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Review

Transannular and intermolecular interactions between chalcogen atoms: syntheses and properties of dichalcogena dications and trichalcogena hypervalent dications

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Abstract

Intramolecular (transannular) and intermolecular through-space interactions between chalcogen atoms have been described. This account includes the following three topics. (1) Various types of bis-chalcogenides and their mono-oxides, which have the two chalcogen atoms in close proximity in a molecule, give the dichalcogena dications upon the oxidation with two equivalents of $NOBF_4$ or treatment with one equivalent of triflic anhydride (Tf_2O). The stability of the dichalcogena dications increases in the order S < Se < Te. The dichalcogena dications with flexible scaffolds cause dealkylation via an S_N1 type reaction to form chalcogenachalcogenonium salts and alkyl cations. (2) The reaction of 2,6-bis[(phenylthio- or phenylseleno)methyl]phenyl phenyl telluride or the corresponding Te–oxide with $NOBF_4$ or Tf_2O affords the positively-charged hypervalent species, dicationic telluranes. Dicationic telluranes can be prepared by the remote oxidation through π-conjugation. The stable sulfenium cation can be isolated by taking advantage of 2,6-bis[(dimethylamino)methyl]phenyl ligand. (3) The remote oxygen migration and Pummerer reactions of *p*-bis(methylthio)-aromatic mono-oxides are discussed in light of an intermolecular through-space interaction between sulfur atoms, and a cyclic bis(dithia dication) dimer is proposed as an intermediate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Transannular interaction; Dichalcogena dication; Trichalcogena hypervalent dication; Sulfenium cation; Remote reaction; Intermolecular interaction

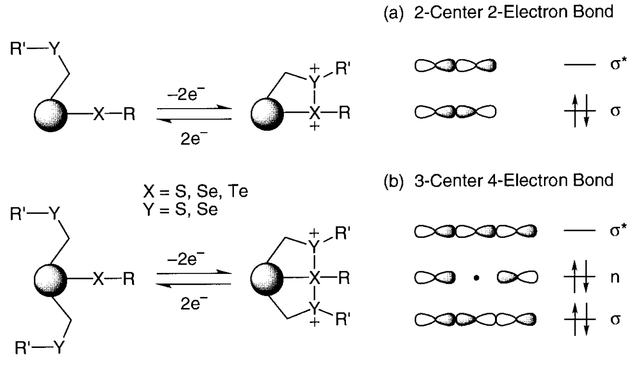

Fig. 1. Schematic representation of (a) a dichalcogena dication: 2c-2e bond and (b) a trichalcogena hypervalent dication: 3c-4e bond.

1. Introduction

Transannular interaction is a well-known phenomenon in organic chemistry [1]. When two chalcogen atoms are arranged appropriately in juxtaposition, a repulsive force between the chalcogen atoms dominates at the neutral state. However, upon removal of two electrons from the chalcogen atoms, an attractive force operates between the chalcogen atoms to create a new σ-bond which is called dichalcogena dication: a two-center two-electron (2c-2e) bond [2]. Furthermore, when a lone pair of electrons attached to a third chalcogen atom participates transannularly in the formation of a dichalcogena dication, a new dicationic species is formed in which the central chalcogen atom is tetracoordinated hypervalently with the two neighboring chalcogen atoms as the apical ligands: a 3-center

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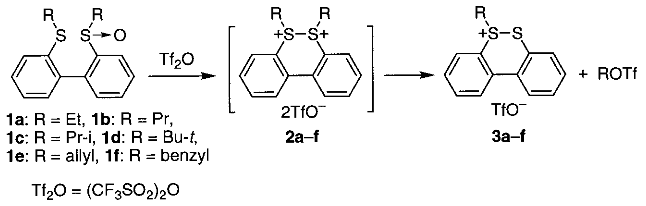


Scheme 1.

4-electron (3c-4e) bond [3]. The simple molecular orbital representation of these bond formations is shown in Fig. 1.

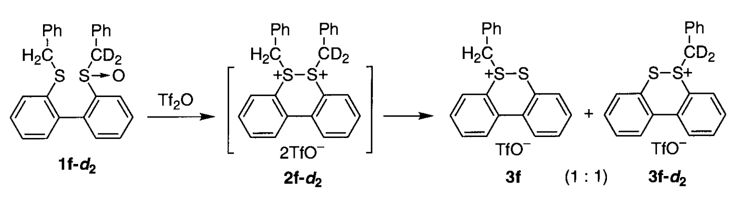
The stability and reactivity of dichalcogena dications and trichalcogena hypervalent dications largely depend on the nature of chalcogen atoms and the conformational flexibility of the scaffold. Dichalcogena dications bearing a rigid conformation such as a cyclic system (1,5-dithiacyclooctane and dibenzodithiocin) are stable and can be isolated, and have been studied extensively [4]. On the other hand, dithia dications generated from an acyclic system have not been studied well because of their instability. We have found the facile dealkylation of dichalcogena dications with a flexible conformation to give chalcogenachalcogenonium salts and alkyl cations. Trichalcogena hypervalent dications with a rigid system have also been studied intensively in our laboratory [5]. We have succeeded in the isolation and full characterization of the trichalcogena hypervalent dications with tellurium atom at the central position, which are generated from an acyclic system. This review describes our recent advances in new types of dichalcogena dications and trichalcogena hypervalent dications. We also propose a cyclic bis(dithia dication) dimer via an intermolecular through-space interaction between sulfur atoms.

2. Intramolecular dichalcogena dications and their dealkylations

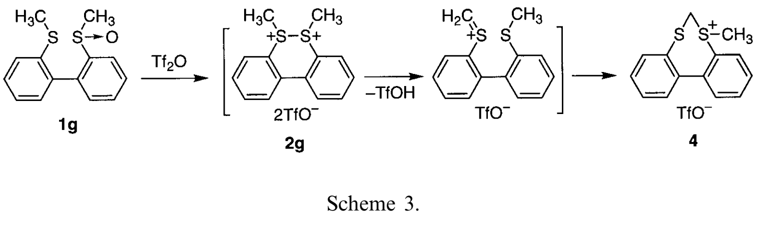
2.1. Dithia dications from 2,2′-bis(alkylthio)biphenyl mono-oxides [6,7]

