A tellura-Baeyer–Villiger oxidation: one-step transformation of tellurophene into chiral tellurinate lactone†‡

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Baeyer–Villiger (BV) oxidation is a fundamental organic reaction, whereas the hetero-BV oxidation is uncharted. Herein, a tellura-BV oxidation is discovered. By oxidizing a tellurophene-embedded and electron-rich polycycle (1) with mCPBA or Oxone, an oxygen atom is inserted into the Te–C bond of the tellurophene to form tellurinate lactone mono-2. This reaction proceeds as follows: (i) 1 is oxidized to the tellurophene Te-oxide form (IM-1); (ii) IM-1 undergoes tellura-BV oxidation to give mono-2. Moreover, the hybrid trichalcogenasumanenes 7 and 8 are, respectively, converted to tellurinate lactones mono-9 and mono-10 under the same conditions, indicating that tellura-BV oxidation shows high chemoselectivity. Due to the strong secondary bonding interactions between the Te=O groups on tellurinate lactones, mono-2, mono-9, and mono-10 are dimerized to form U-shaped polycycles 2, 9, and 10, respectively. Notably, mono-2, mono-9, and mono-10, and their dimers show chirality. This work enables one-step transformation of tellurophene into tellurinate lactone and construction of intricate polycycles.

Introduction

The Baeyer–Villiger (BV) oxidation was discovered more than a century ago,1,2 and great efforts were devoted to making BV oxidation catalytic, along with high chemo-, regio-, and stereo-selectivity.3–7 In BV oxidation, the C–C bond adjacent to the carbonyl is opened and an oxygen atom is inserted to form C–O–C (see Scheme 1a for a typical example). The BV oxidation is an efficient way to transform ketones into esters and/or lactones and is employed to synthesize intricate chemicals.3–7 A variety of oxidants can be used to perform BV oxidation, such as meta-chloroperbenzonic acid (mCPBA), H2O2, Oxone, and so forth.8–10 According to the reaction mechanism of BV oxidation, which involves an intermediate known as the Criegee adduct,11 one may speculate whether it is possible to achieve hetero-BV oxidation. For instance, do organic compounds containing sulf oxide, selenoxide, or telluroxide undergo BV-type oxidation to form the corresponding esters and/or lactones?

Chalcogens (O, S, Se, and Te) have drawn tremendous interest in chemistry and materials science. Tellurium is the heaviest member of this family and shows maverick chemistry.12–17 The emerging development of tellurium compounds is apparent from their application in catalysis,18–21 coordination,22–26 and optoelectronic materials.27–34 The low Pauling electronegativity and high polarisability of tellurium lead to strong secondary bonding interactions (SBIs) and/or...
hypervalent states.\textsuperscript{12,35–38} Meanwhile, embedding Te onto the π-scaffolds of organotellurium compounds will narrow the HOMO–LUMO energy gap,\textsuperscript{39–42} produce intermolecular Te···X SBIs in the solid state,\textsuperscript{43–45} and alter their chemical behavior.\textsuperscript{46–52} Recently, Seferos’s group performed the oxidation of tellurophenes with peroxides and found that they can be converted to various states including dihydroxy tellurophenes, telluroxides and tellurones (Scheme 1b).\textsuperscript{53,54} Further oxidation of tellurophene Te-oxide with mCPBA resulted in ring cleavage to form but-2-ene-1,4-dione instead of tellurinate lactone.\textsuperscript{55}

In BV oxidation, the migration step is rate-determining in most cases and electron-donating substituents in the migrating group will promote the rearrangement\textsuperscript{48–50}.\textsuperscript{55} Herein, with the intention of exploring hetero-BV oxidation, we chose tellurophene-embedded and electron-rich polycycles as substrates. By oxidizing them with mCPBA or Oxone, we discovered a tellura-BV oxidation (Scheme 1c). To the best of our knowledge, this kind of reaction has never been reported so far. This work enables the one-step conversion of tellurophene into tellura,2 0 2 1 ,2 0 2 1 , and yield 82%.

