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Four-membered heterocyclic compounds containing high coordinate group 16 elements

T. Kawashima *

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113,-0033 Japan

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Contents

Abstract

Title compounds containing tetracoordinate sulfur, pentacoordinate sulfur, tetracoordinate selenium and tetracoordinate tellurium together with oxygen or nitrogen were successfully synthesized as stable compounds. Some compounds have the Martin ligand that is well-known to stabilize such high coordinate main group compounds, while others have another four-membered ring. X-ray crystallographic analyses revealed that the compounds have distorted trigonal bipyramidal (TBP) or pseudo TBP structures. In marked contrast to group 13–15 element analogues, which afford the corresponding olefins on heating, their thermolyses gave the corresponding oxiranes or an aziridine except for a few 1,2-oxachalcogenetanes, suggesting the possibility that these compounds are intermediates of the Corey–Chaykovsky reaction of chalcogen ylides with carbonyl compounds or imines. The stereochemistry (retention of configuration) of some oxirane formation reactions as well as compounds synthesized by other groups is also described.

Keywords: High coordinate compounds; Hypervalent compounds; Four-membered heterocyclic compounds; High coordinate 1,2-oxachalcogenetanes; 1,2-Selenazetidines; X-ray crystallographic analysis; Oxirane formation reaction; Thermolysis

1. Introduction

Four-membered heterocyclic compounds containing high coordinate main group elements at the position adjacent to the heteroatom have received much attention, because of their unique structures and reactivity. Particularly, four-membered heterocycles containing an oxygen and a pentacoordinate phosphorus atom have been well-known as intermediates of the Wittig reaction [1]. In the course of our study on such heterocyclic compounds, we have succeeded in the syntheses of intermediates of the Wittig reaction [2], the Peterson reaction [3], and the boron-Wittig reaction [4]. Some of them were isolated as stable compounds by introduction

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* Tel./fax: +81-3-5800-6899.
E-mail address: takayuki@chem.s.u-tokyo.ac.jp (T. Kawashima).

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of the Martin ligand [5]. Furthermore, we have also synthesized spiro compounds bearing two oxetane rings and demonstrated that these compounds, namely, spirobi[1,2-oxaphosphetane] [6] and spirobi[1,2-oxasiletanide] [7] undergo double alkene and alcohol formation reactions, respectively. These results were described in previous accounts and reviews [8]. In this account, we wish to summarize our recent results concerning four-membered heterocycles containing high coordinate group 16 elements, together with some of our previous results [9].

2. High coordinate 1,2-oxachalcogenetanes

2.1. Tetra- and penta-coordinate 1,2-oxathietanes

Since the reactions of sulfur ylides with carbonyl compounds, named as the Corey–Chaykovsky reaction [10], are well known to give oxiranes in sharp contrast to those of phosphorus ylides affording alkenes (the Wittig reaction), it is very interesting to study whether tetracoordinate 1,2-oxachalcogenetanes, group 16 element analogues of pentacoordinate 1,2-oxaphosphetanes, undergo the Wittig-type reaction giving an alkene or reductive elimination giving an oxirane. So, the synthesis of these compounds was attempted.

Target tetracoordinate 1,2-oxathietanes **1a**–**d** with a phenyl group at the 3-position were obtained from **2** via **3** as shown in Scheme 1 and was successfully isolated [11–13]. Tetracoordinate 1,2-oxathietanes without substituents at the 3-position **1e** and **1f** were spectroscopically characterized, but were too moisture-sensitive to be isolated [11].

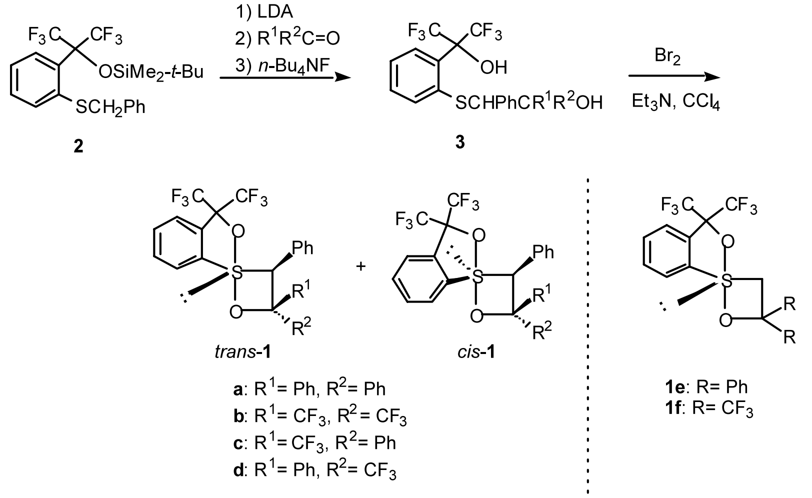
X-ray crystallographic analysis indicated that *trans*-**1a** has a structure similar to those of group 14 and 15 element analogues, although one of equatorial positions is occupied by a lone pair *cis* to the 3-phenyl group [11]. This is the first example of a 1,2λ^4-oxathietane ring system.

Very interestingly, in the thermolysis of *trans*-**1a** equilibration between *trans* and *cis* diastereomers was observed, and oxirane **4a**, benzophenone, and cyclic thioketal **5** were obtained besides **6** and **7** (Scheme 2) [11]. Thioketal **5** seems to be formed by Pummerer-type reaction of a cyclic sulfur ylide generated with benzophenone.