The reaction of 2,2′-bis(alkylthio)biphenyl mono-oxides (**1a**, R = Et; **1b**, R = Pr; **1c**, R = *i*-Pr; **1d**, R = *t*-Bu; **1e**, R = allyl; **1f**, R = benzyl) with one equivalent of triflic anhydride (Tf_2O) in $CHCl_3$ or CH_3CN at −45°C to room temperature (r.t.) gave the corresponding thiasulfonium salts **3a**–**f** as the dealkylated product in quantitative yields together with alkyl triflates, respectively (Scheme 1). For **1a** and **1b**, dithia dications **2a** and **2b** were observed by ^{1}H-NMR spectroscopy during the course of the reaction in CD_3CN at −45°C. For example, in the ^{1}H-NMR spectrum of **1a**, the two sets of peaks showing the unsymmetrical structure in **1a** due to the diastereomers disappear immediately on addition of Tf_2O, and a new set of peaks having a highly symmetrical structure appears in its place at δ 1.43 (t, $J = 7.2$ Hz, 3H) and 3.80–3.95 (m, 2H). The ^{13}C-NMR spectrum under the same conditions shows a similar result. This species generated in situ was treated with two equivalents of thiophenol or H_2O at −45°C to give the bis-sulfide of **1a** and diphenyl disulfide or **1a** in quantitative yield, respectively. These results indicate unambiguously the generation of dithia dication **2a**, which is decomposed gradually to thiasulfonium salt **3a** and ethyl triflate. For **1c**–**f**, dithia dications **2c**–**f** were not detected due to their high instability. However, the reaction of deuterium-labeled **1f**-d_2 afforded a 1:1 mixture of **3f** and **3f**-d_2 (Scheme 2), suggesting that the present reaction proceeds through the formation of dithia dication **2**.

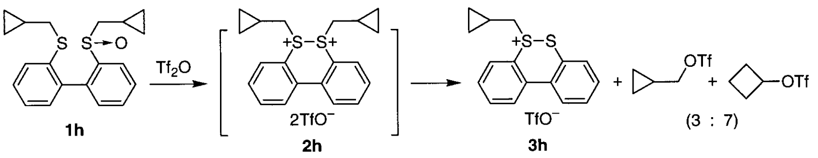
The reactivity of dithia dication **2g** from 2,2′-bis(methylthio)biphenyl mono-oxide **1g** is the only exception, which was converted into cyclic methylsulfonium



Scheme 2.



Scheme 3.



Scheme 4.

salt **4** in 80% yield. The formation of **4** may proceed through dithia dication **2g** followed by its deprotonation and, subsequently, nucleophilic addition by the neighboring sulfide sulfur atom on the carbon atom of the resulting methylidene sulfonium group (Scheme 3). The isotope effect (k_H/k_D) in the step of proton abstraction was 7.7. The study on the intramolecular competitive dealkylation by use of **1** having two kinds of alkyl groups reveals the relative reactivity of alkyl groups on the sulfur atoms of dithia dications **2**, which decreases in the order: benzyl ≫ Et > Pr ≫ Me group for the dealkylation reaction and Me ≫ Et, Pr > benzyl group for the deprotonation.

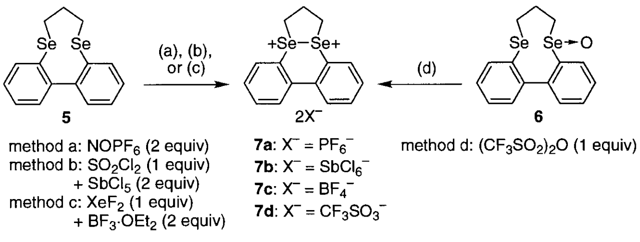
Thus, dithia dications with a flexible structure are highly reactive to result in the facile dealkylation reaction. It is noteworthy that triflate anion, which possesses a very weak nucleophilicity, acts as a nucleophile. The kinetic study using dithia dications **2a** and **2b** generated in situ from **1a** and **1b** with Tf_2O was carried out in CD_3CN. Both dealkylation reactions of **2a** and **2b** obey good first-order kinetics, and their activation parameters are $E_a = 21.5 \pm 1.1$ and 25.2 ± 0.6 kcal mol^{-1}, $\Delta H^{\neq}_{298} = 21.0 \pm 1.1$ and 24.8 ± 0.5 kcal mol^{-1}, and $\Delta S^{\neq}_{298} = 14.8 \pm 4.5$ and 30.4 ± 2.1 eu, respectively. The large positive $\Delta S^{\neq}_{298}$ values in both cases suggest that a transition state for the dealkylation of **2** should be 'loose' where the C–S(+) bond is weakened and lengthened, indicating an S_N1 process. Further evidence for a S_N1 process in the present dealkylation reaction arises from the reaction of 2,2′-bis(cyclopropylmethylthio)biphenyl mono-oxide **1h** with Tf_2O (Scheme 4). When the reaction of **1h** with Tf_2O was carried out at −90°C in CD_2Cl_2, the ^{1}H-NMR spectrum showed the formation of cyclopropylmethyl and cyclobutyl triflates in a 3:7 ratio as well as cyclopropylmethyl thiasulfonium salt **3h**, although the corresponding dithia dication **2h** was not detected at all. The important fact is that the ratio of cyclopropylmethyl and cyclobutyl triflates obtained here remains unchanged below −40°C. This result supports strongly the notion that cyclobutyl triflate is not formed by an isomerization of cyclopropylmethyl trifiate, but is formed in the initial dealkylation step from dithia dication **2h**, indicating a large S_N1 character in the present reaction.

In general, dealkylation of sulfonium salts requires high temperature [8]. On the other hand, the dealkylation of dithia dications **2** proceeds smoothly at less than 0°C. Thus, the formation of dithia dications with a flexible conformation provides a new method for the generation of carbocations [9].

2.2. Diselena dications from 2,2′-bis(alkylthio)biphenyls and their mono-oxides [10]

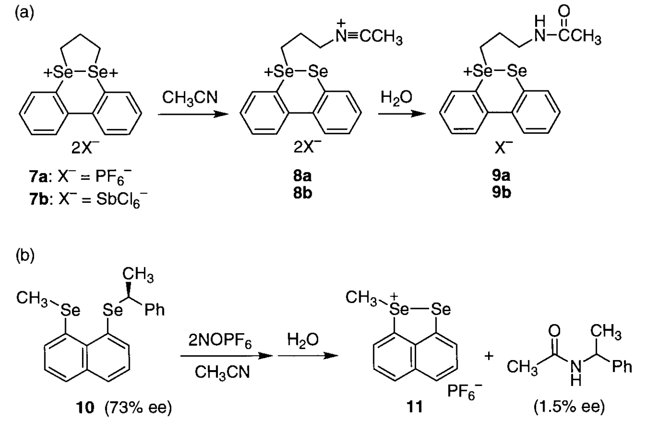
Diselena dications are more stable than the corresponding dithia dications. Diselena dications **7** can be synthesized and isolated at −20°C upon various oxidation methods. The reactions of bis-selenide **5** with two equivalents of $NOPF_6$ (Method a), one equivalent of SO_2Cl_2 and two equivalents of $SbCl_5$ (Method b), and one equivalent of XeF_2 and two equivalents of $BF_3 \cdot OEt_2$ (Method c) in CH_2Cl_2 or CH_3CN at −45 to −20°C gave diselena dications **7a**–**c** in quantitative yields, respectively (Scheme 5). The reaction of the mono-oxide of bis-selenide **6** with one equivalent of Tf_2O (Method d) in CH_2Cl_2 at −45 to −20°C afforded diselena dication **7d**. The ^{77}Se-NMR spectra of **7a**–**d** in CD_3CN at −20°C show only one signal at δ 655 ~ 659, which is shifted downfield by 347 ~ 351 ppm relative to the signal of **5**. These remarkable downfield shifts are characteristic of diselena dications. Diselena dications **7a**–**d** are dealkylated gradually in CD_3CN at r.t.

