Synthesis, Characterization and Molar Conductance
Study of Some New Heterocyclic Tellurium Compounds.

Ammar Al-Baage *

Received on Dec. 20, 1997
Accepted for publication on June 28, 1998

Abstract

Typical heterocyclic tellurium compound, 2-imino-3-tellurapipiderine (I) was prepared by reaction of 1-amino-3-chloropropene with KteCN. New derivatives of compound I(C₄H₇N₂Te(R)X; R=X=Cl; R=X=Br; R=X=I; R=CH₃, X=I; R=CH₂CH₃, X=Br; R=PhCH₂, X=Br; R=PhCOCH₂, X=Br) have been prepared and characterized, IR, ¹HNMR, elemental analysis and molar conductivity in N,N-dimethyl formamide (DMF) and (DMSO) indicate that all these solutes behave as weak electrolytes.

Introduction

The preparation, characterization and solution properties had been described in previous papers [1-5], the synthesis, characterization and solution properties of the series C₄H₇N₂Te(R)X, a hitherto unknown heterocyclic tellurium salt containing nitrogen atom are reported in this manuscript. The newly prepared compounds were stable toward reductive elimination and no reaction between solute and solvent was observed. These observation are compatible with organo tellurium (IV) compounds [5] and inconsistent with the tellurium salts derivatives diphenyl telluride [6,7] and phenoxotellurine [8]. The earlier work assured that in a solvent 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 [1-4] and confirmed by x-ray and other structural studies [9-13].

In the present work a series of new heterocyclic tellurium salts (I-VIII) have been prepared.

© 2002 by Yarmouk University, Irbid, Jordan.
* Department of Chemistry, college of Science, University of Basrah, Basrah, Iraq
Experimental

(a) Physical measurements

Infrared spectra were recorded as KBr pellets in the range of 4000 – 200 cm⁻¹ [Pye – Unicam SP3-300, infrared spectrophotometer]. Elemental analysis were performed using EA-1108 Carlo – Erba elemental analyzer. NMR spectra were recorded in CDCl₃ solution containing TMS as internal standard using Jeol EX-90 instrument. Melting points were determined by Gallen Kamp apparatus and were uncorrected. Conductivity measurements were done with a WTW conductivity meter LBR using a standard conductivity cell with constant of 0.8 cm⁻¹.

(b) Synthesis

- 2-Imino-3-tellurapiperedine (I)

This compound was prepared by alkylation of KteCN with 1-amino-3-chloropropene under purified nitrogen (As previously described by AL-Rubaie et al [16]). We obtained the novel heterocycle (I).

- 2-Imino-3-tellurapiperedine-3, 3-dichloride (II)

Thionyl chloride (1.30g, mmol) in diethyl ether (25 ml) was added slowly to a stirred solution of 2-imino-3-tellurapiperedine (1.70g, 8mmol) in ether (50 ml) at room temperature. A pale yellow precipitate formed immediately. The solution was evaporated to dryness and the residue was recrystallized from ethanol to give white crystals, m.p 87-88°C.

- 2-Imino-3-tellurapiperedine-3, 3-dibromide (III)

A solution of 2-imino-3-tellurapiperedine (1.70g, 8 mmol) in 50 ml of dry ether was added dropwise to a solution of bromine (1.30g, 8mmol) in 20 ml of ether. A yellow precipitate was formed immediately, the solution was evaporated to dryness, and the residue was recrystallized from methanol to give pale yellow crystals, m.p. 112-113°C.

- 2-Imino-3-tellurapiperedine-3, 3-diiodide (IV)

This compound was prepared as previously described by Gysling et al [17] with some modifications as follows:

A solution of iodine (2.03g, 8 mmol) in 50 ml of ether was added dropwise to a stirred solution of 2-Imino-3-tellurapiperedine (1.70g, 8mmol) in 50ml of ether. An orange-red precipitate was formed immediately. The solution mixture was stirred for 5 hours at room temperature. The solvent was evaporated to dryness by a rotary evaporator. The residue was recrystallized from ethanol to give orange crystals, m.p. 121-123°C.

