Synthesis & Characterisation of Organotellurium Compounds of Phenacyl Bromide

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Received 24 August 1987; revised and accepted 4 January 1988

Diphenacyltellurium dihalides, dipseudohalides, dioximes, aniline/piperidine dithiocarbamate derivatives and adducts with some nitrogen donors have been synthesised and characterised. The tetracoordinated organotellurium compounds exhibit keto-enol tautomerism with enol form being present to the extent of (~50%) while the hexacoordinated tellurium adducts exist in the keto form. The proton of the enol form and hydroxyl proton of oximino derivative seem to be attached to the lone pair of tellurium atom forming novel Te-H bonds.

In continuation of our earlier studies, we now report the synthesis and characterisation of some novel organotellurium dihalides, dipseudohalides, dioximes and adducts with some nitrogen donors. Dibenzytellurium compounds have been found to be less stable under the experimental conditions while the diphenacyltellurium derivatives were found to be highly stable, probably due to the presence of the carbonyl group adjacent to the methylene group.

The compounds prepared in the present study are summarised in Table 1.

Diphenacyltellurium dibromide (I) and diiodide (II)

A mixture of phenacylbromide (3.98 g; 0.02 mol) and tellurium metal powder (1.27, 0.01 g. atom) for (I) and sodium iodide (3.00 g; 0.02 mol) for II was heated on a water bath for 14-18 hr. The residue was repeatedly extracted with chloroform/acetone and the compounds were recrystallised from chloroform-acetone-pet. ether (1:1).

Diphenacyltellurium derivatives (III-XIII)

Pseudohalides (III,IV) and aniline/piperidine dithiocarbamate derivatives (V,VI) were prepared by taking a mixture of II (0.619 g; 0.001 mol) and freshly prepared silver salt of thiocyanate/cyanate or ammonium salt of aniline/piperidine (0.002 mol) and refining for ~ 10 hr/refluxing in dry dichloromethane for ~ 6 hr. The separated product was recrystallised from chloroform-pet. ether.

The characterisation data of the compounds are given in Table 1. All the melting points are uncorrected. The IR spectra were recorded in CsI on a Perkin Elmer 577 instrument. The 1H NMR spectra were recorded in CDCl3 on a Varian EM 360L instrument using TMS as an internal reference (chemical shifts are given in δ scale). Silica gel G (GLAXO) was used for TLC.

The IR spectra of compounds (I-XIII) (Table 1) showed characteristic peaks at 1740-1680 cm⁻¹ (C=O). Compound IV showed a peak at 2230 cm⁻¹ due to the C≡N frequency, indicating that the cyan group was covalently bonded to the tellurium metal. The IR spectrum of dithiocyanato compound (III) showed peaks at 2110, 760 and 465 cm⁻¹, characteristic of nitrogen bonded NCS group with the tellurium metal. In the diphenacyltellurium diaminodithiocarbamate (V) and the corresponding piperidino
### Table 1—Characterisation Data of Diphenyltellurium Derivatives

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Mol. formula</th>
<th>m.p. (^\circ)C</th>
<th>Colour</th>
<th>Found (Calc.)</th>
<th>(\nu)Te-H</th>
<th>(\nu)C-O</th>
<th>(\nu)Te-C</th>
<th>(\nu)Te-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C(<em>{16})H(</em>{10})O(<em>{2})TeBr(</em>{2})</td>
<td>130(d)</td>
<td>Brown (65)</td>
<td>24.19, 36.48 (26.52)</td>
<td>2.63</td>
<td>--</td>
<td>2310</td>
<td>1680</td>
</tr>
<tr>
<td>II</td>
<td>C(<em>{16})H(</em>{10})O(<em>{2})TeI(</em>{2})</td>
<td>160(d)</td>
<td>Violet (60)</td>
<td>20.50, 30.92 (30.98)</td>
<td>2.23</td>
<td>--</td>
<td>2315</td>
<td>1700</td>
</tr>
<tr>
<td>III</td>
<td>C(<em>{14})H(</em>{10})O(<em>{2})Te(</em>{2})</td>
<td>115</td>
<td>White (45)</td>
<td>26.42, 44.83 (44.85)</td>
<td>2.86</td>
<td>5.78</td>
<td>2300</td>
<td>1690</td>
</tr>
<tr>
<td>IV</td>
<td>C(<em>{16})H(</em>{10})O(_{2})Te</td>
<td>127</td>
<td>White (50)</td>
<td>30.50, 51.65 (51.72)</td>
<td>3.22</td>
<td>6.64</td>
<td>2320</td>
<td>1710</td>
</tr>
<tr>
<td>V</td>
<td>C(<em>{30})H(</em>{26})O(<em>{2})TeS(</em>{4})</td>
<td>148</td>
<td>Dark yellow (55)</td>
<td>18.14, 51.28 (51.31)</td>
<td>3.65</td>
<td>3.92</td>
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<td>1685</td>
</tr>
<tr>
<td>VI</td>
<td>C(<em>{28})H(</em>{26})O(<em>{2})TeS(</em>{4})</td>
<td>130</td>
<td>Yellow (60)</td>
<td>16.58, 49.07 (49.00)</td>
<td>4.92</td>
<td>4.00</td>
<td>2315</td>
<td>1690</td>
</tr>
<tr>
<td>VII</td>
<td>C(<em>{16})H(</em>{14})O(_{2})Te</td>
<td>110</td>
<td>Light brown (45)</td>
<td>34.86, 52.45 (52.51)</td>
<td>3.80</td>
<td>--</td>
<td>2300</td>
<td>1710</td>
</tr>
<tr>
<td>VIII</td>
<td>C(<em>{16})H(</em>{16})O(_{2})Te</td>
<td>148</td>
<td>Cream (50)</td>
<td>19.60, 29.48 (29.65)</td>
<td>2.39</td>
<td>4.30</td>
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<tr>
<td>IX</td>
<td>C(<em>{16})H(</em>{14})O(_{2})Te</td>
<td>134</td>
<td>White (55)</td>
<td>32.19, 48.50 (48.53)</td>
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<td>7.00</td>
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<tr>
<td>X</td>
<td>C(<em>{24})H(</em>{18})O(_{2})Te</td>
<td>184</td>
<td>Choclate brown (65)</td>
<td>19.06, 43.11 (43.13)</td>
<td>4.72</td>
<td>4.14</td>
<td>--</td>
<td>1710</td>
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<tr>
<td>XI</td>
<td>C(<em>{26})H(</em>{16})N(<em>{2})TeBr(</em>{2})</td>
<td>172</td>
<td>Brown (70)</td>
<td>18.72, 45.59 (45.64)</td>
<td>3.46</td>
<td>4.04</td>
<td>--</td>
<td>1740</td>
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<tr>
<td>XII</td>
<td>C(<em>{26})H(</em>{16})N(<em>{2})TeBr(</em>{2})</td>
<td>204</td>
<td>Light brown (60)</td>
<td>18.28, 44.79 (44.85)</td>
<td>5.12</td>
<td>3.96</td>
<td>--</td>
<td>1690</td>
</tr>
<tr>
<td>XIII</td>
<td>C(<em>{24})H(</em>{18})O(_{2})TeBr</td>
<td>163</td>
<td>Dark brown (55)</td>
<td>18.17, 41.10 (41.16)</td>
<td>4.54</td>
<td>3.91</td>
<td>--</td>
<td>1680</td>
</tr>
</tbody>
</table>