The counter anions of diselena dications **7a** and **7b** have no nucleophilicity. Nevertheless, **7a** and **7b** in CD_3CN at 20°C were completely dealkylated to give selenaselenonium salts **8a** and **8b** bearing a nitrilium moiety at the terminal end of the alkyl chain, respectively, which were converted to selenaselenonium salts **9a** and **9b** bearing an amide group by adding H_2O (Scheme 6(a)). This suggests that the dealkylation of **7** proceeds via an S_N1-like process. Further evidence for the dealkylation process comes from the reaction of a bis-selenide having a chiral alkyl group with $NOPF_6$. If the dealkylation proceeds via an S_N1, S_N2, or a ligand coupling process, the chirality of the resulting alkylamide after quenching with H_2O would be a racemic-,

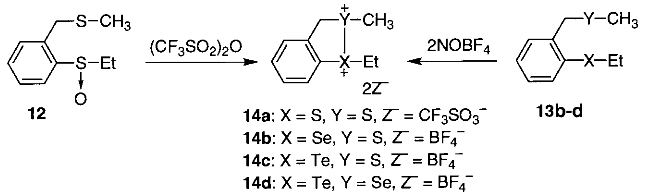


method a: $NOPF_6$ (2 equiv)
method b: SO_2Cl_2 (1 equiv) + $SbCl_5$ (2 equiv)
method c: XeF_2 (1 equiv) + $BF_3 \cdot OEt_2$ (2 equiv)
7a: $X^- = PF_6^-$
7b: $X^- = SbCl_6^-$
7c: $X^- = BF_4^-$
7d: $X^- = CF_3SO_3^-$
method d: $(CF_3SO_2)_2O$ (1 equiv)

Scheme 5.



Scheme 6.



Scheme 7.

inversion-, or retention-form, respectively. The reaction of bis-selenide **10** bearing the chiral α-phenethyl group (73% ee) with two equivalents of $NOPF_6$ in CH_3CN at −40°C, followed by quenching immediately with H_2O, afforded methyl selenaselenonium salt **11** and *N*-α-phenethylacetamide which was almost racemized (1.5% ee) (Scheme 6(b)). This indicates an S_N1 process for the present dealkylation.

2.3. Hybrid dichalcogena dications [11,12]

The stability and reactivity of dichalcogena dications depend largely on the nature of chalcogen atoms. In order to disclose this nature clearly, hybrid dichalcogena dications **14** were prepared and their reactivities were compared. Dithia dication **14a** was prepared from the reaction of sulfoxide **12** with one equivalent of Tf_2O in CH_3CN at −40°C. The hybrid dichalcogena dications, i.e. selenathia dication **14b**, tellurathia dication **14c**, and telluraselena dication **14d**, were prepared from the reactions of bis-chalcogenides **13b**–**d** with two equivalents of $NOPF_6$ in CH_3CN at −40°C, respectively (Scheme 7).

Tellurathia dication **14c** and telluraselena dication **14d** in CD_3CN are stable even at 50°C. In marked contrast, dithia dication **14a** and selenathia dication **14b** in CD_3CN were decomposed gradually to give methyl thiasulfonium salt **15a** and methyl selenasulfonium salt **15b**, respectively, together with ethyl iminium salt which was converted to *N*-ethylacetamide by adding H_2O(Scheme 8). The kinetic study of the deethylation from **14a** and **14b** was carried out in CD_3CN. Both reactions obey good first-order kinetics, and the rate constant of the deethylation at 0°C is calculated to be $k_1 = (9.81 \pm 0.04) \times 10^{-4}\ s^{-1}$ for **14a** and $k_1 = (5.07 \pm 0.28) \times 10^{-4}\ s^{-1}$ for **14b**. The activation parameters of the deethylation from **14a** are $E_a = 20.5 \pm 0.2$ kcal mol^{-1}, $\Delta H^{\neq}_{298} = 20.0 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\neq}_{298} = 0.72 \pm 0.63$ eu. Therefore, the stability of dichalcogena dications decreases in the order Te(**14c**) ≫ Se(**14b**) > S(**14a**).

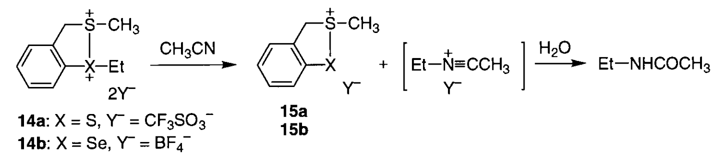
To obtain information on the stability of dichalcogena dications **14a**–**d**, ab initio calculations were carried out at the RHF/3-21G$^{(*)}$ level. The atomic charges were calculated by the natural population analysis. The atomic charges on the central chalcogen atom in these dications were found to be +0.86 (S, **14a**), +1.06 (Se, **14b**), +1.54 (Te, **14c**), and +1.44 (Te, **14d**). The bond orders of X–CH_2CH_3 in these dications are 0.773 (**14a**), 0.816 (**14b**), 0.909 (**14c**), and 0.910 (**14d**). This order agrees with the stability of **14a**–**d** obtained by the experimental results. The dichalcogena dications become more stable as the electronegativity of the central chalcogen atom becomes smaller.

The reaction of chiral α-phenethyl sulfoxide **16** (99% de) with one equivalent of Tf_2O gave methyl thiasulfonium salt **15a** and *N*-α-phenethylacetamide (89%) on hydrolysis, the enantiomer excess of which was only 1.7% ee (Scheme 9). The reaction of 2,2-diphenylethyl sulfoxide **17** with one equivalent of Tf_2O gave **15a** and *trans*-stilbene (75%). These results support that the dealkylation from these dications proceeds via an S_N1 process.

