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Revisiting the addition reaction of $TeCl_4$ to alkynes: The crystal structure and docking studies of 1-chloro-2-trichlorotelluro-3-phenyl-propen-2-ol

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Abstract

Tellurium tetrachloride adds to alkynes via two pathways: a concerted *syn* addition, that yields *Z*-tri- and tetra-substituted alkenes or by an *anti* addition that yields *E*-alkenes. The mechanistic aspects of these divergent pathways have been reevaluated at the light of crystallographic data. The molecules, of the title compound, in the crystal, are associated in a helical fashion with a Te…Te pitch of 6.3492(6) Å. As it exhibits inhibitory activity for cathepsin B and in order to gain more insight of the inhibition mechanism, a docking study was undertaken providing insight on why organic telluranes are more efficient inhibitors than inorganic ones as AS-101.

Keywords: Tellurium tetrachloride; Electrophilic addition; Docking; Cathepsin B; Supramolecular self-assembly

1. Introduction

Recent developments in organic tellurium chemistry have been focused in organotellurium (II) compounds, which have been applied mainly as ligands in transition metal chemistry [1], polymerization catalysts [2], anti-oxidant agents [3] and key synthetic intermediates [4]. Tellurium (IV) compounds, which were intensely studied at the beginning of the development of the organotellurium chemistry [5], in recent years have received less attention. We have found that organotellurium trihalides, specially trichlorides, which are the most intensely studied class of organotellurium (IV) compounds [4c,5], react with aryl alkynes to yield *Z*-vinylic tellurides [6]. Recently, we disclosed new aspects of this transformation, showing that whereas aryltellurium trichlorides react with aromatic alkynes in a *syn*-fashion to give *Z*-vinylic tellurides, reactions with 3-hydroxyalkynes **1** give either the cyclic telluranes **3** or **4** depending on the nature of the substituents at C_3 (Scheme 1) [7]. The cyclic telluranes **3** and **4** are formed likely owing to ring opening of a tellurenium intermediate **2** by the chloride anion, in a stepwise mechanism closely related to that of electrophilic addition of bromine to alkynes [8].

This new synthetic route to cyclic telluranes gained in importance as we have recently demonstrated that **3** and

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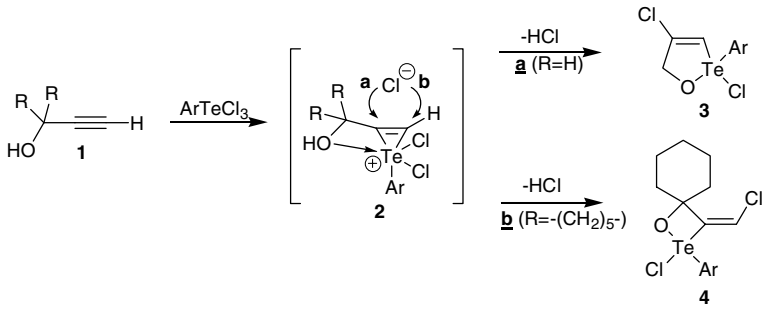


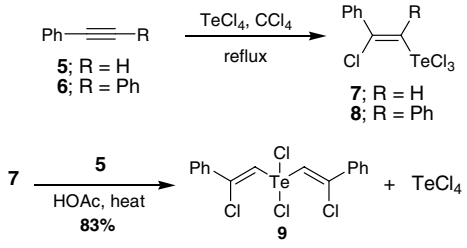
Scheme 1.

4 are efficient inhibitors of human cathepsin B [9]. Tellurium tetrachloride ($TeCl_4$) has been usually found to react similarly to $ArTeCl_3$, both acting as electrophiles in additions to aryl-, alkenyl- and alkynyl groups [4e,4f,4g,4h,4i,5]. Based therefore on the rich chemistry so far found for $ArTeCl_3$ and the expected reactivity similarity with $TeCl_4$, as well as the recently found biological activity of some of the Te(IV) derivatives of $ArTeCl_3$ and $TeCl_4$ [9], we investigated the reactivity of tellurium tetrachloride towards alkynes in order to establish the scope and limitations of this reaction. There have been already three reports on the addition of $TeCl_4$ to alkynes.

In the first report, Petragnani and Campos [10] described the reaction of $TeCl_4$ with both phenylacetylene (**5**) and diphenylacetylene (**6**). The vinylic trichloride **7** resulting from the addition of $TeCl_4$ to (**5**) was further transformed into the bis-vinylic tellurium dichloride **9** on heating in AcOH (Scheme 2). Similarly, Zukerman-Schpector and co-workers [11] reported the addition of $TeBr_4$ to **5** which led to the bis-vinylic dibromide analogue of **9** in good yield.

Uemura and co-workers [12], based on the transformation of the originally formed vinylic tellurium trihalides into *Z*-1,2-dihaloalkenes, concluded that the addition of $TeCl_4$ to aryl alkynes and to 3-hydroxy-1-propyne proceeds both via a *syn* process.