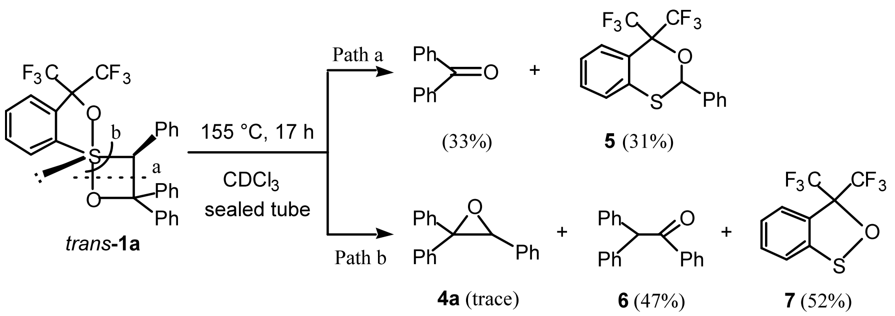
Thus, the thermolysis of oxathietane *trans*-**1a** did not give the alkene in sharp contrast to the oxetanes containing group 13, 14 and 15 elements, indicating that the bond energy of a chalcogen-oxygen double bond is not sufficient to undergo a Wittig-type reaction. In the thermolysis of oxathietane *trans*-**1a**, epimerization and the fragmentation back to the starting benzophenone as well as the formation of an oxirane strongly suggest the possibility that a 1,2λ^4-oxathietane is an intermediate of the Corey–Chaykovsky reaction.

As it is known that the S=O bond energy of a sulfone is larger than that of a sulfoxide, it was expected that sulfurane oxide undergoes a Wittig-type reaction to give the corresponding alkene. Oxidation of *trans*-**1b** with *m*CPBA in the presence of Na_2HPO_4 afforded the corresponding sulfurane oxide **8b**, although the yield was very low. The X-ray crystallographic analysis showed that it has a distorted TBP structure with two endocyclic oxygens at the apical positions and two carbon and exocyclic oxygen atoms at the equatorial positions, indicating that oxidation proceeded with retention of configuration against the central sulfur atom [12]. The bond length of the exocyclic S–O bond is 1.445(6) Å, which is a reasonable value compared with those of the double bond compounds reported as sulfurane oxides [14].

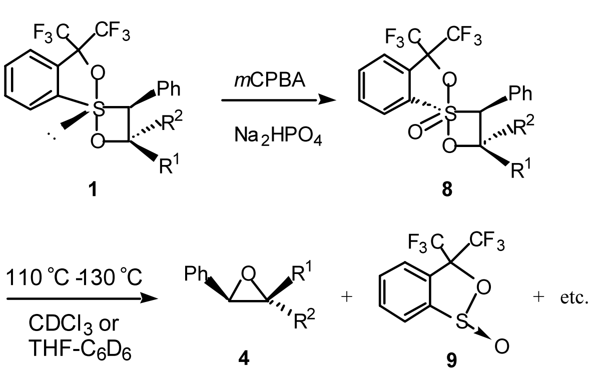
Interestingly, the thermolysis of **8b** gave the corresponding oxirane **4b** and cyclic sulfinate **9** in almost quantitative yield, but the expected alkene was not



Scheme 1.



Scheme 2.



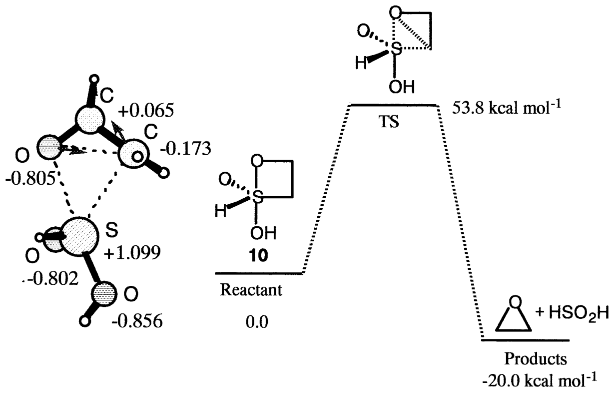
b: R^1= CF_3, R^2= CF_3
c: R^1= CF_3, R^2= Ph
d: R^1= Ph, R^2= CF_3

Scheme 3.

obtained at all (Scheme 3). Taking into consideration that compound **8b** is considered as a formal cycloadduct of an oxosulfonium ylide with a carbonyl compound and that its thermolysis afforded the Corey–Chaykovsky reaction-type oxirane, it is reasonably suggested that high coordinate 1,2-oxathietanes may be intermediates of the Corey–Chaykovsky reaction of the sulfonium and oxosulfonium ylides. It has been proposed that the Corey–Chaykovsky reaction involves the formation of an *anti*-betaine followed by a backside attack of an oxido anion on the β-carbon [15]. But, if the oxathietane is a real intermediate of the Corey–Chaykovsky reaction, S–O bond heterolysis followed by C–C bond rotation is necessary for such an oxirane formation, the latter process of which would be resisted by electrostatic attraction between the oxido anion and the sulfonium cation. In this case, an alternative mechanism such as a concerted mechanism or a front attack of the oxido anion without the C–C bond rotation can be expected to be operative. In order to elucidate these possibilities the stereochemistry of the oxirane formation was investigated [13].

Two diastereomers of pentacoordinate 1,2λ^6-oxathietanes **8c** and **8d** were synthesized and their stereochemistry was determined by differential NOE experiments for **1c** and **1d**. Thermolysis of **8c** gave the corresponding oxirane **4c** along with some other products. In sharp contrast to the thermolysis of **8b**, the yield of oxirane **4c** was quite low, and only a single isomer was obtained. Similarly, the thermolysis of **8d** afforded the other isomer **4d** stereospecifically (Scheme 3) [13]. These results indicate that the oxirane formation proceeds with retention of configuration. That is, the stereochemistry of the oxirane formation was completely reverse to that expected for the backside attack of the oxido anion. Furthermore, formation of the 1,2-oxathietane from a sulfonium ylide and a carbonyl compound was shown to be a no activation process by the previous theoretical calculation [16].