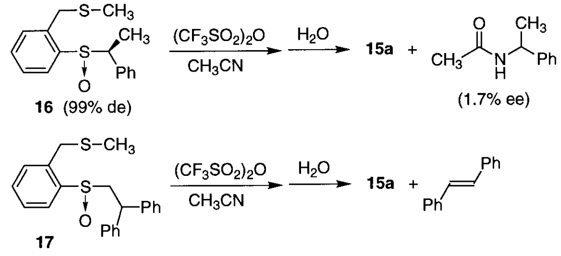
3. Trichalcogena hypervalent dications: 3-center 4-electron bond

3.1. Dicationic telluranes [13]

Recently, considerable interest has focused on the study of positively-charged hypervalent chalco-



Scheme 8.

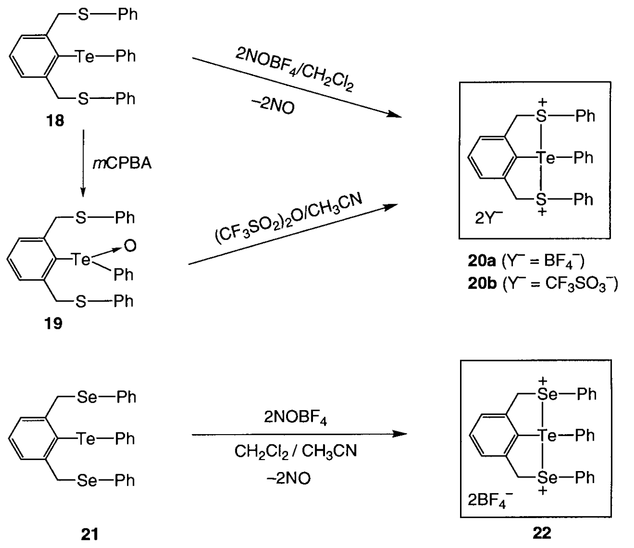


Scheme 9.

genuranes [5,14]. We have described the preparation and characterization of a new type of dicationic σ-telluranes (λ^4-tellane) [10-Te-4(C2X2)$^{2+}\cdot 2Y^-$ (X = S or Se, Y = BF_4 or CF_3SO_3) **20a**, **20b**, and **22** from the new flexible acyclic tris-chalcogenide, 2,6-bis[(phenylthio)methyl]phenyl phenyl telluride **18** and 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluride **21**, and the corresponding telluroxide **19** via transannular bond formation.

Diaryl telluride derivatives **18** and **21** were oxidized readily by adding a solution of anhydrous CH_2Cl_2 containing $NOBF_4$ (two equivalents) dropwise to a solution of anhydrous CH_2Cl_2/CH_3CN containing **18** or **21** at −78°C under an argon atmosphere. After removal of the solvent, the tellurane dication $2BF_4^-$ salts **20a** and **22** were isolated as yellow solids in 92 and 51% yield, respectively. Treating the corresponding telluroxide **19** with trifluoromethanesulfonic anhydride [$(CF_3SO_2)_2O$; one equivalent] in dry CH_3CN under an argon at 0°C resulted in its conversion to the yellow tellurane dication $2CF_3SO_3^-$ salt, **20b** as shown in Scheme 10.

In order to determine the molecular structures of **20a**, **20b**, and **22**, ^{1}H-, ^{13}C-, ^{77}Se-, and ^{125}Te-NMR spectra were measured. The ^{1}H-NMR spectrum of each compound when measured in CD_3CN at 20°C exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.95, 5.21 ($J = 17.3$ Hz) and δ 4.45, 5.15 ($J = 17.1$ Hz); δ 4.45, 5.13 ($J = 17.7$ Hz) and δ 5.09, 5.24 ($J = 17.0$ Hz); and δ 4.26, 5.23 ($J = 16.0$ Hz) and 4.96, 5.23 ($J = 15.0$ Hz) in a 1:1 ratio, respectively. These signals were assigned to the asymmetric bicyclic form. The ^{125}Te-NMR spectra of **20a** and **20b** show a single peak only at 1327.3 and 1330.7 ppm, respectively. However, the ^{125}Te-NMR spectrum of **22** shows one peak at 1174.9 ppm at −40°C with four satellite peaks due to the spin–spin coupling ($^1J_{Te\text{-}Se} = 443$, 491 Hz) between the central tellurium and two asymmetric selenium atoms. The ^{77}Se chemical shifts of **22** appear at 393.6 and 462.3 ppm at −40°C with some satellite peaks. Interestingly, each site shows four satellite peaks not only due to the spin–spin coupling ($^1J_{Se\text{-}Te} = 443$, 491 Hz) between the selenium and tellurium atoms, but also due to the coupling ($^2J_{Se\text{-}Se} = 71$ Hz) between selenium atoms through the tellurium atom. Such an example of spin–spin coupling through a 3c-4e bond has not been reported and is thus an addition to the very interesting behavior of hypervalent chemistry. These results indicate that compound **22** also exists in the asymmetric bicyclic form and supports the bond formation between the tellurium and selenium atoms.



Scheme 10.

In principle, the dications **20a**, **20b**, and **22** could exist as one of the following three possible stereoisomers: *cis–trans*, *trans–cis* (DL-pairs) and/or *trans–trans* (meso) and/or *cis*–cis (meso). The *trans–trans* isomer is expected to be the most sterically stable configuration of the dicationic telluranes. However, the NMR spectra of these compounds indicate that these structures have either a *cis–trans* or *trans–cis* configuration.

The X-ray crystal structure determination of **20a**, **20b**, and **22** establishes that these compounds exist only as one isomer in the solid state. The favored stereoisomer has the *trans–cis* or *cis–trans* configuration, which is in agreement with the NMR results. ORTEP views of **20a** and **22** are shown in Fig. 2.

In order to understand the electronic structure of the dicationic σ-telluranes, single point ab initio calcula-

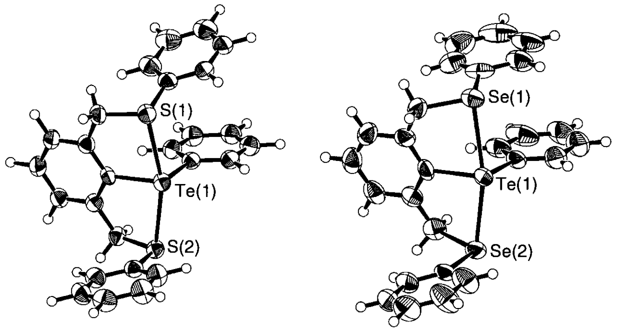
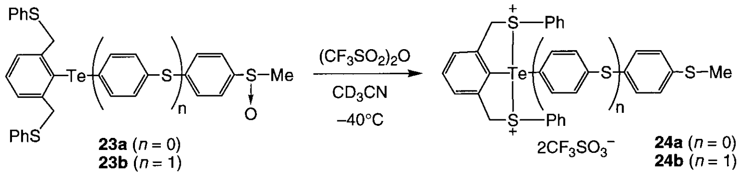


Fig. 2. ORTEP views of dicationic telluranes **20a** and **22**. The counter ions are omitted for clarity.