Considering the scarce data available for this important addition reaction, and based on our recent findings concerning the addition reaction of *p*-methoxyphenyltellurium trichloride to 3-hydroxy alkynes [6,7] and to our interest in the molecular and supramolecular arrangements in Te(IV) compounds [13–15]. We reevaluated the addition of $TeCl_4$ to alkynes and a compilation of what we learned from the study of these reactions are presented herein. Also, due to the nascent application of organic tellurium (IV) compounds as cysteine proteases inhibitors, a docking study was undertaken using the crystal structure of the title compound with human cathepsin B in order to gain more insight of the inhibition mechanism.



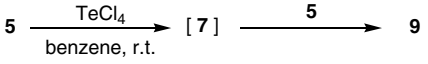
Scheme 2.

2. Results and discussion

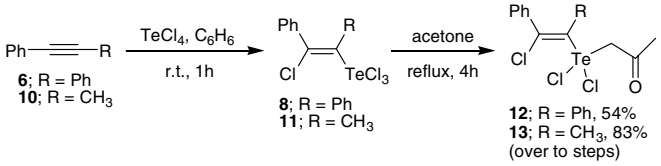
We first re-investigated the reaction of $TeCl_4$ with phenyl acetylene (**5**). The reaction of 1 equiv. of $TeCl_4$ with 1 equiv. of **5** in benzene at room temperature gave **9** in 37% yield (Scheme 2). Although Petragnani and Campos [10] were able to isolate the intermediate **7** we, under the present experimental conditions, could not isolate such intermediate. Using 2 equiv. of **5**, the yield of **9** in this tandem reaction raised to 86% as expected (Scheme 3).

The nascent **7** seems, therefore, to be very reactive, reacting promptly with its precursor **5** even at room temperature to give **9**. An X-ray analysis of **9** [11] confirmed the *syn*-addition of $TeCl_4$ **5** as reported earlier by Uemura [12]. When we reacted $TeCl_4$ with 1-phenyl-1-propyne (**10**) and diphenylacetylene (**6**), no divinyltellurium dichlorides analogous to **9** were formed, and the vinyl tellurium trichloride **8** and **11** were the only isolated products (Scheme 4).

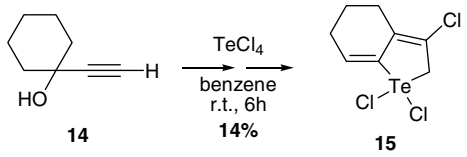
X-ray analysis [16] of **8** confirmed the regio- and stereochemistry proposed by Uemura [12]. Since **8** and **11** are not soluble in common NMR solvents, we prepared diorganotellurium dichlorides derivatives **13** via reaction with excess



Scheme 3.



Scheme 4.



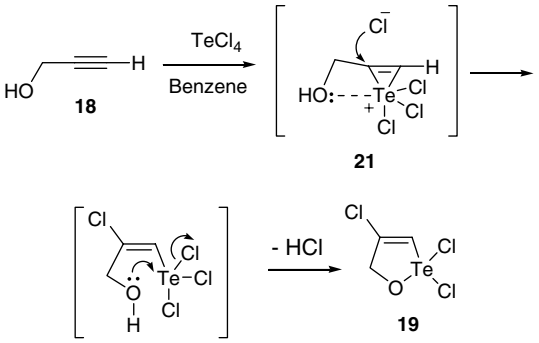
Scheme 5.

of acetone (Scheme 4) [17]. X-ray analysis showed that **13** displays a *Z*-stereochemistry around the C–C double bond [18].

In the reaction of $TeCl_4$ with 1-ethynyl-1-cyclohexanol (**14**), a single and rather unexpected product **15** could be isolated in low yield (Scheme 5), as confirmed by X-ray and spectroscopic methods [19].

As shown in Scheme 6, the alkyl group of **14** allows double bond formation in intermediate **17** upon elimination of water in the acidic reaction medium. In the absence of such alkyl group, common adducts analogous to **16** can be eventually isolated, as we observed for the reaction of $TeCl_4$ with 3-hydroxy-1-propyne (**18**) in benzene. Initially, this reaction gives a crude oil constituted of four products that, by ^{1}H NMR spectroscopy, showed to bear vinylic hydrogens. The major component of the mixture (ca. 58% by ^{1}H NMR) is presumably **19**, which was isolated as its colorless tellurate **20** [20] (Scheme 7) by dissolving the crude oil in absolute ethanol followed by addition of triethylbenzylammonium chloride (TEBAc).

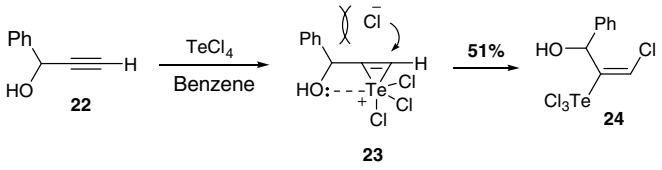
X-ray analysis of the colorless crystals confirmed that indeed **20** is the main product [21], pointing to *anti*-addition of $TeCl_4$ to **18** (Scheme 8). Formation of **20** contrasts therefore with the results of Uemura and co-workers for the same reaction [12], in which a *Z*-stereochemistry for the product resulting from *syn*-addition was reported.



