

Synthesis, structure, and thermolysis of a novel spirotellurane bearing two 1,2-oxatellurethane rings, 1,5-dioxa-4 λ^4 -telluraspiro[3.3]heptane: oxirane and olefin formation reactions

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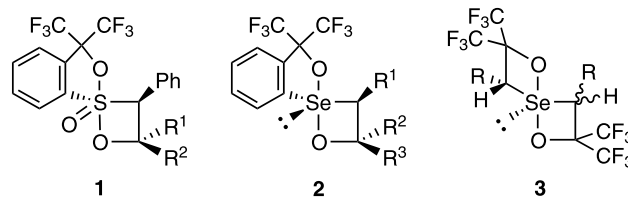
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Abstract—The first 1,5-dioxa-4 λ^4 -telluraspiro[3.3]heptane was synthesized and its structure was determined by X-ray analysis. This tellurane gave the corresponding oxirane and olefin, as well as alcohol, upon heating, which were shown to be formed via a radical pathway. © 2002 Elsevier Science Ltd. All rights reserved.

As part of our study on the intermediates of the Wittig and Peterson-type olefin formation reactions,^{1,2} we have reported the syntheses and isolations of oxetanes bearing highly coordinate main group elements at the position adjacent to the oxygen atom, which give the corresponding olefins on thermolyses.³ Meanwhile, we have found that highly coordinate group 16 element analogues of 1,2-heteraoxetanes bearing the Martin ligand, that is, pentacoordinate 1,2 λ^6 -oxathietanes **1** and tetracoordinate 1,2 λ^4 -oxaselenetanes **2**, yield not the olefins but the oxiranes with retention of configuration,⁴ indicating the deep relationship with the Corey–Chaykovsky reaction.⁵ We have also investigated the synthesis of tetracoordinate 1,5-dioxa-4 λ^4 -selenaspiro[3.3]heptanes **3** bearing two oxaselenetane rings to elucidate the influence of the ring size of the spiro ring system on the reactivity of 1,2-oxachalcogenetanes and found that these compounds undergo double oxirane extrusion. Such an oxirane formation from highly coordinate 1,2-oxachalcogenetanes would proceed regardless of the central chalcogen atom. The chemistry of a 1,2-oxatellurethane, however, has not been explored in detail; there has been only one report on the isolation of a 2-chloro derivative whose thermal reactivity has not yet been investigated.⁷ We report here the

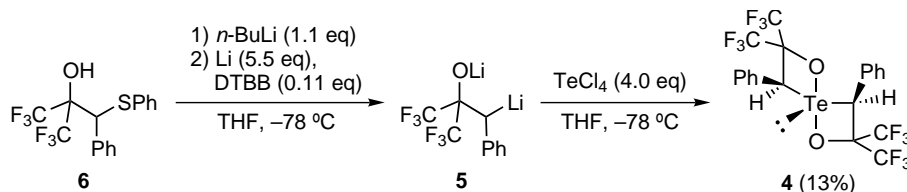
synthesis, crystal structure, and unique thermal behavior of the first 1,5-dioxa-4 λ^4 -telluraspiro[3.3]heptane **4**.



The first trial for the synthesis of **4** by oxidative cyclization of the corresponding bis(β -hydroxyalkyl) tellurides, which was effective for the synthesis of its selenium analogue **3**, failed due to photo instability of the synthetic intermediates, dibenzyl telluride and bis(phenylthiomethyl) telluride. Thus, we took advantage of the direct substitution of tellurium tetrachloride with LiCHPhC(CF₃)₂OLi (**5**) generated by Yus' method.⁸ Successive treatment of β -hydroxyalkyl phenyl sulfide **6** with *n*-BuLi and excess amount of lithium in the presence of catalytic amount of 4,4'-di-*t*-butylbiphenyl (DTBB) in THF at -78°C afforded **5** (Scheme 1). Adding an excess amount of TeCl₄ to **5** at -78°C and further warming the reaction mixture to the room temperature gave a single isomer of 1,5-dioxa-4 λ^4 -telluraspiro[3.3]heptane **4** in 13% yield as a stable solid in the air.⁹ We think the low yield of tellurane **4** is caused by the following reasons: (i) the amount of TeCl₄ for reaction may be insufficient, as the excess amount of lithium, necessary for the lithiation of **6**, reduced and consumed TeCl₄, (ii) benzenethiolato

Keywords: tellurane; tellurium; 1,5-dioxa-4 λ^4 -telluraspiro[3.3]heptane; X-ray analysis; thermolysis.