Scheme 11.

tions were carried out using the crystal structures of **20b** and **22**. The calculations were carried out at the RHF/3-21G$^{(*)}$ level. The atomic charges were evaluated by the natural population analysis. The atomic charges of Te(1), S(1), and S(2) in **20b** were calculated to be + 1.600, + 0.483, and + 0.495, respectively. Thus, the total positive charge of + 2.578 is located exclusively on the three chalcogen atoms of the hypervalent bonding system. The charge is larger than two due to the polarization of Te–C and S–C bonds. In addition, the hypervalent apical bonds seem to be polarized as is observed normally in hypervalent molecules, since the positive charges of S(1) and S(2) are substantially smaller than one (the charge of the sulfur atom in the trimethylsulfonium cation is calculated to be + 0.98 by the same method of calculation). In the case of **22**, the Te(1) atom is less positively charged than in **20b** and the positive charges on Se(1) and Se(2) are larger than those of the sulfur atoms in **20b**, simply reflecting the fact that the electronegativity of selenium is smaller than that of sulfur.

The positive charges are not delocalized onto the phenyl ring systems. This can be explained by the following molecular orbital consideration. Delocalization of the positive charges implies that electrons are pulled into the hypervalent bond and this would require that electrons are placed in the unfavorable antibonding molecular orbital.

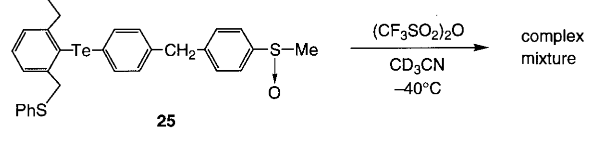
3.2. Synthesis of dicationic telluranes by remote oxidation through a π-conjugated system [15]

As mentioned in the previous section, we have succeeded in the syntheses of the dicationic σ-telluranes **20a**, **20b** and **22** [10-Te-4(C2X2), X = S, Se] by the direct reactions of tellurides or telluroxides having heteroatoms at the 2,6-positions on the benzene ring with oxidizing reagents such as $NOBF_4$ and $NOPF_6$, or $(CF_3SO_2)_2O$. Furthermore, we tried to react the tellurides connecting the sulfinyl group at the 4-position of the tellurophenyl group with $(CF_3SO_2)_2O$ to obtain the corresponding dicationic telluranes. Apparently, the deoxygenation from the sulfinyl group is promoted by the telluride group and 2,6-disubstituted phenylthiomethyl groups via the concerted donation of electrons. We propose that this process proceeds via a new remote oxidation reaction involving electron transfer through π-conjugated bonds like the Domino effect.

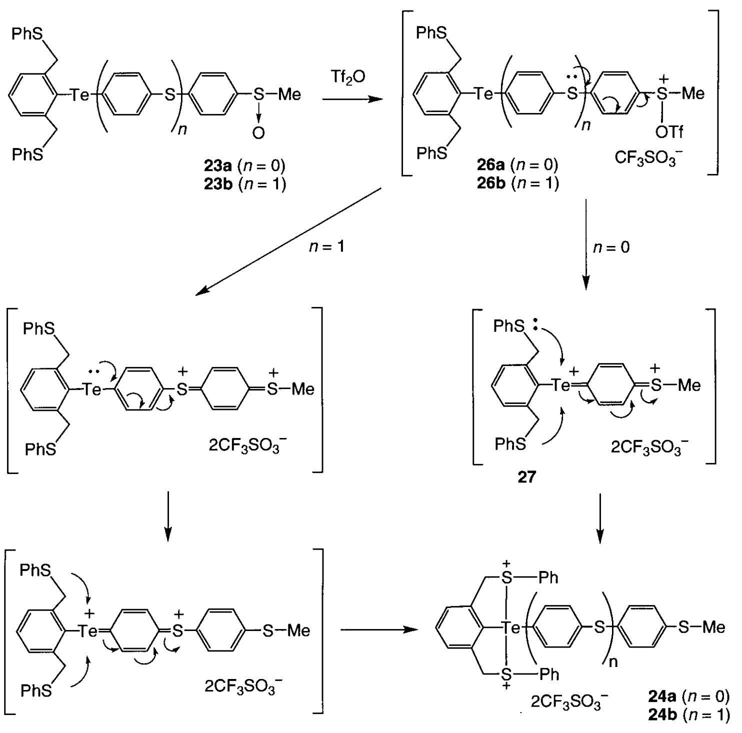
The telluride **23a** was prepared specifically by the initial oxidation of the dicationic tellurane **24a** with *m*-CPBA and then reduction of the dicationic part with PhSH. Treatment of the telluride **23a** with 1.2 equivalents of triflic anhydride (Tf_2O) at − 40°C in CD_3CN readily afforded the corresponding stable dicationic tellurane **24a** (Scheme 11). The ^{1}H-NMR spectrum of the dicationic tellurane **24a** exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.42, 5.26 ($J = 18$ Hz) and 4.90, 5.24 ($J = 17$ Hz) in a 1:1 ratio. These signals were assigned to the asymmetric bicyclic form of the dicationic tellurane as we reported. These results demonstrate that the two sulfur atoms are coordinated directly to the central tellurium atom. The ^{1}H-NMR signals of methyl protons are shifted upfield from δ 2.57 to 2.43 by adding Tf_2O. This indicates that the sulfur atom of the methylsulfinyl group is reduced to form the methylthio group. The ^{125}Te-NMR signal of **24a** appeared at δ 1343 which is similar to that of the corresponding dicationic tellurane **20b** (δ 1331) without a *p*-thiomethyl group. Finally the structure of **24a** was determined by X-ray crystallographic analysis.

The telluride **23b**, prepared similarly to **23a**, having the extended π-conjugated system, was also reacted with Tf_2O to give the corresponding dicationic tellurane **24b** with the reduced methylthio group (Scheme 11). The ^{1}H-NMR spectrum of the dicationic tellurane **24b** also shows two sets of AB quartet signals shifted downfield compared with those of the telluride **23b**. The ^{125}Te-NMR signal of **24b** was observed at δ 1339.7.

In order to determine the mechanism of this type of reaction, the telluride **25**, having no π-conjugated system between the tellurium atom and the sulfinyl group, was treated with Tf_2O. As a result of the reaction, a complex mixture was obtained and no dicationic tellurane was observed (Scheme 12). This result supports the notion that the π-conjugated system is necessary to shift the electrons from the tellurium atom to the sulfur atom in the sulfinyl group and also rules out the intermolecular electron shift between two molecules of **25**.