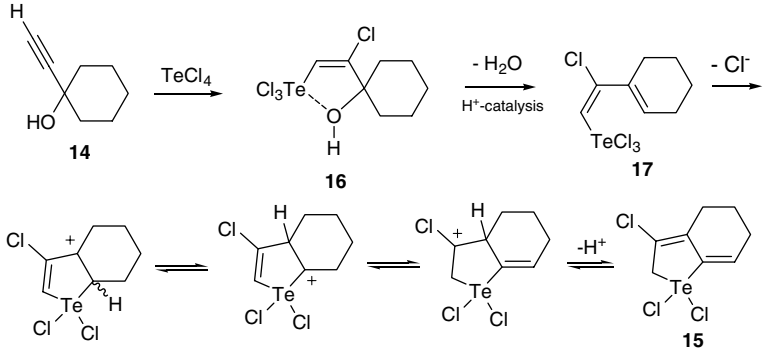
Scheme 8.

Reaction of $TeCl_4$ with 1-phenyl-2-propyn-1-ol (**22**) in benzene at room temperature for 4 h led to an oil, which by crystallization in dry dichloromethane gave colorless crystals identified as the vinylic trichloride **24** (Scheme 9). X-ray analysis confirmed the structure of **24**, showing an interesting and strong intramolecular secondary interaction between the hydroxyl oxygen and the tellurium atom.

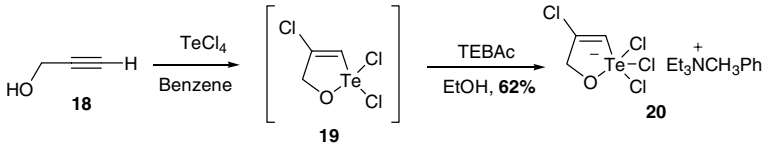
According to the reaction mechanism proposed in Scheme 9, the chloride anion attacks preferentially the non-substituted carbon of the tellurenium (IV) intermediate **23**, probably owing to steric hindrance of the vicinal phenyl group. This hindrance is absent in intermediate **21**



Scheme 9.



Scheme 6.



Scheme 7.

(Scheme 8), which is therefore preferentially attacked by the chloride ion at its substituted carbon.

These findings suggest that $TeCl_4$ indeed reacts with alkynes similarly to *p*-methoxyphenyltellurium trichloride. This similarity is evidenced since they both react with aryl alkynes to form *Z*-vinylic tellurides, whereas reactions with 3-hydroxy alkynes give *E*-vinylic tellurides with structures reflecting the steric demand at the vicinal carbon of the tellurenium ring towards attack of the chloride ion to reaction intermediates, viz., **2** in Scheme 1, **21** in Scheme 8, and **23** in Scheme 9. In their reactions with structurally simple 3-hydroxy alkynes, such as **18** and **22**, acceptable yields of the addition products are obtained, whereas reactions with alkynes prone to carbocation formation and rearrangement give either poor yields of the addition product (1-ethynyl-1-cyclohexanol, **14**) or a complex mixture of products (1-ethynyl-1-cyclopentanol).

3. Crystal structure of Te(IV) trichloride (24)

Details of cell data, X-ray data collection, structure solution and refinement, as well as selected bond distances and angles are given in Tables 1 and 2. A complete list of atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates have been deposited and are available upon request.

Table 1
Crystallographic data and details of the structure refinement of trichloride **24**

Color/shape	Colourless/irregular
Formula	$C_9Cl_4H_8OTe$
Formula weight	401.55
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.441(1)
b (Å)	6.4292(9)
c (Å)	14.755(1)
α (°)	90
β (°)	106.463(9)
γ (°)	90
V (Å°)	1313.7(2)
D_c (Mg m^{-3})	2.030
Z	4
μ (Mo Kα) (mm^{-1})	3.049
Diffractometer/scan	CAD4/$\omega/2\theta$
Radiation/wavelength	Mo Kα/0.71073 Å
F(000)	760
Crystal size (mm)	$0.20 \times 0.15 \times 0.12$
θ Range data collection (°)	1.47–26
Index ranges (*hkl*)	−17/17, −7/0, 0/18
Reflections collected	2676
Independent/observed refls. [$I > 2\sigma(I)$]	2567/1999 ($R_{int} = 0.0185$)
Absorption correction	Ψ-scans
Range of relat. transm. factors	0.711 and 0.581
Refinement method	Full-matrix least-squares on F^2
Data/restraint/parameters	2567/0/136
GOF on F^2	1.104
SHELX-97 weight parameters	0.0293/0.8138
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0249$, $wR_2 = 0.0642$
R indices (all data)	$R_1 = 0.0439$, $wR_2 = 0.0691$
Largest difference in peak and hole (e Å^{-3})	0.357 and −0.326