These results strongly suggest that 1,2-oxathietanes are intermediates of the reaction of the sulfur ylides with carbonyl compounds and decompose to give the oxiranes with retention of configuration. The Corey–Chaykovsky reaction has usually been carried out in the presence of salts, which were formed in the preparation of sulfur ylides. Therefore, we investigated the effect of salts on the stereochemistry of oxirane formation. Thermolyses of both **8c** and **8d** in the presence of lithium bromide in THF-C_6D_6 (6:1) gave a mixture of oxiranes **4c** and **4d**, in sharp contrast to the results in the absence of the salts, indicating that lithium salts can assist the backside attack. This probably explains why the stereochemistry of the typical Corey–Chaykovsky reaction is completely different from that



Structure and net charges of TS Energy diagram

Scheme 4.

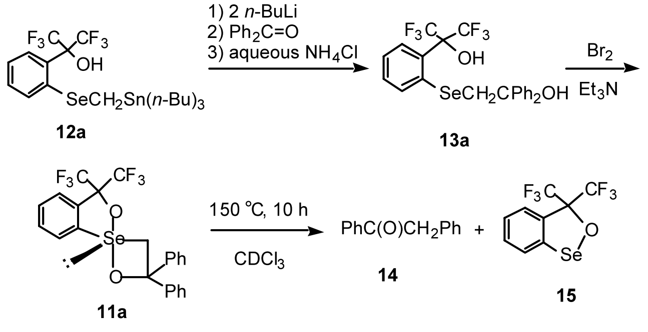
of the present oxirane formation. Therefore, the present reaction can be recognized as a salt-free Corey–Chaykovsky reaction.

The concerted oxirane formation from the 1,2-oxathietane was evidenced by ab initio calculations (RHF/4-31G*). Both the structure of the transition state and energy diagram for the oxirane formation from model compound **10** are shown in Scheme 4 [13]. A similar polarized transition state was reported for the apical-equatorial ligand coupling of sulfuranes [17]. This is the first finding for oxirane formation pathway from 1,2-oxathietanes, which can be recognized as a carbon–oxygen ligand coupling reaction of sulfuranes [18]. Very recently, Aggarwal and co-workers reported theoretical calculations on stereoselective oxirane formation by the reaction of in situ generated sulfur ylide with aldehydes using model compounds. In their system, a tetracoordinate 1,2-oxathietane is not an intermediate and stereoselectivity comes from steric repulsion in nucleophilic attack of carbanion of ylide on the carbon of carbonyl group. They also claimed that their calculations were able to reproduce the X-ray structure of our compound and that the electronic structure of our compound is so different from that of their systems that this observation is not relevant to the standard epoxidation mechanism [19].

2.2. Tetracoordinate 1,2-oxaselenetanes

2.2.1. Tetracoordinate 1,2-oxaselenetanes bearing the Martin ligand

We have described the syntheses and isolation of tetra- and pentacoordinate 1,2-oxathietanes **1** and **8** [11–13] and the oxirane formation reaction with retention of configuration in the thermolysis of **8c** and **8d** [13]. This stereochemistry suggests another possible mechanism for the Corey–Chaykovsky reaction, i.e., the formation and carbon–oxygen ligand coupling reaction of intermediary high coordinate 1,2-oxathietanes, which prompted us to examine the reactivity of such a species on changing a central atom from sulfur to heavier chalcogen. Tetracoordinate 1,2-oxaselenetane **11a** was readily obtained as stable colorless crystals from selenide **12a** via β-hydroxyalkyl selenide **13a** as shown in Scheme 5 [20].



Scheme 5.

The X-ray crystallographic analysis indicated that **11a** has a structure similar to those of tetracoordinate 1,2-oxathietanes [11–13]. This is the first example of a 1,2λ^4-oxaselenetane ring system. Thermolysis of **11a** gave phenyl-migrated ketone **14** and the corresponding cyclic selenenate **15**, and neither the corresponding alkene nor oxirane was obtained at all (Scheme 5) [22].

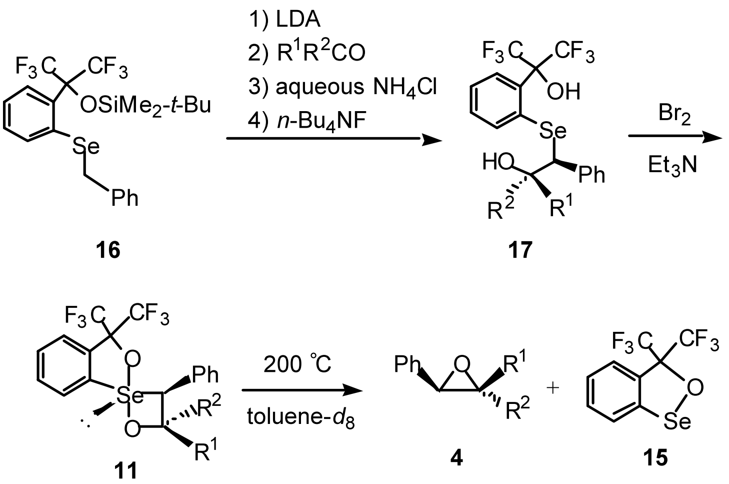
Taking into consideration that 3-phenyl sulfur analogues gave the corresponding oxiranes, 3-phenyl-1,2-oxaselenetanes **11b**–**d** were expected to give the corresponding oxiranes. 3-Phenyl-1,2-oxaselenetanes **11b**–**d** were synthesized from benzyl selenide **16** via **17** as shown in Scheme 6 [21]. The ^{19}F- and ^{1}H-NMR spectra of the crude reaction mixtures showed the signals due to a diastereomeric mixture of *trans*-**11b**–**d** in which the 3-phenyl group was *cis* to the lone pair. However, *cis*-**11b**–**d** were less stable toward hydrolysis than *trans*-**11b**–**d** and gradually decomposed in the course of purification. All compounds *trans*-**11b**–**d** were stable colorless plates at room temperature in the air.