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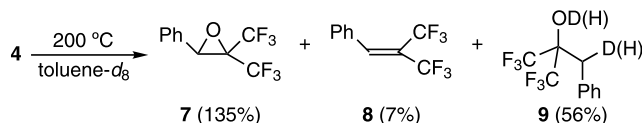
Scheme 1.

anions, which are inevitably generated in the reaction, also consumed TeCl_4 , and (iii) the formation of **4** involves formation of four bonds in a one-pot reaction with overcoming ring strain of the four-membered rings.

In the ^1H , ^{13}C , and ^{19}F NMR spectra of **4**, two 1,2-oxatellurethane rings were observed equivalently. In the ^{125}Te NMR spectra, a signal of **4** (δ_{Te} 1207 in CDCl_3) was observed as a multiplet due to long-range coupling with ^{19}F nuclei. The signal in the extremely low-field region unambiguously supports its tellurane structure.¹⁰ The molecular structure of **4** was finally determined by X-ray crystallographic analysis.¹¹ It was revealed that there are two independent molecules of **4** in the unit cell. Both molecules are very similar to each other. Both phenyl groups at the 3- and 3'-positions are *cis* to the lone pair of the tellurium (Fig. 1A). The apical O–Te–O bond angle ($148.08(10)^\circ$), which is much smaller than that ($160.53(7)^\circ$) of a tellurane bearing two Martin ligands,¹² is considerably deviated from linearity, although the deviation is a common structural feature of the hypervalent species containing a four-membered ring.^{3,4,6,13} Thus, the structure of **4** is intermediate between pseudo trigonal-bipyramidal structure and square-pyramidal structure. The bond lengths in the four-membered rings are almost similar to the previously reported 2-chloro-1,2-oxatellurethane.⁷ Both two four-membered rings in **4** are slightly puckered, judging from the torsion angles of Te1-C1-C2-O1 ($12.0(3)^\circ$) and Te1-C3-C4-O2 ($10.7(2)^\circ$) and from the sum of the angles of the four-membered rings [$358.2(8)^\circ$ and $358.6(8)^\circ$, respectively]. Interestingly, it forms a dimer with intermolecular contacts between $\text{Te1}\cdots\text{O2}'$ and $\text{Te1}'\cdots\text{O2}$ of two independent molecules [$3.195(3)$ and

$3.676(2)$ Å, respectively] in contrast to oxathietanes and oxaselenetanes (Fig. 1B).^{4,6,12,14} This is the first example of the synthesis and structural analysis of a 1,5-dioxaspiro[3.3]heptane derivative.

Thermolysis (toluene- d_8 , 200°C , 180 h in a degassed sealed tube) of **4** gave the corresponding oxirane **7** (135%) and olefin **8**¹⁵ (7%), together with deuterated alcohol **9**⁶ (56%) (Scheme 2).¹⁶ Judging from ^{19}F NMR spectra, the ratio of the products, **7**, **8** and **9**, has not been changed during the reaction. The black precipitates indicate the formation of elemental tellurium or tellurium oxide. This is the first example of oxetanes giving both the corresponding olefin and oxirane in marked contrast to other oxetane analogues with highly coordinate main group elements.^{1,3,4,13,17} The yield of **7**, exceeding 100%, indicates the double oxirane formation from the single molecule of **4**. Although the oxetanes containing a pentacoordinate group 14 or 15 element gave the corresponding olefin,³ the oxachalcogenetanes in the spiro ring systems did not yield the olefins but the oxiranes regardless of the ring size (five- or four-membered ring) of the other ring except for **4**.^{4,6} These results have showed an interesting difference in the reactivity between oxetanes with a tetracoordinate sulfur, selenium, and tellurium. Dicoordinate 1,2-oxatellurethane to be formed in the first step was not observed



Scheme 2.