Table 2
Selected bond distances (Å) and angles (°) for **24**

Te–C(1)	2.119(4)
Te–Cl(1)	2.5022(11)
Te–Cl(2)	2.3262(11)
Te–Cl(3)	2.5045(11)
Cl(4)–C(2)	1.715(4)
C(1)–C(2)	1.327(6)
C(1)–Te–Cl(1)	87.6(1)
C(1)–Te–Cl (2)	95.7(1)
C(1)–Te–Cl (3)	88.6(1)
C(1)–Te–O(1)	58.5(1)
O(1)–Te–Cl(1)	90.96(8)
O(1)–Te–Cl(3)	89.52(8)
Cl(1)–Te–Cl(3)	175.17(4)
Cl(2)–Te–Cl(1)	89.01(4)
Cl(2)–Te–O(1)	154.15(7)
Cl(2)–Te–Cl(3)	88.46(4)

An *E* configuration of the double bond is found for **24** (Fig. 1a), in which the primary geometry about the Te(IV) atom displays the expected disphenoidal (i.e. *pseudo*-trigonal bipyramidal) arrangement in which the Cl(1) and Cl(3) atoms are in axial positions whereas Cl(2) and C(1) are equatorial. It is generally assumed, mainly on the basis of the well known valence-shell electron-pair repulsion (VSEPR) theory [22], that a lone pair occupies a third equatorial position. However, these compounds are seldom monomolecular in the solid state, and they tend to form additional Te···secondary bonds. For **24**, Te(IV) forms one intramolecular secondary bond to the oxygen atom: Te···Ol = 2.476(3) Å, and three intermolecular with chlorine atoms: Te···Cl1^{i} = 3.610(1); Te···Cl2^{ii} = 3.777(1)

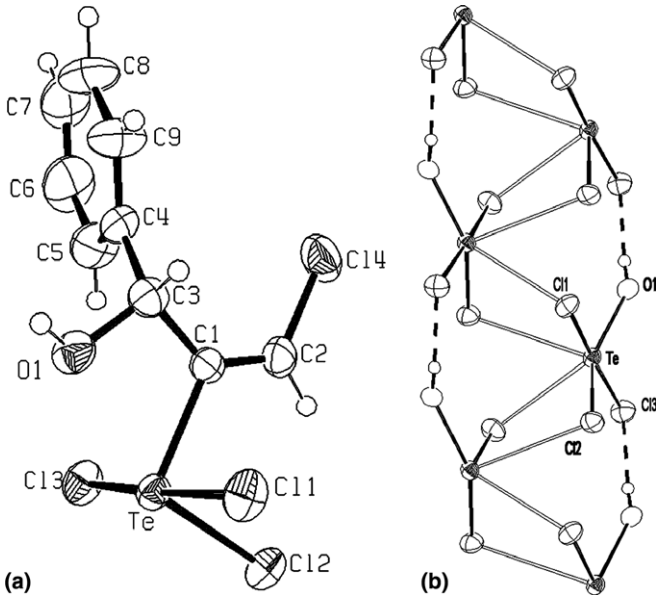


Fig. 1. (a) Projection of trichloride **24** showing the atom labeling. 50% thermal ellipsoids are shown. (b) Supramolecular helicoidal arrangement of **24**.

and Te···Cl4^{iii} = 3.715(1) Å (symmetry operations: (i) = 1 − x, y − 1/2, 1.5 − z; (ii) = 1 − x, 1/2 + y, 1.5 − z; (iii) = x, 1/2 − y, z − 1/2). Owing to the intra- and intermolecular secondary interactions, the polyhedron around the tellurium can be best described as a distorted bicapped octahedron (Fig. 1b) with eight-coordinated tellurium(IV) for which the lone pair is not considered, with O1 capping Cl1–C1–Cl4^{iii} face and Cl2^{ii} capping the Cl1-Cl4^{iii}-Cl1^{i} face. This type of coordination polyhedron is unique and unprecedented [13].

It is worth pointing out that the Te···O1 distance is rather short, indeed a search in the Cambridge Structural Database (CSD version 5.25 plus three updates) [23] using the CONQUEST routine (version 1.6) [24] showed that the shortest Te···O distances found were in 1-ethoxy-2-trichlorotelluro-cycloheptane [25] 2.419 Å and 1-ethoxy-2-trichlorotelluro-cyclohexane [26] 2.643 and 2.657 Å (there are two independent molecules in the asymmetric unit).

4. Supramolecular self-assembly of 24

The molecules are firstly associated into dimeric units through tellurium-chlorine secondary bonds, formed with the participation of Cl1 and Cl2. In turn, the Te_2Cl_2 rings are connected in a helical fashion with a Te1···Te1 pitch of 6.429 Å, moreover these atoms are linked by an hydrogen bond O1–H1O···Cl3: O1···Cl3^{iv} = 3.196(3), H1O···Cl3 = 2.35 Å, O1–H1O···Cl3^{iv} = 176.1° (iv = x, 1 + y, z) (Fig. 2). It is interesting to note that 3_{10} helix, observed in proteins, has a pitch of 6.0 Å [27].