Scheme 12.



Scheme 13.

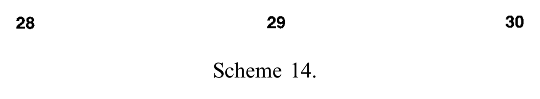
On the basis of this result, the reaction is considered to proceed via the mechanism shown in Scheme 13. The mechanism for the present reactions may proceed initially by the formation of the sulfonium salt **26a** as an intermediate followed by the reaction with Tf_2O. Subsequently, the corresponding dicationic compound **24a** should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic quinoide type compound **27** as an intermediate or a transition state, formed by the electron transfer from the tellurium atom to the sulfur atom in the methylsulfinyl group. The reaction proceeds too rapidly to observe either **26a** or **27** using NMR spectroscopy.

Furthermore, a similar reaction mechanism is predicted in the case of the reaction of the telluride **23b** with Tf_2O. As shown in Scheme 13, the electrons shift from the tellurium atom to the sulfur atom of the methylsulfinyl group through an intramolecular π-conjugation in the benzene rings and the sulfur atom. This sulfur atom is important in connecting the π-conjugated system on the tellurium atom and the sulfur atom of the methylsulfinyl group.

3.3. New sulfenium cation salts stabilized by the coordination of two nitrogen atoms [16]

Sulfenium cation species (RS^+) have long been considered to be unstable and very reactive as strong electrophilic reagents [17]. Although the formation of sulfenium cation salts has been proposed in many studies, it is controversial whether the corresponding free cation exists or not. To date, there is no report describing the actual structure of the sulfenium cation salts. Recently, the analogous selenenium and tellurenium cation salts were first prepared and isolated as a result of their stabilization by employing two neighboring amino ligands, namely, dimethylaminomethyl groups [18]. As a result of applying this ligand, we have succeeded in the isolation of sulfenium cation salts as remarkably stable crystals.

1,3-Bis[(dimethylamino)methyl]benzene **28** was lithiated easily by *n*-BuLi in anhydrous ether at r.t. under an argon atmosphere to yield 1,3-bis(dimethylaminomethyl)-2-lithiobenzene in situ. The ether solution containing the lithiated compound **29** was added dropwise to an equivalent of sulfur dichloride (SCl_2) in dry ether. After the removal of the solvent at r.t., the corresponding sulfenium chloride **29**, having Cl^- as the counter anion, was isolated as stable yellow needle-like crystals in 20% yield. Furthermore, when product **29** was treated with the potassium hexafluorophosphate (KPF_6) in CH_2Cl_2 2,6-[bis(dimethylaminomethyl)-phenyl]sulfenium hexafluorophosphate **30** was produced in 56% yield as shown in Scheme 14.



Scheme 14.

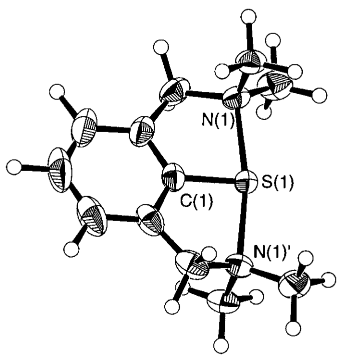


Fig. 3. An ORTEP drawing (drawn at the 50% probability level) of **30**. The counter ion is omitted for clarity.

The ^{1}H-NMR signals of the benzylic and four methyl protons in **29**, measured in $CDCl_3$ at r.t., appear as singlets at 4.31 and 2.96 ppm, respectively. These chemical shifts of those protons of **29** appear at a lower field than those of 1,3-bis(dimethylaminomethyl)-2-methylthiobenzene. These results indicate that each amino group coordinates to the cationic sulfur. The ^{1}H-NMR spectrum of **30**, measured in $CDCl_3$ at r.t., exhibits almost the same signals as **29**, and no significant difference in their chemical shifts was observed. The proton-decoupled ^{31}P and ^{19}F signals of **30** appeared at -145.4 ppm as a septet and -73.5 ppm as a doublet due to the spin–spin coupling between the phosphorus and fluorine nuclei ($^{1}J_{P-F} = 707$ Hz) which is derived from the PF_6^- counter anion. The molecular structures of both **29** and **30**, except for their counter anions, were characterized reasonably by the fragmentation peaks derived from their parent peaks in their EIMS spectra.

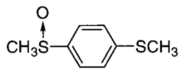
Furthermore, the solid state structure of the sulfenium cation **30** was determined by X-ray diffraction ($R = 0.037$, $R_w = 0.034$). An ORTEP view of **30** is shown in Fig. 3. In the solid state, the two neighboring amino nitrogen atoms coordinate directly to the sulfur atom. Each of the S–N distances is equal to 2.063(1) Å, which is longer than a single covalent bond (1.74 Å). The N(1)–S(1)–N(1)′ angle, 168.54(9)°, is distorted from a linear arrangement. The counter anion, PF_6^-, is independent of the cationic part of the sulfenium cation, since the closest contact (S(1)···F(3) = 3.786(2)) is longer than the sum of the van der Waals radii of a sulfur and a fluorine atom (2.20 Å). The bicyclo ring on the sulfur and nitrogen atoms are distorted and the angle between the N(1), S(1), N(1)′ and the benzene ring planes exhibited is 14.3(1)°. This X-ray data indicates clearly that in the solid state significant interactions exist between the sulfur and nitrogen atoms and the sulfenium cation is stabilized by the neighboring-group participation of the two nitrogen atoms.

In order to understand the electronic structure of sulfenium cation species single-point ab initio calculations were carried out using the crystal structure coordinates of **30**. The charge on the S atom in **30** was calculated to be $+0.550$ and the two nitrogen atoms are negatively charged. The Mulliken and Löwdin bond orders of S(1)–N(1) of **30** are 0.379 and 0.539, respectively. These results indicate that the N–S–N bond has a 3c-4e hypervalent bonding system. The sulfur atom possesses ten formal valence electrons, the two S–N bonds being polarized strongly toward the nitrogen atoms. Finally, we notice that the total 3d orbital population evaluated by the natural population analysis is very small (0.025) indicating that the d orbitals are not concerned primarily with the 3c-4e bond in agreement with the current view of hypervalent species.

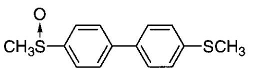
4. Intermolecular dithia dication: cyclic bis(dithia dication) dimer as an intermediate

4.1. Remote Pummerer reactions via intermolecular through-space interaction between sulfur atoms [19]

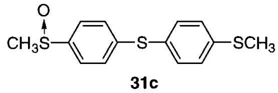
Despite the accumulation of a large body of information about dithia dications, a dithia dication formed by intermolecular reaction has not been explored extensively [20] because a transannular effect is unavailable. Our attention has been focused on whether an intermolecular interaction of the sulfur atom of acyloxysulfonium salt with a sulfur functional group occurs essentially and on whether an intermolecular or through-bond interaction is more favorable. To this end, we have chosen the Pummerer reaction and *para*-bis(methylthio)-aromatic mono-oxides **31** as a model.



