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Raman and Ir Spectra of Carbonyl Functionalized Z-Vinyllic Tellurides: Additional Evidences of the Intramolecular Tellurium-Oxygen Interaction

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Several carbonyl functionalized Z-vinyllic tellurides were synthesized. Infrared spectra of compounds **1** showed a peculiar pattern. Appreciable shifts to lower wavenumbers for both the $\nu_{C=C}$ and $\nu_{C=O}$ modes, as well as extensive mixing of such modes were observed. This behaviour could be rationalized in terms of a proposed Te-O interaction.

Keywords: vinyllic substitution; Z-functionalized vinyllic tellurides; infrared and Raman spectroscopy; intramolecular Te-O interaction

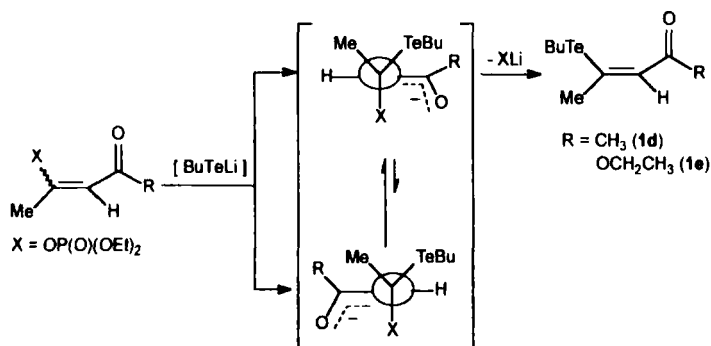
INTRODUCTION

Organo tellurium compounds have awakened considerable interest over recent years due to their applications in organic synthesis^[1,2] and as precursors of semiconductors or materials.^[3] Notwithstanding such interest very few of them were the subject of more detailed spectroscopic investigations, particularly Raman and IR. In fact some dialkyl tellurides have been characterized by vibrational spectroscopy over recent years,^[4] but this is not the case for the more complex functionalized tellurides, where more specific interactions are present. In particular, the intramolecular through space interaction of tellurium and oxygen atoms in several classes of organo tellurium compounds has been postulated as responsible for their stereochemistry,^[5] as seems to be the case for ketovinyllic tellurides.

In a recent publication, some of us^[5] reported a new method for the preparation of tri and tetrasubstituted vinyllic tellurides from β -dicarbonyl compounds, noting that only the Z isomer is formed. Such behavior can be rationalized on basis of a through space interaction of the carbonyl oxygen with the tellurium atom, as shown schematically in Scheme 1 for a particular compound of this family.

In a recent paper^[7] calculations were performed for a series of β -chalcogenovinylaldehydes, in close agreement with the experimentally observed peculiarities of the O \rightarrow chalcogen (S, Se, Te) interactions. In particular, the authors highlight the fact that for some of the carbonyl vinyllic tellurides the calculated O-Te distance is almost coincident with that of a normal covalent Te-O bond, i.e., 2.08-2.10Å. With such motivation we decided to investigate the vibrational spectra of a series

of carbonyl vinylic tellurides, displaying some distinctive features that in our view represent additional evidences of the previously mentioned interaction.



SCHEME 1: The trough space interaction involving tellurium and oxygen as responsible for the Z-stereochemistry.

EXPERIMENTAL

The synthesis of **1** and of several other members of the series was reported recently.^[6]

The IR spectra were obtained for the neat liquid in a FTIR Perkin-Elmer 2000 spectrophotometer, as a film between KBr windows.

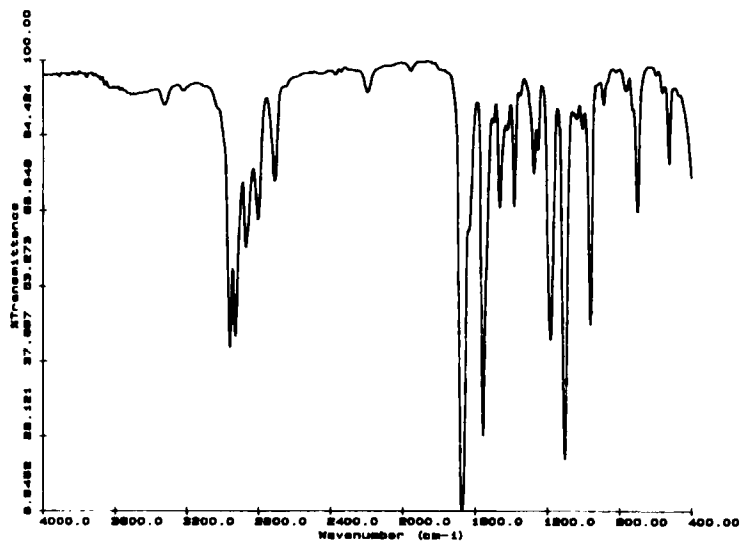
The Raman spectra were obtained in a Renishaw microRaman spectrometer using the 514.5 nm line from an Ar⁺ laser for excitation. The power was kept at ca. 10 nW to prevent local heating of the deep yellow sample, and the possibility of photodecomposition was