5. Docking studies

Ligand docking is designed to find the best mode of interaction between a small ligand and a large macromolecular receptor. It is one of the most widely used tools in ligand and drug design/screening. As it can provide information about how ligands bind to a receptor a docking study was undertaken.

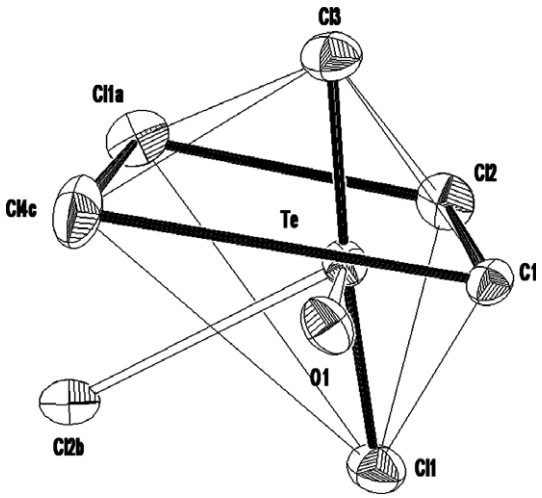


Fig. 2. The coordination polyhedra of **24**.

Docking experiments, performed using the DOCK 4.0 program [28], were carried out using the protein crystal structure obtained from the protein data bank as a PDB file entitled 1GMY-C (1.9 Å structure resolution), which is human cathepsin complexed with the inhibitor APD-DFA (3-methylphenylalanine-diphenylacetic acid). As for the ligands, the crystal structure for **24,** which is described in this paper, and for AS101 the data deposited in the Crystal Structure Database under the reference code PORSOE [29], were used. To verify and check the docking procedure, we first applied the protocol to the experimentally known complex (1GMY).

A probe of 1.4 Å radius was used to trace a 4 dots/Å^2 negative image of the protein molecular surface, according to Connolly's method [30]. The resulting data were used to generate clusters of overlapping spheres with the SPHGEN program [31]. To describe the shape characteristics of the docking site a 9 Å cutoff radii was used, centered on Ser28-Cys29-Trp30. As it was postulated that the inactivation of cathepsin B by organotellurium (IV) compounds can be due to the high nucleophilic character of the thiol residue at the active site combined with the electrophilic character of the tellurium atom[9], in all calculations the Cys29 was considered as a Cyx, and the histidines were protonated as Hid. MOPAC [32] charges were used for the ligands.

Initially, a three-step procedure was used for the docking of **24**: (a) the docking calculation was performed using the neutral ligand and involving contacts and force field, (b) the same calculation was repeated using a charged ligand, that is, one of the chlorine atoms, attached to the Te atom, was removed, and (c) this third step consisted in a docking calculation but considering only contacts, still using the charged ligand. In order to obtain a meaningful statistical result, an energy cutoff was set in order to select a group of 15–20 complexes with the most favorable scores for the first and second steps. These scores represent an estimation of the ligand–protein interaction energy, which is calculated using the ligand atoms and the potential energy grid, generated by the CHEMGRID subroutine of the program DOCK 4.0. After the calculations the analysis and selection of the obtained complexes was done in two steps, first a graphical analysis was performed, using the O program [33,34], mostly in order to prevent the selection of complexes presenting steric clashes, then, the complexes with almost the same ligand-site relative orientation were clustered together and within each cluster the complex with the best fitting was preserved for further analyses. Following mean interaction energies (total, Coulomb and van der Waals) were calculated for all the selected complexes (Table 2). Finally, to establish the *binding patterns*, defined as the binding modes with enough statistical weight, a series of parameters were considered: (i) favorable energy score; (ii) complementary atomic contacts; (iii) high percentage of repetition in a docking calculation (see Table 3).

Table 3
Total, coulombic and van der Waals energies of the complexes obtained in steps (a) and (b)

Step	Total energy (kcal/mol)	Coulomb energy (kcal/mol)	van der Waals energy (kcal/mol)
(a)	−20.700	−3.474	−17.226
(b)	−36.701	−23.233	−13.468

The first step calculation positioned the Te and SG at a distance of 7.84 Å as shown in Fig. 3a. The second step resulted, not only in a Te...SG distance of 5.97 Å, but also in a very favorable position of the Te lone pair towards the SG, as can be seen in Fig. 3b. The results of the third step, showed that the not only the position attained is very favorable but, also the Te...SG distance obtained, of 3.87 Å (Figs. 3c and 4), is less than the sum of the tellurium and sulphur van der Waals radii of 4.05 Å [35]. As already stated this calculation was carried out taking into account only contacts, this was done in order to push a covalent bond.