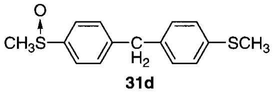
31a



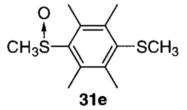
31b



31c



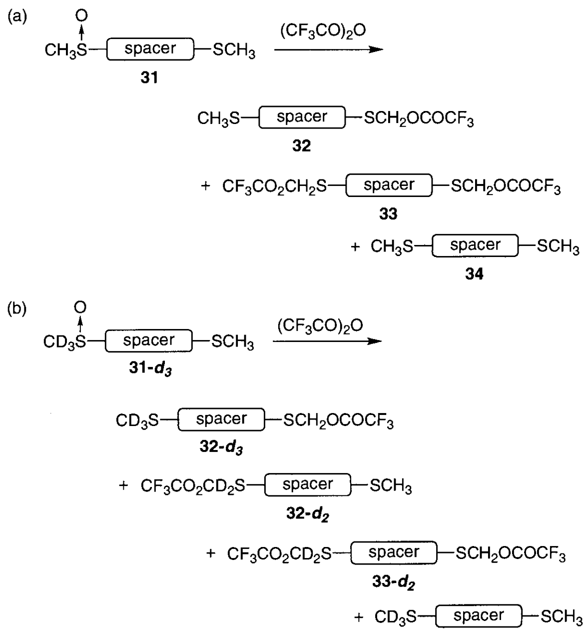
31d



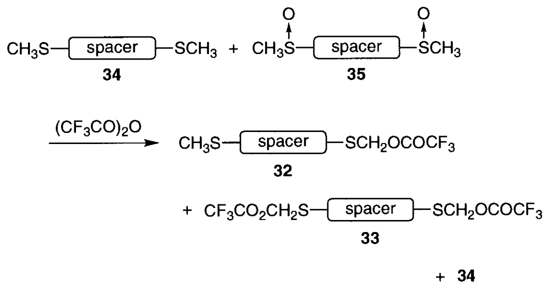
31e

The two sulfur atoms in **31**, which are separated intramolecularly by aromatic spacers so as not to contact each other, may allow an intermolecular through-space or intramolecular through-bond interaction.

The reaction of *para*-bis(methylthio)-aromatic mono-oxides **31a**–**e** with five equivalents of $(CF_3CO)_2O$ (TFAA) in CH_2Cl_2 at -20°C to r.t. gave a quantitative mixture of mono-Pummerer products **32a**–**e**, bis-Pummerer products **33a**–**e**, and bis-sulfides **34a**–**e** in an n:1:1 ratio ($n = 2.1$–12.8) (Scheme 15(a)). In all cases,



Scheme 15.

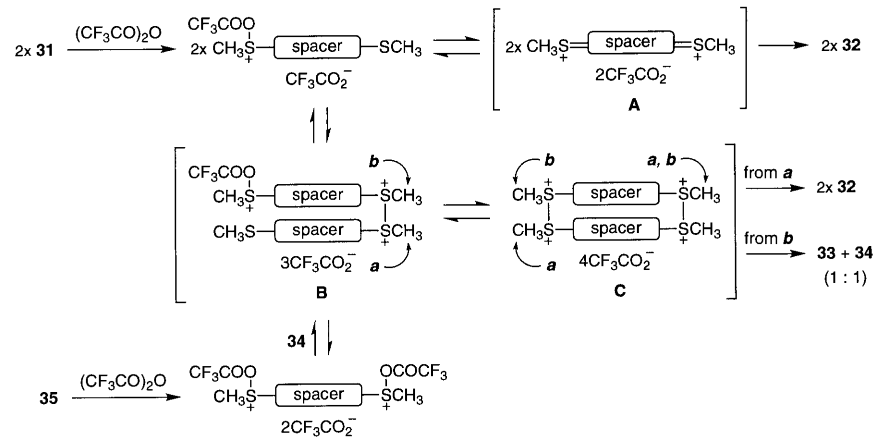


Scheme 16.

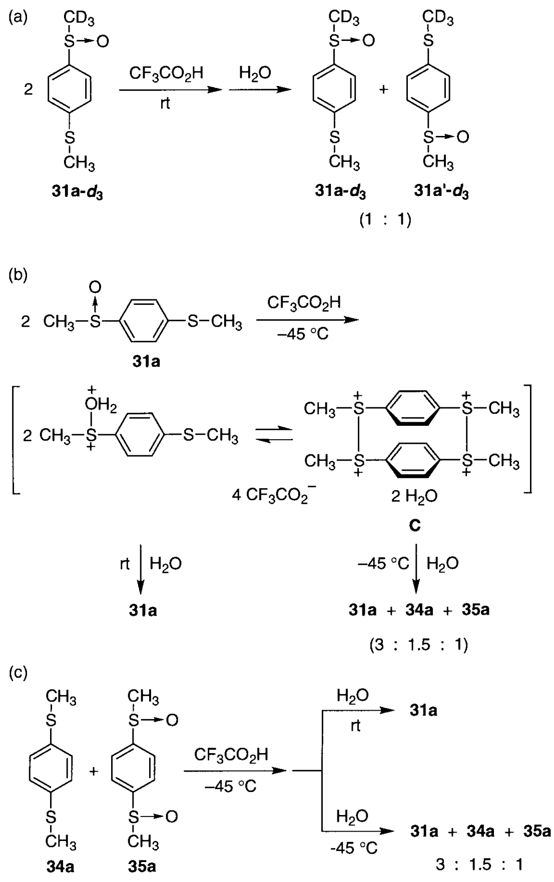
the product ratio of **33** to **34** is constantly 1:1. This result suggests that the formation of **33** and **34** could be attributed to an intermolecular reaction. In all cases, the ratio of **32**, **33**, and **34** is almost independent of the concentration of **31**. The reaction of trideuterium-labeled mono-sulfoxides **31**-d_3 with TFAA afforded a mixture of **32**-d_3, **32**-d_2, **33**-d_2 and **34**-d_3 (Scheme 15(b)). It is noted that the ratio of mono-Pummerer products, **32**-d_3:**32**-d_2, obtained from **31a**-d_3–**31d**-d_3 is significantly large and in the range 3.5 ∼ 10. In general, the Pummerer reaction should proceed at the methylsulfinyl group, but not at the methylthio group. In the present reaction, this is not the case. This result indicates unambiguously that the formation of **32** occurs at both methylsulfinyl and methylthio groups in **31**, which are located at the remote position by the intervention of spacers. This suggests an intermolecular through-space and/or intramolecular through-bond interactions between sulfur atoms. In marked contrast, the product ratio of **32e**-d_3:**32e**-d_2 from **31e**-d_3 as a sterically hindered analog of **31a** was 0.47.