Expectedly, thermolysis of *trans*-**11b** (toluene-d_8, 200 °C, 6 d) afforded the corresponding oxirane **4b** quantitatively, so the stereochemistry of this reaction was investigated using diastereomers **11c** and **11d**, whose stereochemistry was determined also by differential NOE experiments. Thermolyses of *trans*-**11c** (toluene-d_8, 200 °C, 30 h) and *trans*-**11d** (toluene-d_8, 200 °C, 5 h) gave oxiranes **4c** and **4d** stereospecifically in high yields with retention of the relative stereochemistry of the starting oxaselenetanes, respectively, though a small amount (2%) of an inverted product was obtained from **11c** (Scheme 6) [25]. These results suggest that such a concerted oxirane formation from high coordinate oxachalcogenetanes generally proceeds regardless of the central atom or its coordination number.

2.2.2. 1,5-Dioxa-4λ^4-selenaspiro[3.3]heptanes

For the purpose of elucidating the influence of ring size of the spiro-ring system on the reactivity of the heterocyclobutanes, we studied the synthesis and reactivity of tetracoordinate 1,5-dioxa-4λ^4-selenaspiro[3.3]heptanes, a novel type of a spiroselenurane bearing two 1,2-oxaselenetane rings [22].

Sequential treatment of $(PhSCH_2)_2Se$ (**18**) with lithium diisopropylamide (LDA), with freshly generated hexafluoroacetone (HFA), and then with aqueous NH_4Cl gave mono(2-hydroxyalkyl) selenide **19** (28%). Diastereomeric mixture of bis(2-hydroxyalkyl) selenides **20** was obtained from **19** by repetition of the same procedure as the addition of HFA to **18**. Separation by flash column chromatography (SiO_2) gave *dl*-**20** (7%) and *meso*-**20** (61%). Oxidative cyclization of *dl*-**20** and *meso*-**20** with Br_2 in the presence of Et_3N afforded the corresponding tetracoordinate 1,5-dioxa-4λ^4-selenaspi-



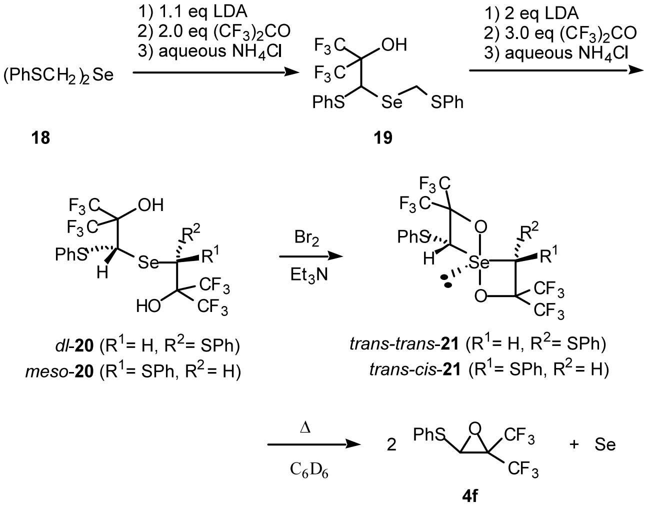
16 **17** **11** **4** **15**

b: R^1= CF$_3$, R^2= CF$_3$
c: R^1= CF$_3$, R^2= Ph
d: R^1= Ph, R^2= CF$_3$

Scheme 6.

ro[3.3]heptanes *trans–trans*-**21** (30%) and *trans–cis*-**21** (49%), respectively.

In the ^{1}H, ^{13}C, and ^{19}F-NMR spectra of *trans–trans*-**21**, the two oxetane rings were observed equivalently, whereas those of *trans–cis*-**21** were nonequivalent. Downfield shifts from *dl*-**20** (δ 4.98, δ_C 52.31) to *trans–trans*-**21** (δ 6.35, δ_C 88.07) were observed for the proton and carbon of the methine adjacent to the central selenium, which is a common spectral feature for tetracoordinate 1,2-oxachalcogenetanes [8d,11-13,21]. In the ^{77}Se-NMR spectra of *trans–trans*-**21** (δ_{Se} 835.3) and *trans–cis*-**21** (δ_{Se} 882.0) were observed multiplets due to the long-range coupling with ^{19}F nuclei. The large downfield shifts in δ_{Se} from **20** (δ_{Se} 521.1 (*dl*), 521.7 (*meso*)) to **21** and their chemical shifts close to those of compounds **11** (**11a**: δ_{Se} 840.8; **11b**: δ_{Se} 781; **11c**: δ_{Se} 793) [20,21] strongly support the selenurane structure for **21**. We have also synthesized *trans–trans*-**22** with two phenyl groups instead of two phenylthio groups of *trans–trans*-**21**.



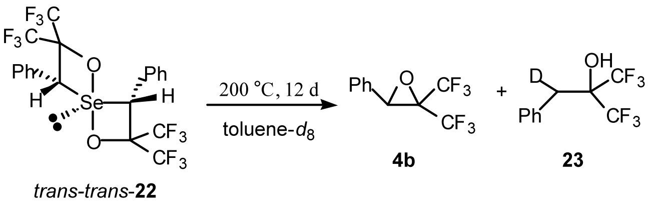
(PhSCH$_2$)$_2$Se **18** **19**

dl-**20** (R^1= H, R^2= SPh)
meso-**20** (R^1= SPh, R^2= H)

trans-trans-**21** (R^1= H, R^2= SPh)
trans-cis-**21** (R^1= SPh, R^2= H)

2 **4f** + Se

Scheme 7.



trans-trans-**22** **4b** **23**

Scheme 8.