In the description of 1GMY [36], the authors showed that an important interaction of the ligand with cathepsin B is with Gly74 [37]. The results of the third step in our docking calculations with **24**, showed interactions with Gly73, Gly74, Tyr75, Asn72, and Gly198, in particular the finding of a C–H...π T-shaped arrangement of the aromatic ring of the ligand with the phenyl ring of Tyr75 is shown in Fig. 5.

We also performed a similar docking calculation with the inorganic tellurane, trichloro(dioxyethylene-*O*,*O*′)tellurate (AS101) to compare it with tellurane **24**. It was previously demonstrated that AS101 acts as an inhibitor of papain and cathepsin B [37], although it is less potent than organic telluranes [9]. The docking of the AS101 showed that it closes the channel to where the Cys29 is located, and that it only makes interactions with Gly73, Gly74, Tyr75 (Fig. 6).

In structural terms, it should be noted that all the mentioned residues are part of two β-sheets which are located in the entrance of the channel leading to Cys29 where, using the nomenclature of Schechter and Berger [38], are located the binding subsites S1 (Gly 72, Gly73, Gly74), S2 (Asn 72, Gly198) and S3 (Tyr75). Both compounds, **24** and AS101, interact with S1 and S3 subsites residues, Gly73, Gly74, Tyr75. Due to its size, compound **24** interacts also with residues of the S2 subsite, where the interaction with Asn72 and Gly198, can likely favor a more appropriate orientation of the ligand before the formation of the Te–SG covalent bond, and the inactivation of the enzyme (Fig. 7).

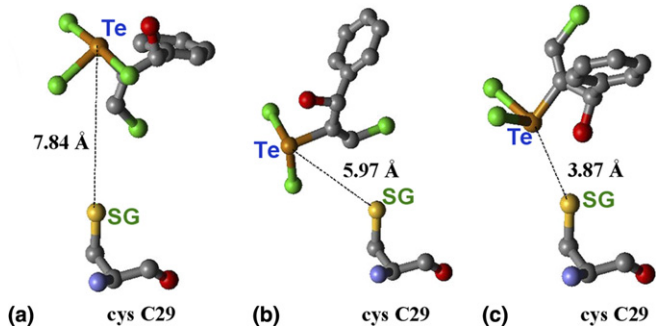


Fig. 3. The optimal positional poses obtained in steps (a), (b) and (c) of the docking.

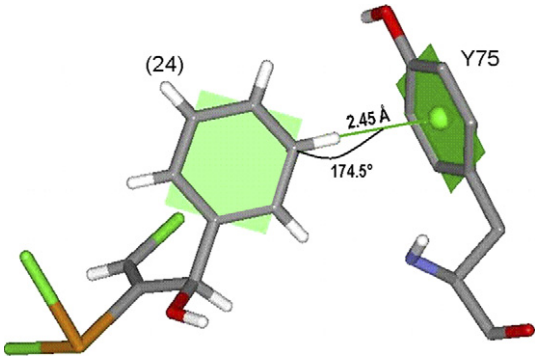


Fig. 5. C–H...π T-shaped interaction of Tyr75 with **24**.

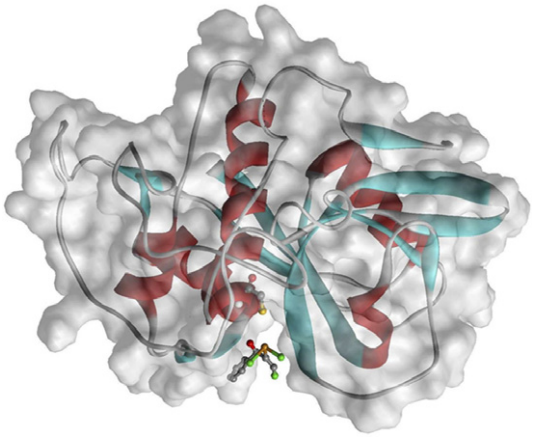


Fig. 4. Probable interacting mode of **24** with cathepsin B.

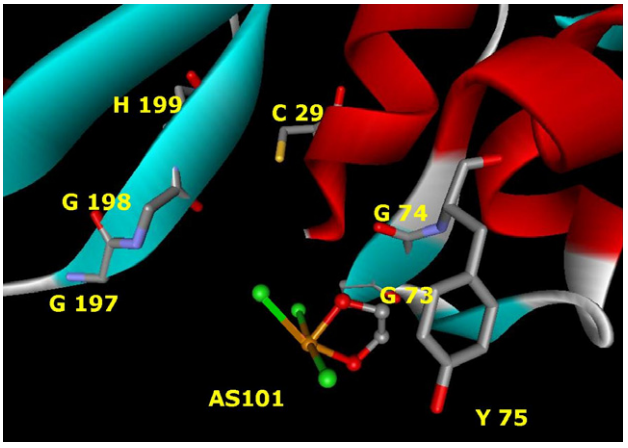


Fig. 6. Docking result of AS101 in 1GMY, showing that it is closer only to residues of one of the β-sheets (subsites S1 and S3).

