over NaOH and distilled under reduced pressure, ^{1}H NMR data were obtained using a Brucker WH 90 DC spectrometer.

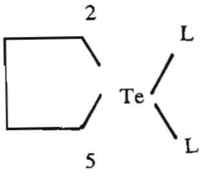
Result and Discussion

Compounds (I-VI) were prepared (80-86% yield). The ^{1}H NMR spectra (DMSO-d6, relative to TMS) (Table 1) of compounds (I-VI) showed both aliphatic and aromatic protons resonance. With the exception of compound I, the chemical shift of well resolved signals of the 2,5-methylene ring protons revealed a significant deshielding which was dependent upon the substituent. Compound (VI) showed the largest downfield shift of (0.4-0.6) ppm compared with those of compounds (I-V). This is consistent with the deshielding effect expected to the tellurium nucleus due to the inductive effect of the two nitro groups. This is in good agreement with previous investigations demonstrating the deshielding of the Te^{125} chemical shift relative to the counter ion electronegativity (Zumbulyadis and Gysling 1980 and Al-Rubaie and McWhinnie 1982).

The molar conductance Λ_m of the telluronium salts in 10^{-3} of DMSO solution were determined (Table 2).

Table 1. ^{1}H NMR data for the 1,1-bis (phenoxy derivatives)-1-telluracyclopentane, $C_4H_8TeL_2$ compounds (I-VI)

	Compounds	**Chemical Shift (ppm); TMS = O ppm**
I		H(2,5): 3.1-3.3(t) J=6 Hz; H(3,4): 2.6-2.8(m); Ar-H: 6.4-7.1 (complex overlapping).
II		H(2,5): 2.66-3.08(t) J=6 Hz; H(3,4): 2.22-2.84(m); CH_3: 1.8(S); Ar-H: 6.24-7.45 (complex overlapping).
III		H(2,5): 2.8-3.0(t) J=5.9 Hz; H(3,4): 1.8-2.0(m); CH_3O: 3.7(S): Ar-H: 6.30-7.40 (complex overlapping).
IV		H(2,5): 3.0-3.2(t) J=6 Hz; H(3,4): 2.5-2.9(m); Ar-H: 6.40-7.52 (complex overlapping).
V		H(2,5): 3.2-3.4(t) J=5.8 Hz; H(3,4): 1.9-2.0(m); Ar-H: 6.40-7.52 (complex overlapping).
VI		H(2,5): 3.6-3.8(t) J=5.8 Hz; H(3,4): 2.7-2.9(m) (6̀) - Ar-H: 7.3 (d); (5̀) Ar-H: 8.35-8.50 (q); (3̀) -Ar-H: 8.85 (d)



I-VI

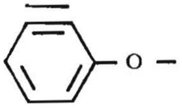
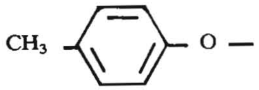
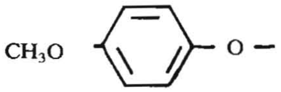
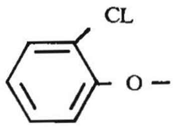
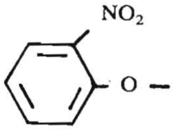
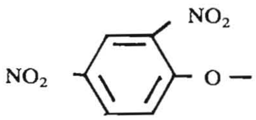
Compound	L
I	
II	
III	
IV	
V	
VI	

Table 2. Conductivity data of 1,1-bis (phenoxy derivatives)-1-telluracyclopentane. $C_4H_8TeL_2$ Compounds I-VI

Cmpd.	**L**	**Molar Conductance Λ_m (Ohm^{-1} $cm^2.mol^{-1}$ (10^{-3} M, DMSO)***	**Limiting Molar conductance $\overset{o}{\Lambda}_m$**
I	C_6H_5O-	27.66	60.5430
II	$p-CH_3OC_6H_4O-$	28.16	58.8620
III	$p-CH_3C_6H_4O-$	23.26	56.4470
IV	$o-ClC_6H_4O-$	41.32	68.8700
V	$o-NO_2C_6H_4O-$	32.42	90.8700
VI	$o,p-(NO_2)_2C_6H_3O-$	38.20	190.1848