Thermolyses of *trans–trans*-**21** (C_6D_6, 120 °C, 11 h) and *trans–cis*-**21** (C_6D_6, 60 °C, 19 h) in a degassed sealed tube gave oxirane **4f** in 144 and 166% yields [23], respectively, with black precipitates and minor unidentified products, indicating that both compounds underwent double oxirane extrusion reaction. The formation of elemental selenium (black precipitates) was confirmed by observation of the signal due to tris(dimethylamino)phosphine selenide (δ_P 84.9) after treatment of the reaction mixture with tris(dimethylamino)phosphine (δ_P 121.5). On the other hand, the thermolysis of *trans–trans*-**22** (toluene-d_8, 200 °C, 12 d) gave a somewhat complicated mixture containing the oxirane **4b** (62%) and deuterated alcohol **23** (38%) (Scheme 8) [23]. The formation of **23** indicates that the radical species were generated by homolytic bond cleavage, probably because drastic conditions were necessary for the thermolysis.

Although the oxetanes containing a pentacoordinate group 14 or 15 element gave the olefins, the spiro oxachalcogenetanes yielded the oxiranes, regardless of the ring size (five or four membered ring). This indicates that the thermal reactivity mainly depends on the bond energy of the oxygen and the central atoms.

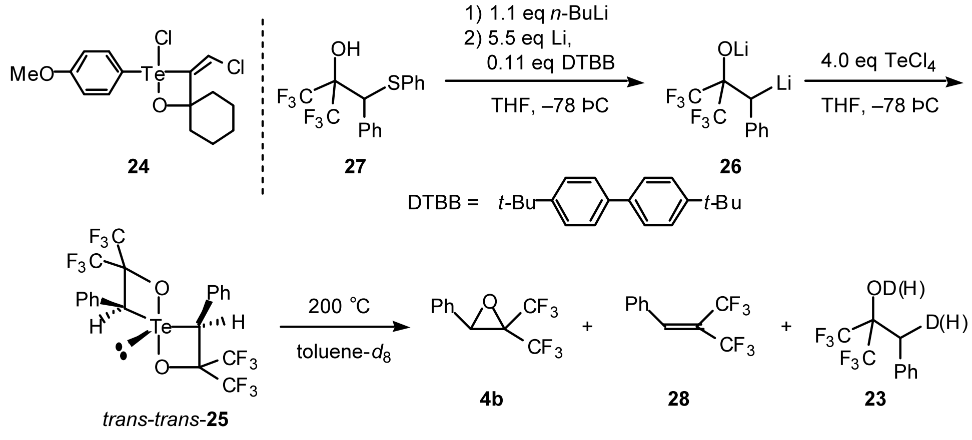
2.3. 1,5-Dioxa-4λ^4-telluraspiro[3.3]heptanes

As described above, we have found that pentacoordinate 1,2λ^6-oxathietanes **8c** and **8d** and tetracoordinate 1,2λ^4-oxaselenetanes **11c** and **11d** bearing the Martin ligand do not yield the olefins, but the oxiranes with retention of configuration, indicating the deep relationship with the Corey–Chaykovsky reaction and also found that tetracoordinate 1,5-dioxa-4λ^4-selenaspiro[3.3]heptanes **21** bearing two oxaselenetane rings undergo double oxirane extrusion. Such an oxirane formation from high coordinate 1,2-oxachalcogenetanes is expected to proceed regardless of the central chalcogen atom. The chemistry of a 1,2-oxatelluretane, however, has not been explored in detail; there has been only one report on the isolation of a 2-chloro derivative **24** whose thermal reactivity has not yet been investigated [24]. We next tried to examine the synthesis, crystal structure, and unique thermal behavior of the first 1,5-dioxa-4λ^4-telluraspiro[3.3]heptane **25**.

The first trial for the synthesis of **25** by oxidative cyclization of the corresponding bis(2-hydroxyalkyl) tellurides, which was effective for the synthesis of its selenium analogue **21** as shown in Scheme 7, 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 $\mathrm{LiCHPhC(CF_3)_2OLi}$ (**26**) generated by Yus' method [25]. Successive treatment of 2-hydroxyalkyl phenyl sulfide **27** 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 **26** (Scheme 9) [26]. Adding an excess amount of $\mathrm{TeCl_4}$ to **26** at −78 °C and further warming the reaction mixture to the room temperature gave a single isomer of 1,5-dioxa-4λ^4-telluraspiro[3.3]heptane **25** in 13% yield as a stable solid in the air.

In the ^{1}H, ^{13}C, and ^{19}F-NMR spectra of **25**, two 1,2-oxatelluretane rings were observed equivalently. In the ^{125}Te-NMR spectra, a signal of **25** (δ_{Te} 1207 in $\mathrm{CDCl_3}$) 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 [27]. Its structure was finally determined by X-ray crystallographic analysis. It was revealed that there are two independent molecules of **25** in the unit cell. The two molecules are very similar, with the phenyl groups at the 3- and 3′-positions *cis* to the lone pair of the tellurium. The apical O–Te–O bond angle (148.08(10)°), which is much smaller than that (160.53(7)°) of a tellurane bearing two Martin ligands [28], deviates considerably from linearity, a common structural feature of the hypervalent species containing a four-membered ring [8,9]. The bond lengths in the four-membered rings are similar to the previously reported 2-chloro-1,2-oxatelluretane [24]. Interestingly, it forms a dimer with intermolecular contacts between Te and O in contrast to oxathietanes and oxaselenetanes [11,12,20,22,28,29]. This is the first example of the synthesis and structural analysis of a 1,5-dioxa-4λ^4-telluraspiro[3.3]heptane derivative.