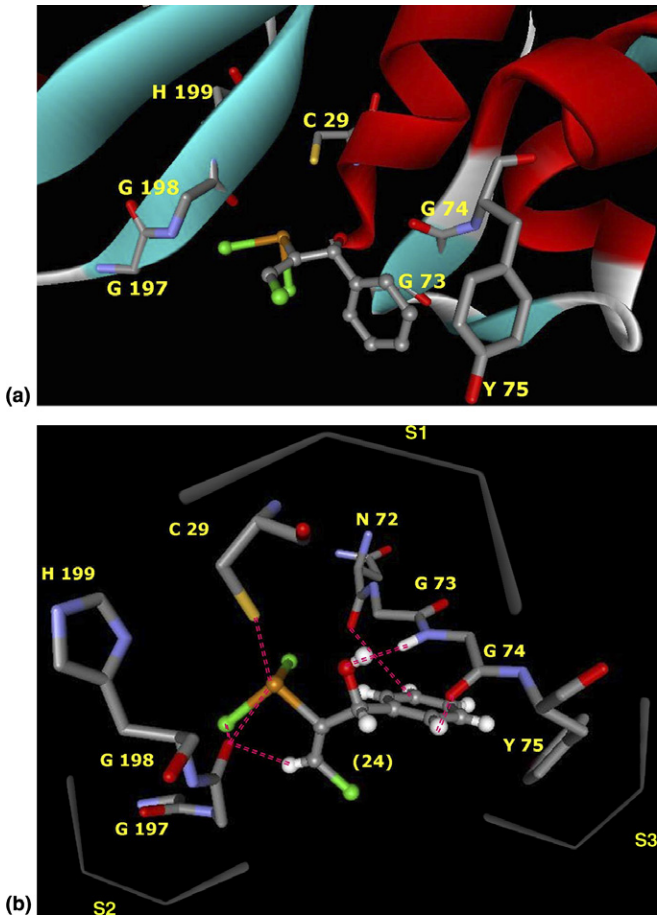


Fig. 7. Docking result of **24** in 1GMY showing the probably interacting mode (a) and the important residues (b).

6. Conclusion

In summary, we have reinvestigated the addition reaction of $TeCl_4$ to some alkynes. $TeCl_4$ presented a similar reactivity as observed for *p*-methoxyphenyltellurium trichloride towards alkynes. Aromatic and 3-hydroxy-alkynes react by different mechanisms, which explain the stereochemistry of the obtained products. The crystal structure of **24** showed a new coordination polyhedron around the Te atom and a supramolecular arrangement that resembles a 3_{10} helix. The docking results showed that the interaction with non-prime subsites of Cathepsin B (S1, S2 and S3) should be important in the positioning of the compounds, and the size of the ligands, which allow additional interactions, should be also important to the potency of this class of protease inhibitors.

7. Experimental

All solvents and chemicals used were previously purified according to the usual methods [39]. Tellurium tetrachloride was prepared according to the literature procedure [40]. ^1H and ^{13}C NMR spectra were recorded on either a Varian DPX-300, Bruker DRX-500 or a Bruker AC-200 spectrometers using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. The ^{125}Te NMR spectra were also recorded on a Bruker DRX-500 spectrometer and referenced to a diphenylditelluride solution (1 M in $CDCl_3$) as a external standard (419.536 ppm). Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz and multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet) and br (broad). Infrared spectra were recorded on a Bomem MB-100 spectrophotometer. Peaks area reported in cm^{-1}. Low resolution mass spectrometry was performed in a Shimadzu CGMS-17A/QP5050A instrument. Elemental analysis was performed at the Microanalytical Laboratory of the Chemistry Institute – University of São Paulo. The IUPAC names were obtained using the software ChemDraw Ultra®, version 7.0.1.

7.1. General procedure for the addition reaction of tellurium tetrachloride to alkynes

In a one-necked round bottomed flask equipped with a $CaCl_2$ guarding tube it was added $TeCl_4$ (0.54 g, 2 mmol) and dry benzene (15 mL). The desired alkyne (2.2 mmol) was added dropwise and the mixture was stirred, at room temperature, for 1 h. The solution thus obtained was filtered out and the solvent was evaporated giving the corresponding chloro alkenyl tellurium trichloride as an amorphous syrup.

1,1-Dichloro-telluro-bis-[(2-chloro-2-phenyl)-ethene] (**9**): Pale yellow crystals crystallized from dry H_2Cl_2/hexane mixture at room temperature (0.653 g, 86%). ^1H NMR (300 MHz, $CDCl_3$/10% DMSO-d^6) δ 8.98 (s, 2H), 7.84–7.81 (m, 4H), 7.52–7.50 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 144.0, 132.7, 130.1, 127.6, 125.9, 122.5. ^{125}Te NMR (158.04 MHz, $CDCl_3$) δ ppm 625.5. IR (KBr) cm^{-1} 3031, 1955, 1889, 1804, 1582, 1558, 1492, 1445, 1206, 901, 730, 681, 611. Anal. Calc. for $C_{16}H_{12}Cl_4Te$: C, 40.57; H, 2.55. Found: C, 40.46; H, 2.62%.