discarded by the reproductibility of several spectra obtained in 10 sec intervals.

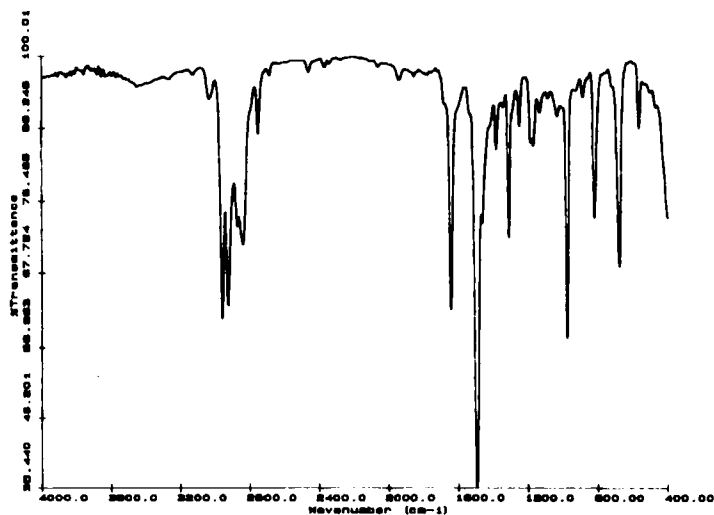
RESULTS AND DISCUSSION

Some years ago, carbonyl functionalized vinylic tellurides **2** were prepared from the corresponding propyolic aldehyde.^[8] The analysis of the IR spectrum of a *E*-vinylic telluride (**2a**, Figure 1a), showed the usual relative intensities pattern for the C=C and C=O stretching vibration absorption bands; however, when the stereochemistry is *Z* (**2b**, Figure 1b), an important change on the relative intensities of these bands was observed, suggesting the occurrence of some intramolecular interaction that would be responsible for modifying the vibrational modes of the molecule.

In analogy, we found out that other carbonyl functionalized *Z*-vinylic tellurides **1a-i** showed the same pattern. The corresponding wavenumber values are listed in Table 1, together with a tentative assignment of the more characteristic modes. As representative examples, the IR and Raman spectra of **1d** and **1e** (see Figure 3 and 4) will be discussed in further detail.



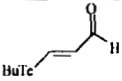
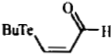
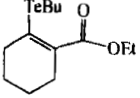
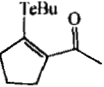
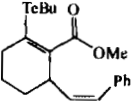
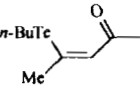
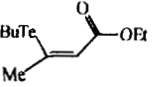
2a



b

FIGURE 1. IR spectra of **2a** and **2b**

TABLE 1: IR data for functionalized vinylic tellurides.

Telluride	Wavenumber (cm ⁻¹)	Absorbance (%)	Tentative assignment
	1673	96	ν _{C=O}
2a	1553	66	ν _{C=C}
	1642	21	ν _{C=O}
2b	1493	46	ν _{C=C}
	1678	16	ν _{C=O}
1a	1566	28	ν _{C=C}
	1635	30	ν _{C=O}
1b	1522	36	ν _{C=C}
	1676	14	ν _{C=O}
1c	1556	22	ν _{C=C}
	1614	17	ν _{C=O}
1d	1518	21	ν _{C=C}
	1682	35	ν _{C=O}
1e	1577	33	ν _{C=C}

 1f	1647	17	$\nu_{C=O}$
	1527	26	$\nu_{C=C}$
 1g	1638	17	$\nu_{C=O}$
	1528	24	$\nu_{C=C}$
 1h	1634	15	$\nu_{C=O}$
	1520	26	$\nu_{C=C}$
 1i	1607	85	$\nu_{C=O}$
	1554	53	$\nu_{C=C}$