Thermolysis (toluene-d_8, 200 °C, 180 h in a degassed sealed tube) of *trans–trans*-**25** gave the corresponding oxirane **4b** (135%) and olefin **28** (7%), together with deuterated alcohol **23** (56%) (Scheme 9) [23]. Judging from ^{19}F-NMR spectra, the ratio of the products, **4b**, **28** and **23**, 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 high coordinate main group elements [1–4,6–9,11–13,20–23]. The yield of **4b**, exceeding 100%, indicates the double oxirane formation from the single molecule of **25**. Although the oxetanes containing a pentacoordinate group 14 or 15 element gave the corresponding olefin [8], the oxachalcogenetanes in the spiro ring



Scheme 9.

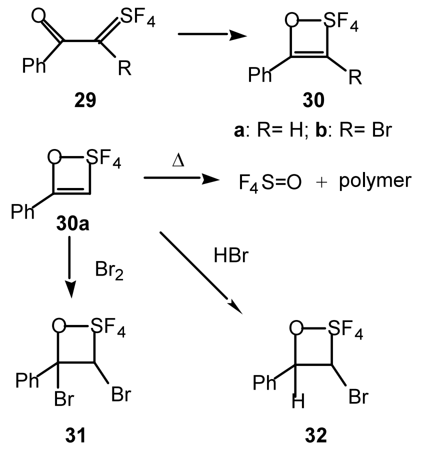
systems did not yield the olefins but the oxiranes regardless of the ring size (five- or four-membered ring) of the other ring except for **25** [20,21]. These results have showed an interesting difference in the reactivity between oxetanes with a tetracoordinate sulfur, selenium, and tellurium. Dicoordinate 1,2-oxatelluretane to be formed in the first step was not observed in the reaction mixture by NMR spectroscopy, probably because of its instability under the reaction conditions. The formation of alcohol **23** is reasonably explained by the generation of the radical species through homolytic bond cleavage. Thermolysis of **25** using cumene as a solvent afforded **4b** (20%) and **23** (180%) without the formation of **28**. The loss of **4b** and **28** together with the gain of **23** clearly indicates that **4b** and **28** were formed mostly via the radical pathway. It cannot be ruled out that a part of **4b** 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 **28** might be formed by concerted mechanism if homolytic bond fission of Te–C (or Te–O) of **25** is reversible and if this process competes with concerted and/or ionic stepwise mechanisms [20,21].

Depending on the substrates, the reactions of telluronium ylides with carbonyl compounds were reported to give Wittig type products and/or Corey–Chaykovsky type products, respectively, while the reaction mechanism has not been elucidated yet [10]g[10]h[10]i. 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 [10]h. 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 ylides with a carbonyl compound. In this study, we have demonstrated the unprecedented formation of the oxirane and olefin from a 1,5-dioxa-4λ^4-telluraspiro[3.3]heptane.

3. High coordinate 1,2-oxachalcogenetes

3.1. Hexacoordinate 1,2-oxathiete

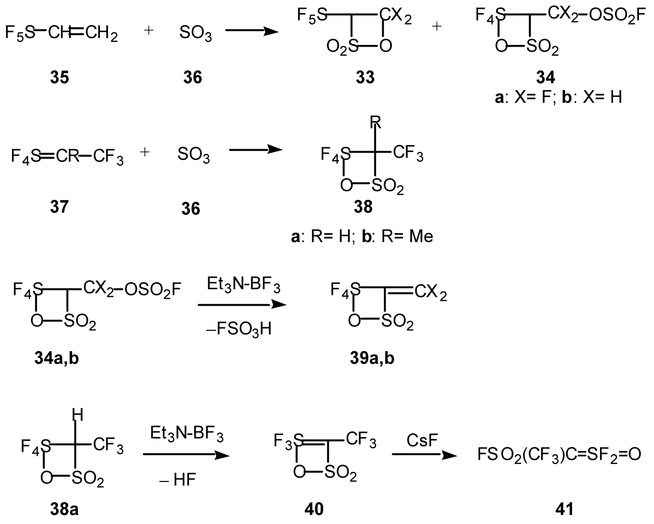
This class of compound was reported by Seppelt and co-workers [30]. Benzoylalkylidene sulfur tetrafluoride **29** isomerized to 1,2-oxathiete **30**. The structure was determined by X-ray analysis. Thermolysis of **30a** gave the $F_4S{=}O$ and polymer, and Br_2 and HBr added to the carbon-carbon double bond of **30a** gave the corresponding 1,2-oxathietanes **31** and **32**, respectively (Scheme 10).



Scheme 10.

3.2. 1,2,4-Oxadithietanes and 1,2,4-oxadithietes

In the course of a study on the synthesis of (pentafluoro-λ^6-sulfanyl)sultone **33**, Seppelt and co-workers found that 1,2,4-oxadithietanes **34** and **38** were synthesized by the reaction of pentafluorosulfuranylethene **35** with two mole equivalents of sulfur trioxide (**36**) and by the reaction of alkylidenesulfurane **37** with **36**, respectively [31]. Exocyclic elimination of fluorosulfonic acid from **34a** and **34b** with $Et_3N{-}BF_3$ gave the corresponding 3-methylene-1,2,4-oxadithietanes **39a** and **39b**, while endocyclic loss of hydrogen fluoride from **38a** with $Et_3N{-}BF_3$ afforded 1,2,4-oxadithiete **40**. Their structures were supported by NMR spectral data and finally determined by the X-ray crystallographic analysis. In the case of compound **34a** the major diastereomer has been found to have relative stereochemistry of *RR* or *SS*. Compound **40** is not stable at room temperature but decomposes to a ring-opened product **41**. Cesium fluoride can catalyze this transformation as shown in Scheme 11.



Scheme 11.