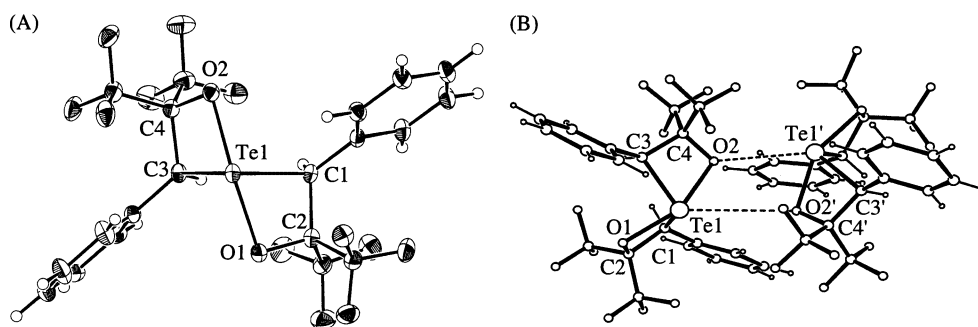


Figure 1. (A) ORTEP drawing of **4** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å) and bond angles ($^\circ$): Te1-O1 , 2.091(3); Te1-O2 , 2.112(3); Te1-C1 , 2.160(3); Te1-C3 , 2.155(3); C1-C2 , 1.567(5); C2-O1 , 1.397(4); C3-C4 , 1.562(5); C4-O2 , 1.407(4); O1-Te1-O2 , $148.08(10)$; C1-Te1-O1 , $67.30(12)$; Te1-C1-C2 , $89.0(2)$; C1-C2-O1 , $105.2(3)$; Te1-O1-C2 , $96.7(2)$; C1-Te1-C3 , $98.29(14)$. (B) Intermolecular interaction of **4**. Intermolecular distances (Å): $\text{Te1}'\cdots\text{O2}$, $3.195(3)$; $\text{Te1}\cdots\text{O2}'$, $3.676(2)$.

in the reaction mixture by NMR spectroscopy, probably because of its instability under the reaction conditions. The formation of alcohol **9** is reasonably explained by the generation of the radical species through homolytic bond cleavage. Thermolysis of **4** in the presence of cumene (20 equiv.) as a radical trapping reagent at 220°C for 30 h gave oxirane **7** (120%), olefin **8** (8%), and alcohol **9** (72%). Furthermore, a similar reaction using cumene as a solvent afforded **7** (20%) and **9** (180%) without the formation of **8**. The loss of **7** and **8** together with the gain of **9** clearly indicates that **7** and **8** were formed mostly via the radical pathway. It cannot be ruled out that a part of **7** might be formed by the carbon–oxygen ligand-coupling or heterolytic cleavage of the tellurium–oxygen bond and the successive attack of the oxide anion at carbon, and that a part of **8** might be formed by concerted mechanism if homolytic bond fission of Te–C (or Te–O) of **4** is reversible and if this process competes with concerted and/or ionic stepwise mechanisms.^{4,6}

Depending on the substrates, the reactions of tellurium ylides with carbonyl compounds were reported to give Wittig type products and/or Corey–Chaykovsky type products, respectively, while the reaction mechanism has not yet been elucidated.^{18,19} However, it was thought that the latter reaction proceeds through the backside attack of the oxide anion of the betaine, which was formed by the ring opening of the transient four-membered ring and successive rotation around carbon–carbon bonds.¹⁹ The study on a tetracoordinate 1,2-oxatelluretane which decomposes under milder conditions, where homolytic bond cleavage does not take place, would provide any information concerning the possibility that such a species is an intermediate of the reaction of a telluronium ylide with a carbonyl compound. In this study, we have demonstrated the unprecedented formation of the oxirane and olefin from a 1,5-dioxa-4 λ^4 -tellurasp[3.3]heptane.

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