1-Chloro-2-trichlorotelluro-3-phenyl-propen-3-ol (**24**). ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.70–7.68 (m, 2H), 7.56 (d, J 2.87 Hz, 1H), 7.46–7.43 (m, 3H), 6.18 (d, J 2.85 Hz, 1H), 2.30 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 157.4, 138.6, 130.6, 130.2, 129.9, 127.4, 76.1. ^{125}Te NMR (158.04 MHz, $CDCl_3$) δ ppm 1239. IR (KBr) cm^{-1} 3327, 3064, 3030, 2891, 1949, 1874, 1636, 1492, 1455, 1198, 970, 851, 802, 724, 689, 457. Anal. Calc. for $C_9H_8OCl_4Te$: C, 26.92; H, 2.01. Found: C, 26.98; H, 1.92%.

7.2. General procedure for the functionalization of the chloro alkenyl trichlorides with acetone

In a one-necked round bottomed flask equipped with a reflux condenser, the 2-chloro-1-alkenyl tellurium trichloride was dissolved in acetone (20 mL) and the obtained solution was refluxed for 2 h. The mixture was cooled,

the excess of acetone was removed and the solid obtained was recrystallized from dry CH_2Cl_2 yielding crystals of the corresponding tellurium dichloride.

1-{Dichloro[(*Z*)-2-chloro-1-methyl-2-phenylethenyl]-λ^4-tellanyl}acetone (**12**): Colorless needles (0.653 g, 83%). mp: (164–166) °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.46 (m, 5H), 4.70 (s, 2H), 2.52 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 138.1, 129.4, 128.6, 116.3, 55.7, 29.8. ^{125}Te NMR (158.04 MHz, $CDCl_3$) δ 724.6. IR (KBr) cm^{-1} 3444, 1705, 1614, 1355, 1239, 769, 530. Anal. Calc. for $C_{12}H_{13}OCl_3Te$: C, 35.40; H, 3.44. Found: C, 35.46; H, 3.31%.

1-{Dichloro[(*Z*)-2-chloro-1,2-diphenylethenyl]-λ^4-tellanyl}acetone (**13**): Pale yellow needles (0.395 g, 54%). mp: (192–195) °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.52 (m, 10H), 4.74 (s, 2H), 2.56 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 140.1, 138.4, 131.7, 129.4, 128.4, 127.7, 127.2, 122.3, 55.8, 29.9. ^{125}Te NMR (158.04 MHz, $CDCl_3$) δ 731.2. IR (KBr) cm^{-1} 3448, 1720, 1624, 1362, 1231, 762, 534. Anal. Calc. for $C_{17}H_{15}OCl_3Te$: C, 43.51, H, 3.22. Found: C, 43.78; H, 3.43%.

7.3. General procedure for the tellurate salt formation

In a one-necked round bottomed flask with a solution of the mixture obtained from the reaction of $TeCl_4$ and propargylic alcohol (5 mmol scale) in absolute ethanol (40 mL) it was added dropwise a solution of triethylbenzylammonium chloride (5.18 g, 5.2 mmol) in absolute ethanol (15 mL) at room temperature. The mixture thus obtained was stirred for 1 hour and a off-white precipitate was formed. The solution was filtered out and the solvent evaporated giving a pale yellow syrup. The syrup was dissolved in dry dichloromethane and colourless crystals were obtained at room temperature after two days. The crystals was recrystallized from dichloromethane yielding 1.57 g (61%) of the tellurate as colourless crystals (m.p.:94–95 °C).

Triethylbenzylammonium 2,2,2,4-tetrachloro-2,5-dihydro-1,2-λ^6-tellurate (**20**): ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.75 (t, *J* 2.3 Hz, 1H), 7.67–7.53 (m, 5H), 5.28 (d, *J* 2.25 Hz, 2H), 4.67 (s, 1H), 3.45 (q, *J* 7.25 Hz, 6H), 1.53 (t, *J* 7.21 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 147.8, 140.0, 133.5, 131.4, 130.1, 128.4, 76.8, 61.4, 53.6, 8.35. ^{125}Te NMR (158.04 MHz, $CDCl_3$) δ ppm 1239. IR (KBr) cm^{-1} 1601, 1477, 1390, 1037, 755, 533. Anal. Calc. for $C_{16}H_{25}ONCl_4Te$: C, 37.19; H, 4.88; N, 2.71. Found: C, 37.19; H, 4.88; N, 2.69%.

7.4. X-ray crystallography

The structure was solved by direct methods [41]. Refinement was based on F^2 by full-matrix least-squares technique [42]. The hydrogen atoms were located on stereochemical grounds, except that of the hydroxyl moiety which was localized on a difference Fourier map, all were assigned a temperature factor of 1.2 times the U_{eq} of the atom they were attached to. CCCD deposition No. 607494.

7.5. Computational details

Please see Section 5 and references cited.

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