4. Tetracoordinate 1λ^4,2-selenazetidines

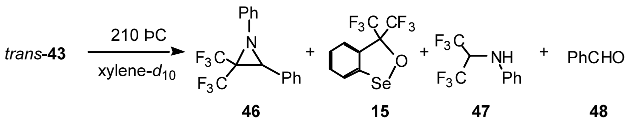
In the course of our study on the heteracyclobutanes, we previously reported the olefin formation reactions of such oxetanes bearing high coordinate group 13, 14, and 15 elements. Furthermore, we also reported the synthesis of 1,2-azaphosphetidines **42**, nitrogen versions of oxaphosphetanes [32], which undergo a Wittig-type reaction to give the olefins on their thermolysis. On the contrary to such heteracyclobutanes, we have described so far that high coordinate 1,2-oxachalcogenetanes do not give the corresponding olefins and that some of them gave the corresponding oxiranes. These reactions giving the corresponding three membered ring compounds on their thermolysis are expected to proceed for other heteracyclobutanes, e.g., a 1,2-selenazetidine with a high coordinate selenium atom. However, there has been no report on the compounds with such a ring system. The synthesis of tetracoordinate 1,2-selenazetidines **43** takes advantage of the Martin ligand, for which the crystal structure has been determined and thermolysis has been examined.

Sequential treatment of benzyl selenide **16** with LDA, (hexafluoroisopropylidene)aniline (HFIA), and aqueous solution of NH_4Cl gave β-aminoalkyl selenide **44** (90%) (Scheme 12) [33]. The oxidation of β-aminoalkyl selenide **45**, which was quantitatively obtained by the desilylation of **44** with n-Bu_4NF, with mCPBA gave a mixture of two diastereomers of tetracoordinate 1,2-selenazetidines *trans*-**43** and *cis*-**43**. The chromatography of the mixture afforded *trans*-**43** (40%) and *cis*-**43** (8%) separately as stable colorless crystals.

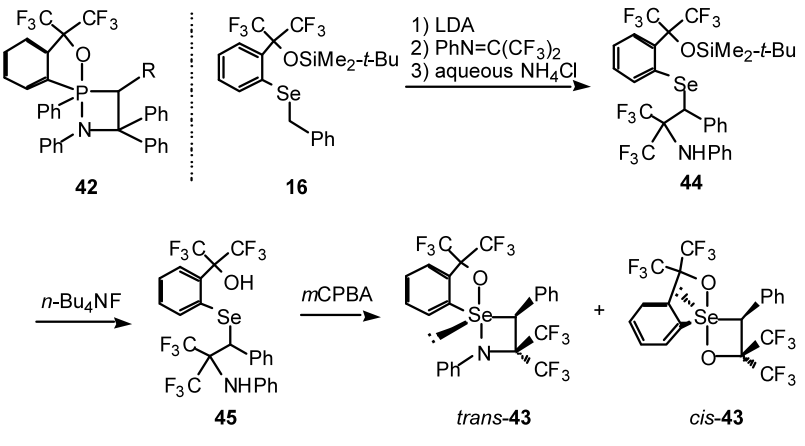
In the ^{19}F-NMR spectra of *trans*-**43** and *cis*-**43** (xylene-d_{10}), four sets of quartets for the trifluoromethyl groups derived from HFIA unit and the Martin ligand unit were observed due to their nonequivalence emerging from the ring formation. Downfield shifts of the ^{77}Se resonance ($CDCl_3$) in going from **45** (δ_{Se} 435.1) to *trans*-**43**(δ_{Se} 713.0) and *cis*-**43**(δ_{Se} 759.5), respectively, are consistent with tetracoordinate selenurane structures [34,35]. In the ^{1}H-NMR spectra ($CDCl_3$) of *trans*-**43** and *cis*-**43**, the ortho proton of the 'Martin ligand' resonated at low field (δ_H 7.96 and 8.08, respectively), which is a typical feature of compounds with a trigonal bipyramidal (TBP) or a pseudo TBP structure bearing a polar apical bond [8]. These spectroscopic features support their structures as tetracoordinate 1,2-selenazetidines.

The X-ray crystallographic analysis of *trans*-**43** revealed its distorted pseudo TBP structure with oxygen and nitrogen atoms at two apical positions and two carbon atoms and the lone pair at three equatorial positions. This is the first example of the synthesis and structural analysis of a 1,2-selenazetidine. Interestingly, the nitrogen atom of *trans*-**43** is not trigonal planar in marked contrast to that of **42**, which is isoelectronic to *trans*-**43**, though other structural features of *trans*-**43** are almost same as those of **11a** and **42** [20,32]. Pyramidal configuration for the nitrogen atom of *trans*-**43** would emerge from the steric repulsion between the Martin ligand and the phenyl group on the nitrogen atom.

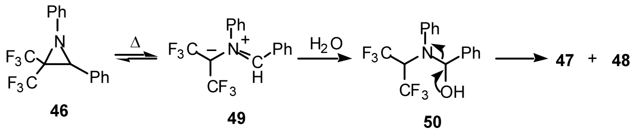
Thermolysis of *trans*-**43** (xylene-d_{10}, 210 °C) was monitored by ^{1}H and ^{19}F-NMR spectroscopy (Scheme 13). The signals due to the corresponding aziridine **46** and cyclic selenenate **15** increased with the decrease in those of *trans*-**43**. Finally, **46** (78%), **15** (100%), **47** (16%) and **48** (16%) were obtained after complete consumption of *trans*-**43**. Formation of the corresponding olefin was not observed in sharp contrast to the phosphorus analogue **42**. This is the first finding for aziridine



Scheme 13.



Scheme 12.



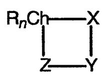
Scheme 14.

formation pathways from heteracyclobutanes with high coordinate main group elements. Compounds **47** and **48** are most likely formed by the ring opening reaction of aziridine **46** giving azomethine ylide **49**, followed by the hydrolysis of **49** with water in the reaction mixture via **50**, indicating that **47** and **48** are the secondary products of **46** (Scheme 14).