- 3-Methyl-3-iodo-2-imino-3-tellurapiperedine (V)

666
An excess of freshly distilled iodo methane was introduced with 2-imino-3-tellurapipерidine (1.70g, 8 mmol) in a flask flushed with dry nitrogen. The reaction gave a pale yellow crystals of m.p. 153-154°C.

- **3-Ethyl-3-bromo-2-imino-3-tellurapipерidine (VI)**

  An excess of freshly distilled bromoethane was placed with 2-imino-3-tellurapipерidine (1.70g, 8 mmol) in a flask flushed with dry nitrogen. A white precipitate formed after 3 hours. Recrystallization from ethanol/water (3/1) gave white crystals of m.p. 176-178°C.

- **3-Benzyl-3-bromo-2-imino-3-tellurapipерidine (VII)**

  An excess of freshly distilled benzelbromide (1.70g, 8 mmol) in a flask flushed with dry nitrogen. A yellow precipitate formed after 5 hours. Recrystallization from ethanol/water (3/1) gave yellow crystals of m.p. 201-203°C.

- **3-Phenacyl-3-bromo-2-imino-3-tellurapipерidine (VIII)**

  A mixture of 2-imino-3-tellurapipерidine (1.70g, 8mmol) and phenacyl bromide (8 mmol) in ethanol (50 ml) was stirred in a flask flushed with dry nitrogen. A pale yellow precipitate formed after 3 hours. The precipitate was filtered off, washed with water, rinsed with acetone, and air dried. Recrystallization from isopropyl alcohol gave pale yellow crystals of m.p. 189-190°C.

The melting points, the elemental analysis of compounds I-VIII are listed in Table I.

**Results and Discussion:**

Tellurocyanate route to heterocyclic tellurium salt is one of the simplest and most efficient routes for the preparation of 2-imino-3-tellurapipерidine and its derivatives (3,3-dihalide and 3-organyl-3-halide). Addition of 1-amino-3-chloropropane to potassium tellurocyanate [14] gives a novel heterocyclic tellurium compound (I) containing nitrogen. Treatment of (I) with halogen or thionyl chloride afforded the corresponding dihalides in 70-86% yield. Its treatment with alkyl halide as the oxidants afforded the corresponding (V-VIII) in 25-72 % yield. All compounds are soluble in DMF and DMSO, their physical properties and elemental analysis are listed in Table I. The infrared spectra (KBr disc) of all compounds show two bands in the range 540-425 cm⁻¹ due to $\nu$(Te-Calkyl) and $\nu$(Te-CH$_3$) as shown in Table I. The IR spectra for solid (VIII) showed a $\nu$(C=O) band at 1660 cm⁻¹. The slight lowering of the $\nu$(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 a symmetrical bidentate ligand [2]. The imino group showed medium band in the range 3260-3320 cm⁻¹. Other characterized bands are shown in Table I.
$^1$HNMR spectra for compound I was measured in CDCl₃. This compound gave multiple signals at δ 3.1-3.8 integrates to four protons due to $C_4$ and $C_6$. The signals were shifted when compound (I) was oxidized by SOCl₂, Br₂, I₂ or alkyl halide to the organotellurium (IV) derivatives. Table 2 shows two sets of aliphatic signals, one due to the alkyl group attached to tellurium and the other due to the methylene in the ring protons.

Compounds VII and VIII gave complex aryl proton signals at δ 7.0 – 8.15 and broad signal due to NH protons at the range δ 6.5 – 9.25 for all compounds. The resulting spectrum shows that the intensities of line (N-H) for amino proton and (=N-H) for imino proton of the unsymmetric species are equal because of the tautomerization shown in Figure 1. The results are summarized in Table 2.

The molar conductance values (Table 2) for all compounds (except compound (I) which is not an electrolyte) give good indication for the suggested reaction mechanism via the coordination of the halogen or alkyl halide with tellurium giving organotellurium (IV) derivatives.