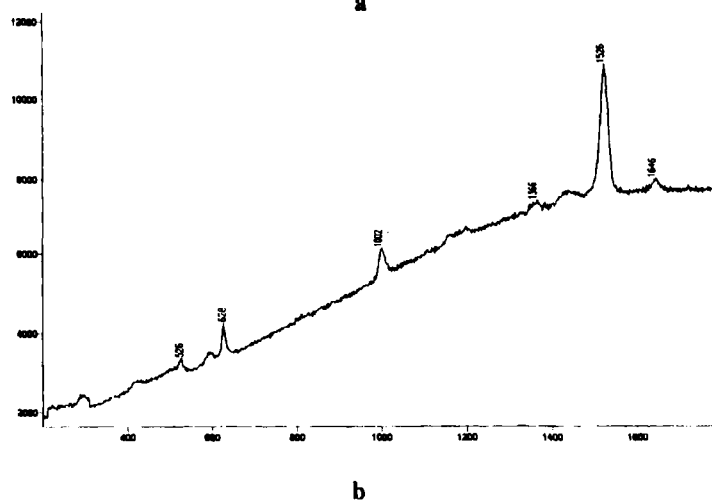
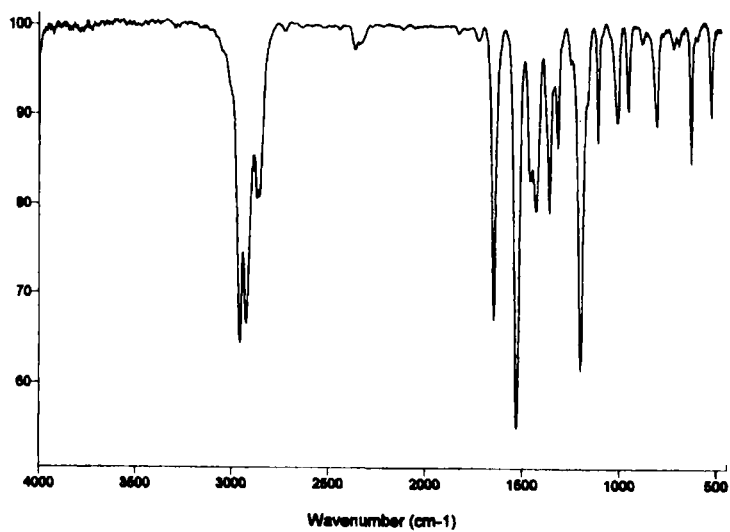
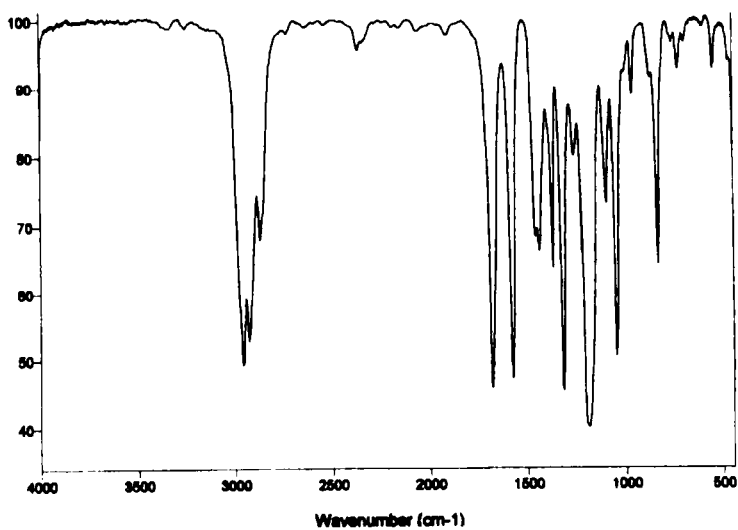
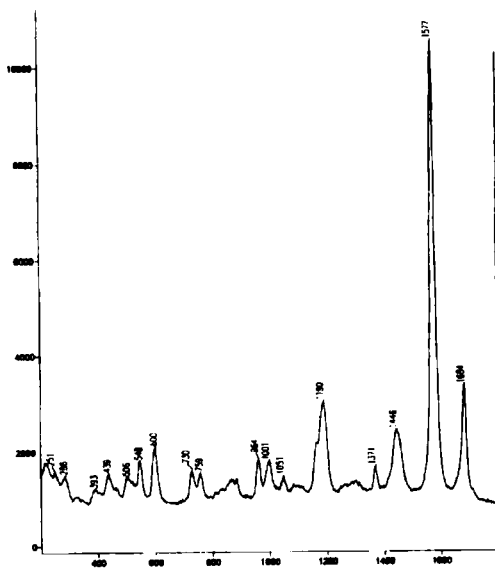


FIGURE 2. IR (a) and Raman (b) spectra of **1d**.