* 10^{-3} M Solutions Et_4NCl, (DMSO) 30.Ohm^{-1}. cm^2. mol^{-1}

$\overset{o}{\Lambda}_m$ Conductance at infinite dilution (estimated)

Each compound was studied as a function of concentration over the range $10^{-3}-10^{-6}$M. Plots of Λ_m *vs.* (conc.)$^{1/2}$ showed a marked curvature for compounds I-V. This is typical of weak electrolytes. Compound (VI) showed more ionic behaviour by the almost linear plot which was obtained. A plot of (concentration x Λ_m) *vs.* ($1/\Lambda_m$) for each compound gave a straight line from which the values of limiting molar conductance $\overset{o}{\Lambda}_m$ was estimated (Table 2).

The limiting molar conductance values $\overset{o}{\Lambda}_m$, clearly show the influence of substituents upon the ionic character of compounds I-VI. The presence of two nitro groups of compound VI revealed the largest effect which was consistent with the almost linear plot of Λ_m *vs.* (conc.)$^{1/2}$ and the largest deshielding of the 2,5-methylene protons resonance. This leads to the suggestion that in DMSO, the compounds I-VI exist in an ionic form which is similar to that for the tellurium dihalides with formulation of $[C_4H_8TeL]^+$ $[L]^-$ (Ziolo and Guenther 1978). The ionic character of the compounds follows the order VI$\rangle$ V$\rangle$ IV$\rangle$ I$\rangle$ II$\rangle$ III, based upon their molar conductances. This is in good accord with the electronic character (donating/withdrawing) of the substituent.

The infrared spectra (KBr disc) of the compounds (I-VI), displayed common features and characteristic bands in certain regions. The I.R. spectra showed the ν ($Te-C_{2,5}$) bands between 465-475 cm^{-1} and broad bands characteristic of ν (Te-O) were located at (350-385) and (600-615) cm^{-1}. These assignments are in good agreement with that previously reported (Pant *et al.* 1973 and Mehdi *et al.* 1984). In addition, the compounds V and VI show bands characteristic of the nitro group modes at 1510, 1260 and 620 cm^{-1} which represent the unsymmetrical, symmetrical, and bond stretching modes respectively. Relevant I.R. data are presented (Table 3). Further investigation of such salts is in progress.

Table 3. I.R. Data of 1,1-bis (phenoxy derivatives)-1-telluracyclopentane. $C_4H_8TeL_2$ Compounds (I-VI)

I	II	III	IV	V	VI	Assignment	
3065	3050	3065	3055	3075	3085	Ar.C–H	stretching
2850	2860	2850	2865	2855	2860	Aliph.C–H	stretching
1450	1455	1450	1465	1455	1450	Aliph.C–H	bending
1460	1485	1480	1480	1480	1485	Ar.C=C	stretching
475 w	465 w	475 m	470 w	465 w	470	(Te–$C_{2,5}$)	
600 s	615 s	615 s	610 s	605 s	600 s	(Te–O)	
380 w	350 w	365 w	350 w	385 w	380 w		
–	–	–	–	1510 s	1510 s	NO_2	stretching

References

Al-Rubaie, A.Z. and **McWhinnie, W.R.** (1982) The synthesis and spectroscopic examination of Telluronium salts based on the 1-organo-3, 4-benzo-1-telluracyclopentane cation. *J. Organomet. Chem.* **234:** 287-298.

Al-Rubaie, A.Z., Alshirayda, H.A., and **Auoob, A.I.** (1988) 2-Methyl-1-organo-1-halo-1-telluracyclopentane. Synthesis, solution properties, and configurational studies. *J. Organomet. Chem.* **356:** 49-55.

Al-Rubaie, A.Z., Alshirayda, H.A., Granger, P. and **Chapelle, S.** (1985) Synthesis and spectroscopic investigations of 1-organo-1-halo-1-telluracyclopentane. *J. Organomet. Chem.* **287:** 321-327.