Interpretation of characteristic parameters of an electrolyte solution from conductance data in $10^{-3}$ mol. L.⁻¹ of DMF and DMSO showed that the values in Table 2 approach those expected for 1:1 electrolytes in both solvents. [1-4,15]. Plots of (ohm⁻¹. cm². mol⁻¹) against (concentration)¹/² for compounds II-VIII, showed a typical behavior of weak electrolytes. Fig.2 is the plot for compound II. It is represented as an example of the plots. As it is well known [5] that the conductivity of the stable cyclic tellurium salts depends on the nature of the counter anion. It appears that there is an ion-pair interaction between the anion and the tellurium cation.

\[
\text{H}_{2}\text{N} - \text{CH}_2 - \text{CH}_2 - \text{Cl} + \text{KteCN} \xrightarrow{\text{Dry DMSO}}
\]

\[
\begin{align*}
\text{H}^+ &- \text{N-H} \\
\text{Te} \quad \text{C} & \\
\text{N} \quad \text{N} & \\
\text{R} & \\
\text{X} & \\
\text{N} & \\
\text{H} &
\end{align*}
\]

(II: R = Cl⁻, X = Cl⁻;
IIV: R = Br⁻, X = Br⁻;
IV: R = I⁻, X = I⁻);

V : R = CH₃, X = I⁻;
VI : R = CH₂CH₂, X = Br⁻;
VII : R = PhCH₂, X = Br⁻;
VIII : R = PhCOCH₂, X = Br⁻).

\textbf{Scheme 1: Methods of preparation of new cyclic telluride and its derivatives.}

668
복합 및 종합의 전기물성의 위해 있는 비환원 전화의 폐쇄

عمار يعو

ملخص

تضمن البحث تحضير سلسلة جديدة من مركبات التلوريوم العضوية الحلقية حيث تم تحضير التلورید الحلقي الجديد 2 - ايميتو - 3 تلوروبريدين من مفاعل 1 - ايميتو - 3 - كلاكروبيريان مع C₄H₄N₂TeCl(R)X تلوروسينينتيل والبولسوم ومجموعة سلسلة جديدة من مركبات التلوريوم من نوع حيث = بثيل واثيل ونيليل وفيفينيل و X = كلور أو بروم او يود. وقد شُكِّرت هذه المركبات ودرست اطية الشعكة تحت الحمارة وأطيف الزيني الهيرو المخاطيسي وتبّحيل العقاق DMSO و DMF وكذلك تحت دراسة التوصيلية المولارية لمركبات التلوريوم في مذبي C.H.N حيث تسلك سلوك الكثربليت ضعيفة.

References


669


### Table 1. Analytical data and IR data for compounds [I – VIII].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
<th>Anal. Found (wt%)</th>
<th>Calc. (wt%)</th>
<th>IR (cm⁻¹)</th>
<th>Other selected bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Yellow</td>
<td>78-80</td>
<td>74</td>
<td>12.9</td>
<td>15.8</td>
<td>3250 s</td>
<td>3270 w 530-490 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(22.7)</td>
<td>(24.9)</td>
<td>1520 w</td>
<td>1530 w 1450 w 1360 w 1120 w</td>
</tr>
<tr>
<td>II</td>
<td>White</td>
<td>87-85</td>
<td>70</td>
<td>17.1</td>
<td>9.5</td>
<td>3270 s</td>
<td>3270 w 530-475 s 1300 s 930 w 1450 w 1360 w 1000 s 350 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(18.9)</td>
<td>(12.8)</td>
<td>1360 w</td>
<td>1360 w 1320 w 1080 w 1040 w</td>
</tr>
<tr>
<td>III</td>
<td>Pale yellow</td>
<td>112-113</td>
<td>88</td>
<td>12.5</td>
<td>2.5</td>
<td>45 w</td>
<td>3250 w 3200-4250 s 2650 s 1850 w 1450 w 1360 w 1000 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(12.9)</td>
<td>(7.5)</td>
<td>1300 s</td>
<td>1300 w 1280 s 1260 s 1180 w 1060 w</td>
</tr>
<tr>
<td>IV</td>
<td>Orange</td>
<td>121-123</td>
<td>76</td>
<td>10.4</td>
<td>6.2</td>
<td>3250 w</td>
<td>3250 w 530-460 w 1310 w 1300 w 1280 w 1075 w</td>
</tr>
<tr>
<td>V</td>
<td>White</td>
<td>159-154</td>
<td>95</td>
<td>17.3</td>
<td>7.5</td>
<td>45 w</td>
<td>3200 w 5200-4700 s 1270 w 1350 w 1450 w 1300 s 1100 s</td>
</tr>
<tr>
<td>VI</td>
<td>White</td>
<td>176-178</td>
<td>82</td>
<td>23.1</td>
<td>8.5</td>
<td>3220 s</td>
<td>3220 w 530-450 w 1285 w 1260 w 1450 w 1370 w 1140 w</td>
</tr>
<tr>
<td>VII</td>
<td>Pale yellow</td>
<td>201-203</td>
<td>72</td>
<td>35.9</td>
<td>7.1</td>
<td>3250 w</td>
<td>3250 w 5250-4600 w 1280 w 1450 w 1560 w 1460 w 1050 w</td>
</tr>
<tr>
<td>VIII</td>
<td>Pale yellow</td>
<td>169-190</td>
<td>67</td>
<td>34.8</td>
<td>7.3</td>
<td>3250 w</td>
<td>3250 w 5250-4600 w 1290 w 1350 w 1300 w 1460 w 1050 w</td>
</tr>
</tbody>
</table>