2



b

FIGURE 3. IR (a) and Raman (b) spectra of 1e.

An examination of Figure 2 and 3 reveals some distinctive features of the vibrational spectra of **1d** and **1e**, i.e.:

1) The wavenumbers of the bands assignable to the $\nu_{(\text{C}-\text{C})}$ and $\nu_{(\text{C}=\text{O})}$ are substantially lower than for analogous compounds where Te is replaced by O or S.

2) The relative intensities of the bands assignable to $\nu_{(\text{C}-\text{C})}$ and $\nu_{(\text{C}=\text{O})}$ do not follow the usual pattern, that is, the $\nu_{(\text{C}=\text{O})}$ mode is more intense than the $\nu_{(\text{C}=\text{C})}$ mode.

On the other hand, the Raman spectra show the expected pattern of relative intensities, with the $\nu_{(\text{C}=\text{C})}$ mode being more intense than the $\nu_{(\text{C}=\text{O})}$ one.

It is well known that alternate $-\text{C}=\text{C}-$ and $-\text{C}=\text{O}$ moieties greatly favor the extensive mixing of the corresponding vibrational modes, the typical example being *p*-benzoquinone, where normal coordinate calculations reveal almost 50% to 50% composition for the $\nu_{(\text{C}-\text{C})}$ and $\nu_{(\text{C}=\text{O})}$ modes. A similar situation seems to be present in the case of compound **1**. If one considers that a rather strong Te-O interaction is present, leading to a five member ring, as depicted in Figure 4, and that such a structure is stabilized by charge transfer $\text{O} \rightarrow \text{Te}$ interaction and by the π electron delocalization over the ring, a reduction in the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bond orders can be anticipated.

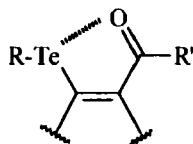


FIGURE 4. Proposed interaction between Te and O atoms.

In this way, the appreciable shifts to lower wavenumbers for both the $\nu_{(C=C)}$ and $\nu_{(C=O)}$ modes, as well as the extensive mixing of such modes can be rationalized in terms of the proposed Te-O interaction.

It should also be pointed out that for a series of carbonyl vinylic tellurides the IR spectra show the $\nu_{(C=C)}$ and $\nu_{(C=O)}$ modes as bands of comparable intensities and in some cases the former as a stronger band.

On the other hand, for all the investigated compounds the Raman spectra show, consistently, the $\nu_{(C=C)}$ as a stronger band (ca. 10 times), that is, the normal pattern for carbonylic compounds bearing $-C=C$ bonds.

In conclusion, it seems reasonable to attribute the peculiar observed effects on dipole moments to a Te-O interaction, rather than to polarizability counterparts, although confirmation of such hypothesis will require further detailed investigation.

ACKNOWLEDGMENTS

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References

- [1] N. Petragnani, *Tellurium in Organic Synthesis*, Best Synthetic Methods, Academic Press: London, U.K., 1994.
- [2] R.E. Barrientos-Astigarraga and J.V. Comasseto, *Aldrichimica Acta* **33**, 66 (2000).
- [3] V.J. Minkin, I.D. Sadekov, B.B. Rivkin, A.V. Zakharov, V.L. Nivorozhkin, E. Kompan and Y.T. Struchkov, *J. Organomet. Chem.* **233**, 536 (1997).
- [4] K. Karaghiosoff, T.M. Klapötke, B. Krumm and O.P. Ruscitti, *J. Organomet. Chem.* **577**, 69 (1999) and references cited therein.
- [5] V.J. Minkin, I.D. Sadekov, B.B. Rivkin, A.V. Zakharov, V.L. Nivorozhkin, O.E. Kompan and Y.T. Struchkov, *J. Organomet. Chem.* **536**, 233 (1997).
- [6] R.E. Barrientos-Astigarraga, C.Y. Sumida, P. Castelani and J.V. Comasseto, *Tetrahedron Lett.* **40**, 7717 (1999).
- [7] R.M. Minyaev and V.I. Minkin, *J. Can. Chem.* **76**, 776 (1998).
- [8] L.H.S. Rahmeier and J.V. Comasseto, *Organometallics* **4**, 671 (1997).