Mehdi, R.T., Miller, J.D. and **Tahir, T.A.** (1984) A kinetic and mechanistic study of photochemical degradation of a diarylditelluride in toluene solutions containing alcohol. *Inorg. Chim. Acta.* **90:** 85-89.

Morgan, G.T. and **Burstall, F.H.** (1931) Cyclotellurobutane (Tetrahydrotellurophen). *J. Chem. Soc.* 180-184.

Pant, B.C., McWhinnie, W.R., and **Dance, N.S.** (1973) Organotellurium carboxylates and related compounds. Structural and synthetic considerations. *J. Organomet. Chem.* **63:** 305-310.

Thavornyutikarn, P. (1973) Tellurium analysis in organotellurium compounds by atomic absorption spectroscopy. *J. Organomet. Chem.* **51:** 237-239.

Wieber, M., and **Kaunzinger, E.** (1977) Organotellurium (IV) compounds. Esters of diorganotellurium dihydroxide. *J. Organomet. Chem.* **129:** 339-346.

Ziolo, R.F. and **Guenther, W.H.H.** (1978) The synthesis and characterization of α and β-1, 1-diiodo-3, 4-benzo-1-telluracyclopentane, $C_8H_8TeI_2$. *J. Organomet. Chem.* **146:** 245-251.

Zumbulyadis, N. and **Gysling, H.J.** (1980) Tellurium-125 NMR Spectra of tellurium heterocycles. *J. Organomet. Chem.* **192:** 183-188.

(Received 13/10/1991;
in revised form 08/02/1992)

تخليق ودراسات طيفية لأملاح التلورونيوم المشتقة من ١ ، ١ - ثنائي (مشتقات الفينوكسي) - ١ - تيلورا البنتان الحلقي

هاتف الشريدة[١] و إبراهيم صالح النعيمي[٢] و علاء أيوب[١] و خالد العديلي[١]

[١] قسم الكيمياء - كلية العلوم - جامعة البصرة - البصرة - العراق
[٢] قسم الكيمياء - كلية العلوم - جامعة قطر - ص. ب : ٢٧١٣ - الدوحة - قطر

يشمل هذا البحث على تخليق سلسلة جديدة من أملاح التلورونيوم الحلقية ثنائية الفينوكسي المشتقة من تيلورا البنتان الحلقي من نوع $C_4H_8TeL_2$ حيث

(III) $p\text{-}CH_3OC_6H_4O\text{-}$, (II) $p\text{-}CH_3C_6H_4O\text{-}$, (I) $C_6H_5O\text{-} = L$

(VI) $o,p\text{-}(NO_2)_2C_6H_3O\text{-}$, (V) $o\text{-}NO_2C_6H_4O\text{-}$, (IV) $o\text{-}ClC_6H_4O\text{-}$

وقد تم تحضير هذه المركبات من خلال إضافة فينوكسيد الصوديوم ومشتقاته إلى محلول إيثانولي ساخن من 1,1 - ثنائي أيودو - ١ - تيلورا البنتان الحلقي بنسبة (٢ : ١).

وقد تَبَيَّنَ من خلال نتائج الرنين النووي المغناطيسي لذرة الهيدروجين لهذه المركبات والتوصيلات المولارية لها في ثنائي ميثيل السلفوكسيد وجود سلوك أيوني كبير وخصوصاً في المركبات المحتوية على مجموعة نيترو بديلة لتأخذ هذه المركبات الشكل الأيوني $[C_4H_8Te]^+[L]^-$ وتكون الخاصية الأيونية تبعاً للتسلسل VI > V > IV > I > II > III ، الذي يتفق مع الخاصية الالكترونية للمجموعة البديلة (المجموعات الطاردة والمجموعات الساحبة للإلكترونات). كما يشتمل البحث على دراسة مختصرة لأطياف الأشعة تحت الحمراء لهذه المركبات.