Results and discussion

An electron-rich polycycle 1 containing a tellurophene moiety was prepared from 2,3,6,7,10,11-hexabutoxytriphenylene (HBT) via the dilithiation and insertion of tellurium in one-pot (see the ESI†).\textsuperscript{56–58} Upon oxidation of 1 by mCPBA (2 equiv., condition a) in CH\textsubscript{2}Cl\textsubscript{2} at room temperature (r.t.), compound 2 was obtained in a yield of 52% (Scheme 2). The yield of 2 remained almost unchanged when excess mCPBA was used. On the other hand, compound 2 was harvested with a yield up to 82% by oxidizing 1 with Oxone (2 equiv., condition b) in a mixed solvent of THF–deionized water (4 : 1, v/v). It is worth noting that the yield of 2 was distinctly lowered when tap water was used during the oxidation of 1 with Oxone. The reason is that the residual Cl\textsuperscript{−} in tap water is converted to chlorine in the presence of Oxone,\textsuperscript{59,60} and chlorine will react with the tellurophene on 1 to form a hypervalent adduct.\textsuperscript{46–49,57}

Scheme 2. Transformation of 1 into dimeric tellurinate lactone 2. Reagents and conditions: (a) mCPBA (2 equiv.), CH\textsubscript{2}Cl\textsubscript{2}, r.t., 4 h, and yield 52%; (b) Oxone (2 equiv.), THF–deionized H\textsubscript{2}O (4 : 1, v/v), r.t., 4 h, and yield 82%.

The structure of 2 was also determined through X-ray single crystal structure analysis. Referring to the crystal structure of 1 (Fig. 1), the tellurophene ring on 1 was opened and an oxygen atom was inserted to form six-member rings (A and B moieties). The bond lengths for the newly formed Te-O and O-C bonds in the A and B moieties are 2.02(1) and 1.36(1) Å, respectively (Fig. 1a). The A and B moieties are connected with a “Te\textsubscript{2}O\textsubscript{2}” four-member ring. The tellurium atoms in the “Te\textsubscript{2}O\textsubscript{2}” unit take the so-called four-center ten electron (10-E-4) hypervalent state.\textsuperscript{12} The “Te\textsubscript{2}O\textsubscript{2}” four-member ring is nearly perpendicular to the A and B moieties. As a result, compound 2 adopts a U-shaped conformation (Fig. 1b). According to the molecular structure of compound 2, this compound is non-centrosymmetric, and therefore it is a chiral molecule. However, a pair of enantiomers coexists in its crystal.

There are two kinds of Te-O bonds in the “Te\textsubscript{2}O\textsubscript{2}” four-member ring of 2 with bond lengths of 1.91(1) and 2.09(1) Å (Fig. 1a). The former is close to the Te==O bond length (1.89(1) Å) in PhTeO\textsubscript{2} (ref. 61) and (C\textsubscript{6}F\textsubscript{5})\textsubscript{2}TeO,\textsuperscript{62} and the latter is longer than the Te-O bond (1.97 Å) in X[R\textsubscript{2}TeO\textsubscript{3}]TeR\textsubscript{2}X.\textsuperscript{63,64} It was reported that the Te-X bond (where X is more electronegative than Te) is more polar in Te=X, leading to stronger SBIs.\textsuperscript{12} For instance, the telluroxides usually exist as dimers owing to the strong intermolecular O → Te SBIs.\textsuperscript{64–67} Therefore, compound 2 can be regarded as a dimer of mono-2 formed through the intermolecular SBIs between the Te==O bonds (Scheme 2). Accordingly, the two kinds of Te-O bonds in “Te\textsubscript{2}O\textsubscript{2}” can be reasonably assigned to Te==O (1.91(1) Å) and O → Te (2.09(1) Å).

Consistent with the above deduction, we observed the ionic peak of mono-2 (C\textsubscript{42}H\textsubscript{36}O\textsubscript{7}Te + H\textsuperscript{+}, 821.3257) in the high resolution mass spectrum (HRMS) of 2 as shown in Fig. 2a. This result implies that the dimerization of mono-2 to form 2 would be reversible under certain conditions. In this context, we carried out 1H NMR spectroscopic investigation of 2 at different concentrations (Fig. 2b). The transformation between mono-2 and 2 occurs indeed. It is found that compound 2 exists in the solution with a concentration higher than 4 × 10\textsuperscript{−4} mol L\textsuperscript{−1}. As the concentration decreases, mono-2 gradually appears. When the concentration is below 8 × 10\textsuperscript{−5} mol L\textsuperscript{−1}, compound 2 completely transforms into mono-2. On the other hand, the single crystals of 2 were harvested by slowly evaporating the solution of mono-2 (c ≤ 8 × 10\textsuperscript{−5} mol L\textsuperscript{−1}). Therefore, mono-3 is
the intrinsic product for the oxidation of 1 under condition a or b.