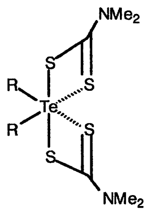
The result described above shows that a 1,2-selenazetidine has reactivity similar to that of 1,2-oxaselenetanes **11b** at the point of giving the corresponding three-membered ring compound on thermolysis. Such ligand coupling reactions on selenium would be favorable compared with the olefin formation, because the energy gain obtained by the formation of double bond between selenium and oxygen or nitrogen is too little to be the driving force of the latter reaction. We previously reported the possibility that the 1,2-oxachalcogenetanes are intermediates of the Corey–Chaykovsky reaction of chalcogenonium ylides with carbonyl compounds [13,21]. In addition, such an aziridine formation of a sulfonium ylide with a cyclic imine was previously reported as a nitrogen version of the Corey–Chaykovsky reaction [36]. The result of thermolysis of *trans*-**43** giving **46** indicates that a 1,2-selenazetidine might be the intermediate of the selenium version of this reaction. Similarly, thermolysis of *cis*-**43** (xylene-d_{10}, at 210 °C) also gave **46** (79%), **15** (100%), **47** (15%) and **48** (16%) as final products with isomerization to *trans*-**43**. These results indicate that *cis*-**43** isomerized to *trans*-**43** before its thermolysis.

Table 1
Selected bond lengths and bond angles and torsion angles of four-membered heterocyclic compounds containing high coordinate group 16 elements

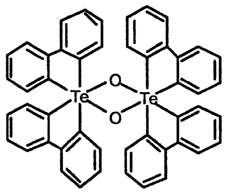
Compound	Ch	X	Y	Z	*n*	Ch-X/A	Ch-Z/A	ZX-Ch-Z/deg	Ch-X-Y-Z/deg	References
trans-**1a**	S	C	C	O	2	1.837(8)	1.764(5)	77.2(3)	−7.5(5)	[11]
trans-**1b**	S	C	C	O	2	1.859(3)	1.901(2)	73.1(1)	17.9(2)	[12]
8b	S	C	C	O	3	1.852(8)	1.822(7)	74.8(4)	6.8(7)	[12]
11a	Se	C	C	O	2	1.923(7)	1.902(4)	72.5(2)	4.7(4)	[20]
trans–*trans*-**22**	Se	C	C	O	2	1.979(6)	1.971(4)	71.1(2)	−5.9(5)	[22]
	Se	C	C	O	2	1.978(6)	1.955(4)	71.9(2)	−6.1(5)	
24	Te	C	C	O	2	2.177(5)	2.050(3)	66.3(2)	360.0 [a]	[24]
trans–*trans*-**25**	Te	C	C	O	2	2.160(3)	2.091(3)	67.30(12)	12.0(3)	[26]
						2.155(3)	2.112(3)	–	10.7(2)	
30a	S	C	C	O	4	1.785	1.687	75.6	374.6 [a]	[30]
34a	S	C	S	O	4	1.844(3)	1.696(2)	82.5(1)	361.9 [a]	[31]
40	S	C	S	O [b]	3	1.573(6)	1.715(5)	84.8(9)	359.7 [a]	[31]
trans-**43**	Se	C	C	N	2	1.991(2)	1.972(2)	69.72(8)	21.6(1)	[33]
51a	Te	S	C	S [c]	4	2.654(2)	3.173(2)	61.0(3)	–	[37]
	Te	S	C	S		2.621(2)	3.167(2)	61.1(3)	–	
	Te	S	C	S [c]	4	2.629(2)	3.244(2)	59.8(3)	–	
	Te	S	C	S		2.605(2)	3.182(2)	61.1(3)	–	
51b	Te	S	C	S	4	2.621(1)	3.186(2)	61.0(1)	–	[38]
52	Te	O	Tc	O	4	2.005(6)	2.006(6)	77.8(2)	360[a]	[39]



R= Alkyl, Ar, O
n = 2 ~ 4



51a: R= Me
51b: R= Ph



52

[a] Sum of inernal angles of the four-membered ring.
[b] CH–X bond is a double bond.
[c] Two independent molecules are present in the unit cell.

Thus, we have revealed that tetracoordinate $1\lambda^4$,2-selenazetidines give the corresponding aziridine and the cyclic selenenate on their thermolysis, which indicates the possibility that a high coordinate 1,2-heterachalcogenetane may provide the corresponding heteracyclopropane regardless of the heteroatoms.

Selected bond lengths, bond angles, and torsion angles of four-membered heterocyclic compounds containing high coordinate group 16 elements are summarized in Table 1. Tetracoordinate and pentacoordinate compounds have distorted pseudo TBP and TBP structures, while hexacoordinate compounds distorted octahedral structures. Bond angles X–Ch–Z are scattered from 59.8 to 84.8°, depending on the kind of the central atom. Judging from the torsion angles or sum of the internal angles of the four membered ring, the four-membered ring was found to be intermediate between a planar structure and a significantly puckered one.

5. Conclusion

We have described our recent results concerning isolable four-membered heterocyclic compounds containing high coordinate group 16 elements. X-ray crystallographic analyses have revealed that tetracoordinate and pentacoordinate compounds have distorted pseudo TBP structures and distorted TBP structure, respectively, with two atoms adjacent to the central atom constructing the four-membered ring at the equatorial and apical positions, respectively. One of typical reactions for this kind of ring compound is formation of the corresponding three-membered ring compound and the reaction is observed for various types of the ring compound regardless of the kinds of central atom, coordination number, and size of the other ring. Although the stereochemistry still remains unclear for some reactions, the reaction may be classified as a ligand coupling reaction between apical and equatorial ligands. These results strongly suggest the possibility that these compounds are intermediates of the Corey–Chaykovsky reactions.

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