Notes:

I. For compound (VI), a single peak at 960 and 980 cm\(^{-1}\) respectively due to \(\nu\)CSS indicated their monodentate nature\(^{10}\). The IR spectra of halides (I,II), pseudohalides (III,IV) and telluride (VII) exhibited bands at 1710-1680 cm\(^{-1}\) (\(\nu\)C=O), tertiary C-H bending at 1350-1310 cm\(^{-1}\), \(\nu\)OH at 3490-3410 cm\(^{-1}\) and OH bending vibrations (1390-1370) indicating the partial conversion of keto form into enol (\(~50\%\)). The appearance of a new band around 2300 cm\(^{-1}\) is due to Te-H (enolic) bond\(^{5.11}\). The intensity ratio between the peaks originating from the C = O and OH groups seems to depend also on the nature of the anion attached to tellurium atom.

The IR spectra of oximino derivatives (VIII, IX) showed \(\nu\)C=N (oxime) at 1650 cm\(^{-1}\) and \(\nu\)OH (bonded) at 3310 cm\(^{-1}\) indicating the presence of oxime function in the compounds. A new peak occurring in (IX) at 2330 cm\(^{-1}\) is assigned to \(\nu\)Te-H\(^{6}\) (oximino OH) mode. The IR spectra of adducts (X-XIII) showed strong bands due to \(\nu\)C = O and \(\nu\)C-H whereas \(\nu\)OH bands were completely absent indicating presence of purely keto function. The donor molecules, viz., pyrrolidine, pyridine, piperidine and morpholine exhibited bands in the range 3400-3170 cm\(^{-1}\), attributable to \(\nu\)NH mode. The spectra of adducts showed, in general, an appreciable lowering of the characteristic peaks due to the coordination with tellurium atom, but in the case of adduct with pyridine there was a positive shift in the pyridine ring stretching vibrations\(^{12}\) which was indicative of back bonding from tellurium atom to pyridine through the formation of an extensive \(\pi\) bonding. In the far IR region, bands due to \(\nu\)Te-C\(^{13}\), \(\nu\)Te-N\(^{14}\) and \(\nu\)Te-S\(^{15}\) appeared at 535-510, 425-410 and 280-270 cm\(^{-1}\), respectively.

In the \(^1\)H NMR spectra of compounds (I—VII), aromatic protons appeared as multiplets in the region \(\tau\)3.2-1.6, while in the adducts (X—XIII) these were deshielded (\(\tau\)1.2-0.6) probably due to the steric hindrance by the donor molecules around the tellurium atom. The OH proton of the enol form (\(~50\%) attached to the lone pair of tellurium atom, forming a
novel Te-H bond\textsuperscript{15,16}, gave a singlet between \(\tau\) 10 and 9.2. The methylene protons appeared in the regions \(\tau\) 7.9-7.3 and \(\tau\) 7.1-6.6; probably the drift in the electron density around tellurium atom changes the electronic environment of the adjacent methylene groups. The spectra of adducts showed only one signal for two methylene protons and no signal was observed for Te-H bond.

The \(^1\)H NMR spectrum of oximino derivatives (VIII) showed aromatic multiplets between \(\tau\) 2.8 and 2.2 and broad singlet at \(\tau\) 3.8 due to OH proton whereas the oximino derivative (IX) from telluride, in which the bulky iodine atoms had been removed, showed phenyl protons as multiplets between \(\tau\) 2.8 and 1.8 and two singlets, one at \(\tau\) 3.1 due to OH proton and another at \(\tau\) 8.9 due to Te-H proton. The steric hindrance exhibited by the bulky iodine atoms prevented the formation of Te-H bond\textsuperscript{6} in derivative (VIII).

Thanks are due to Dr R S Kapil, CDRI, Lucknow for providing spectral facilities and Dr Mohd. Athar, ITRC, Lucknow, for helpful discussions.

References