### Table 2. ¹H NMR data and Conductivity data for the new organotellurium (IV) compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shifts (ppm)*; DMSO-δ ppm</th>
<th>¹H NMR * (DMSO)* (\text{M} \cdot \text{cm}^2 \text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.29 (CH₃, s, 2H) 3.45 (CH₃, t, 2H) 6.3 (NH, s, 2H)</td>
<td>46.20 86.21</td>
</tr>
<tr>
<td>II</td>
<td>2.3-3.05 (CH₃, m, 2H) 3.35 (CH₃, s, 2H) 8.5 (NH, s, 2H)</td>
<td>59.25 89.56</td>
</tr>
<tr>
<td>III</td>
<td>2.30-4.14 (CH₃, m, 2H) 3.8 (CH₃, s, 2H) 9.3 (NH, s, 2H)</td>
<td>62.56 92.57</td>
</tr>
<tr>
<td>IV</td>
<td>2.4-3.3 (CH₃, m, 2H) 5.9 (CH₃, t, 4H) 6.35 - 7.5 (NH, s, 2H)</td>
<td>35.86 60.64</td>
</tr>
<tr>
<td>V</td>
<td>2.2 (CH₃, s, 2H) 2.7-3.2 (CH₃, m, 4H) 3.48 (C, s, 4H) 9.3 (NH, s, 2H)</td>
<td>37.38 77.38</td>
</tr>
<tr>
<td>VI</td>
<td>1.13 (CH₃, s, 2H) 1.15 (CH₃, m, 2H) 5.25-5.30 (CH₃, m, 2H) 3.3 (CH₃, s, 2H) 7.5 (NH, s, 2H)</td>
<td>32.34 88.75</td>
</tr>
<tr>
<td>VII</td>
<td>4.1 (CH₃, m, 2H) 2.2 (CH₃, s, 2H) 3.45 (CH₃, t, 4H) 3.14 (CH₃, s, 2H)</td>
<td>30.91 84.57</td>
</tr>
<tr>
<td>VIII</td>
<td>4.3 (CH₃, s, 2H) 2.25-3.35 (CH₃, m, 2H) 3.12 (CH₃, t, 4H) 6.9 (CH₃, s, 2H)</td>
<td>30.91 84.57</td>
</tr>
</tbody>
</table>

* a 10⁻¹ M solution; R₅NC₁ MX (DMSO) 40 M, DMF 95 ohm⁻¹ cm² mol⁻¹
Fig. 1: Tautomerization of compound I.

Fig. 2: Plot of $\Lambda$ vs. (concentration)$^{1/2}$ for compound II.