The product mono-2 possesses a tellurinate lactone moiety, which would have originated from the oxidation of tellurophene Te-oxide. The formation of tellurinate lactone can be rationalized with a tellura-BV oxidation mechanism. We have proposed a mechanism for this transformation by employing mCPBA as an oxidant (Scheme 3). The tellurophene on 1 is first oxidized by mCPBA to afford a tellurophene Te-oxide intermediate IM-1. Owing to the highly polarized Te==O bond, the IM-1 is easily attacked by mCPBA to form an intermediate IM-2, which resembles the Criegee adduct in BV oxidation. Finally, IM-2 undergoes a rearrangement to afford mono-2. Then mono-2 is
dimerized in the concentrated solution and/or in the solid state to give 2. The reaction of 1 with Oxone would also follow the similar procedure. The high yield of 2 under condition b can be attributed to the acceleration of the rearrangement step, because the electron-deficient leaving group will facilitate the rearrangement.3−7

To gain more insight into the mechanism, an attempt was made to identify the key intermediate IM-1 along the reaction pathway. It is known that tellurophene can be transformed into its Te-oxide form by oxidation with mCPBA.53 Thus, we

**Scheme 3** Proposed mechanism for converting 1 to 2 via tellura-BV oxidation.

**Scheme 4** Oxidation of 1 with mCPBA (1 equiv.) in CH₂Cl₂ at r.t.
We then studied the electronic effect on tellura-BV oxidation. Employing a similar synthetic approach to that of compound 1, a polycycle containing a tellurophene moiety (compound 4) was prepared from phenanthrene. In comparison with 1, compound 4 doesn’t possess the electron-rich substituents. As shown in Scheme 5, oxidation of 4 with excess mCPBA didn’t afford tellurinate lactone 6, and only 5 was isolated. The formation of 5 is attributed to the transesterification during the purification of crude products via column chromatography, where the eluent contains formic acid. Along with previous reports, the present result further indicates that electron-donating substituents are essential for tellura-BV oxidation.

To further understand tellura-BV oxidation, we intend to clarify the chemoselectivity of this reaction. Considering that

**Scheme 5** Oxidation of 4 with excess mCPBA in CH2Cl2.

**Fig. 4** Crystal structure of 10, with n-Bu groups and hydrogen atoms omitted for clarity: (a) and (b) are molecular structures, respectively, projected perpendicular and parallel to the Te2O2 four-member ring; (c) packing motif with intermolecular contacts shown in grey dashed lines. The Se atoms are shown in pink.

**Fig. 3** Crystal structure of 3, with n-Bu groups and hydrogen atoms omitted for clarity. (a) and (b) are, respectively, projected perpendicular and parallel to the HBT ring. The mCBA moieties are omitted in (b). The Cl atoms are shown in orange.

**Fig. 4** Crystal structure of 7, with n-Bu groups and hydrogen atoms omitted for clarity.
structure of 10 is reminiscent of that of 2. Two *mono-10* are dimerized via a “Te₂O₂” four-member ring to form a non-centrosymmetric U-shaped structure. The tellurium atoms on the “Te₂O₂” four-member ring take the “10-E-4” hypervalent state (Fig. 4a). Two kinds of Te-O bonds in “Te₂O₂” are observed with bond lengths of 1.91(1) and 2.07(2) Å, respectively, assigned to Te–O and O → Te. Compound 10 forms helical arrays in the crystal with various intermolecular atomic contacts between neighboring molecules (Fig. 4c), *i.e.*, Te⋯C (3.44–3.70 Å), Te⋯O (2.95–3.33 Å), Te⋯Te (4.06–4.09 Å), and O⋯O (2.85–3.02 Å). While 10 is a chiral molecule, a pair of enantiomers coexists in its crystal.

It is worth noting that 2, 9, and 10 show good thermal stability at a decomposition temperature higher than 200 °C (Fig. S1 and Table S1 in the ESI†). 2, 9, and 10 are solvable in organic solvents such as CH₂Cl₂, CHCl₃, toluene, and THF, whereas they show poor solubility in methanol.

We elucidated the influence on electronic states by converting tellurophene into tellurinate lactone and its dimerized form. Herein, we take 8, *mono-10*, and 10 as representative examples, and those for the 1 and 7 series show similar phenomena. Theoretical studies reveal that the HOMO energy levels remain almost unchanged for 8, *mono-10*, and 10. The LUMO energy levels of *mono-10* and 10 are the same, and both are clearly lower than that of 8 (Fig. 5a). This is caused by the electron-withdrawing unit (Te=O) in *mono-10* and 10. Consequently, the HOMO–LUMO energy gaps (ΔE) of *mono-10* (ΔE = 3.75 eV) and 10 (ΔE = 3.78 eV) are narrower than that of 8 (ΔE = 4.19 eV). Consistent with the theoretical study, the UV-Vis absorption spectra in CH₂Cl₂ for *mono-10* (c = 1 × 10⁻⁵ mol L⁻¹) and 10 (c = 5 × 10⁻⁴ mol L⁻¹) are almost identical (Fig. 5b). The compounds *mono-10* and 10 exhibit broad absorption bands at 382–440 nm originating from the HOMO–LUMO transition, which is red-shifted compared to that of 8 (368–414 nm). The compounds *mono-10* and 10 are non-emissive at r.t., but they show emissions at 77 K (Fig. 5c), ascribable to phosphorescence. The emission of 10 is clearly red-shifted compared to that of *mono-10*, which would be due to the excimer emission since the two π-frameworks of 10 are arranged face-to-face (see Fig. 4b). Similar phenomena are also observed for 2 and 9 (Fig. S26 and S27†).

Referring to Fig. 5d, the UV-Vis absorption of 10 is distinctly changed upon adding trifluoroacetic acid (TFA). Acidification of 10 also leads to a clear down-field shift of ¹²⁵Te NMR (Fig. 6a). On the other hand, the original absorption bands and ¹H NMR spectra of 10 will be restored when the acidified solution of 10 is neutralized by triethylamine (TEA) as shown in Fig. S25.† Thus, it is a reversible process and a proposed mechanism is shown in Fig. S25.† Variations in absorption spectra and ¹H NMR of 10 are also observed in the presence of HCl (3 N, aqueous). However, the original spectra of 10 are not recovered by neutralization. 10 was quantitatively converted into a new product when it was reacted with HCl (3 N, aqueous). Single crystal structure analysis reveals that the tellurinate lactone moiety of 10 is destroyed and two Cl atoms are attached onto the Te atom to give compound 12 (Fig. 6b). The mechanism for the formation of 12 is shown in Scheme 7.

2, 9, and 10 possess chirality, whereas they are obtained as enantiomers. We separated the enantiomers of 2, 9, and 10 via chiral HPLC on a Daicel CHIRALPAK IF (IF00CE:SL018) column (elucent: hexane/CH₂Cl₂ = 50/50). Fig. 7a shows the chiral
Chromatogram of 10 as a typical example. Two fractions of 10 have retention times of 3.4 min and 5.3 min, and are isolated with >93% ee. Circular dichroism (CD) spectra of the two fractions show a mirror symmetry (Fig. 7b), indicating that they have opposite chirality. According to the positive and negative Cotton effects at 378 nm, the two fractions are denoted as (+)-10 and (−)-10. Based on the molecular structure of 10 in a single crystal, we performed CD spectra simulation via TD-DFT calculation at the TD-PBE0/Def2-SVP level, where the butyl groups on (+)-10 and (−)-10 were replaced with methyl groups to give (+)-1′0 and (−)-1′0. The simulated CD spectra of (+)-1′0 and (−)-1′0 are in good agreement with the experimental results, and give the structure of each isomer as shown in Fig. 7c.

Conclusions

In summary, we have discovered a tellura-BV oxidation which enables the one-step transformation of tellurophene into the chiral tellurinate lactone. Owing to the strong SBIs between Te=O groups, the resulting tellurinate lactone is dimerized via the formation of a hypervalent “Te2O2” four-member ring in the solid state. This reaction shows good chemoselectivity, i.e., tellura-BV oxidation selectively occurs when the telluro-, seleno-, and thiopeu moieties coexist in the substrates. It was also found that electron-donating substituents are essential for tellura-BV oxidation. Employing tellura-BV oxidation as a vital step, the hybrid trichalcogenasumanenes are transformed into the U-shaped polycycles. Further investigation will be directed to the development of stereoselective tellura-BV oxidation as well as the asymmetric synthesis and application of the U-shaped polycycles. Such work is ongoing in our laboratory.

Author contributions

S. W. conducted the synthesis, crystal structure analysis, and most of the measurements. C. Y. carried out the theoretical calculation. W. Z. supported the synthesis. X. L. contributed to the analysis of NMR spectra (including 2D NMR). H.-L. Z. contributed to the analysis and discussion on optical spectra. X. S. conceived the ideas and designed the project. S. W. and X. S. wrote the paper. All authors approved the final version of the manuscript.

Conflicts of interest

There is no conflict of interest to report.

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