In the presence of TFAA (five equivalents), bis-sulfide **34** itself remained completely unchanged, whereas bis-sulfoxide **35** afforded exclusively the bis-Pummerer product **33**. On the other hand, the reaction of a 1:1 mixture of **34** and **35** with five equivalents of TFAA gave a quantitative mixture of mono-Pummerer product **32**, **33**, and **34** (Scheme 16). It is noteworthy that the product ratios for the reactions of **34a**–**d** with **35a**–**d** are **32a**–**d**:**33a**–**d**:**34a**–**d** = n:1:1 ($n = 2.3 \sim 13.2$) and are similar to those for the reactions of mono-sulfoxides **31a**–**d**, respectively. These results suggest strongly that both reactions shown in Schemes 15 and 16 proceed via the same intermediate by an intermolecular interaction between sulfur atoms.

On the basis of these observations, the following three types of intermediates are envisaged in the present reactions (Scheme 17): a dithiaquinodimethane-like dication **A**, a dithia dication dimer (or oligomer) **B**, and a cyclic bis(dithia dication) dimer **C**. Coexistence of two reaction pathways, where mono-Pummerer product **32** results from an intermediate **A**, and bis-Pummerer product **33** and bis-sulfide **34** arise from intermediates **B**



Scheme 17.



Scheme 18.

and/or **C**, is not plausible, because the product ratio in the present Pummerer reaction is independent of the concentration of **31**. It is also decisive that the product ratios of **32a**–**d**, **33a**–**d**, and **34a**–**d** for the reactions of mono-sulfoxides **31a**–**d** with TFAA are similar to those for the reactions of a 1:1 mixture of bis-sulfides **34a**–**d** and bis-sulfoxides **35a**–**d**, respectively, and that the 1:1 formation of **33** and **34** is invariable in all cases (Schemes 15(a) and 16). The most plausible mechanism which could fit all the results described above should involve intermediates **B** and/or **C** but not **A**.

Further evidence for the proposed mechanism comes from the following two types of experiments. First, the reaction of **31d**-d_3, in which an intramolecular through-bond interaction is not available due to the insulation of π-conjugation by the methylene bridge, gave the ratio of **32d**-d_3:**32d**-$d_2 = 4.6$ in mono-Pummerer products, which is in the range of those from **31a**-d_3–**31c**-d_3 having π-conjugate spacer (Scheme 15(b)). Second, the reaction of **31e**-d_3 as a sterically hindered analog of **31a** gave the ratio of **32e**-d_3:**32e**-$d_2 = 0.47$, which is in marked contrast to the ratio of 3.5 obtained from **31a**-d_3. This result shows that a normal Pummerer reaction at the methylsulfinyl group dominates in **31e** probably due to the disadvantage of an intermolecular through-space interaction between sulfur atoms by steric hindrance of the methyl groups at the 2,6-positions of the aromatic ring. These results suggest strongly that an intermolecular through-space interaction between sulfur atoms (**B** and/or **C**) is much more favorable than an intramolecular through-bond interaction (**A**).

4.2. Remote oxygen migration reaction between sulfur atoms [21]

The reaction of trideuterium-labeled mono-sulfoxide **31a**-d_3 with 30 equivalents of CF_3CO_2H (TFA) at r.t. afforded a 1:1 mixture of **31a**-d_3 and **31a′**-d_3 after quenching with H_2O (Scheme 18(a)). When the reaction was conducted in $CDCl_3$ at −45°C, the ^{1}H-NMR spectrum shows that the protonated **31a** almost disappears and instead a new species **C** exhibiting two singlet peaks at δ 3.07 (s, 6H) and 8.02 (s, 4H) appears. The ^{13}C-NMR spectrum shows absorptions at δ 41.4, 125.8, and 144.7. The NMR data indicate that **C** should have a highly symmetrical structure. There is an equilibrium between **C** and protonated **31a**, depending on the reaction temperature.

The quench of the reaction mixture containing **C** as the main component with excess of H_2O at −45°C afforded a mixture of **31a**, **34a**, and **35a** in a 3:1.5:1 ratio (Scheme 18(b)). The reaction of a 1:1 mixture of bis-sulfide **34a** and bis-sulfoxide **35a** with 30 equivalents of TFA at −45°C followed by quenching with H_2O at −45°C gave a mixture of **31a**, **34a**, and **35a** in a 3:1.5:1 ratio, whereas quenching at r.t. afforded only **31a** (Scheme 18(c)). It is noteworthy that the product ratio from the reaction of **34a** and **35a** is exactly the same as that from the reaction of **31a** at the respective temperature. These results support the cyclic bis(dithia dication) dimer **C** as an intermediate in the present oxygen migration reaction.

5. Concluding remarks

This account has summarized our recent advances in new types of dichalcogena dications and trichalcogena hypervalent dications. (1) The stability of dichalcogena dications from acyclic systems decreases in the order Te > Se > S. Dichalcogena dications with a flexible conformation cause the facile dealkylation to give chalcogenachalcogenonium salts and alkyl cations, which provide a new method for the generation of carbocations. (2) Trichalcogena hypervalent dications from acyclic systems can be stabilized and isolated by the use of tellurium atom at the central position of trichalcogena hypervalent dications. These dicationic telluranes can also be prepared by the remote oxidation through π-conjugation. This system may open a way to a molecular hysteresis and a molecular switch in future. (3) Intermolecular through-space interaction between sulfur atoms has been demonstrated by the remote Pummerer reaction as a model. The results may provide for the understanding of electric conductivity mechanisms of the materials bearing sulfur functionalities.

Acknowledgements

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References

[1] (a) N.J. Leonard, Acc. Chem. Res. 12 (1979) 423. (b) K.-y. Akiba, K. Takee, Y. Shimizu, K. Ohkata, J. Am. Chem. Soc. 108 (1986) 6320. (c) N. Tandura, M.G. Voronkov, N.V. Alekseev, Top. Curr. Chem. 131 (1986) 99. (d) J.G. Verkade, Acc. Chem. Res. 26 (1993) 483.

[2] (a) W.K. Musker, Acc. Chem. Res. 13 (1980) 200. (b) H. Fujihara, N. Furukawa, J. Synth. Org. Chem. Jpn. 49 (1991) 636. (c) N. Furukawa, K. Kobayashi, J. Synth. Org. Chem. Jpn. 55 (1997) 1006. (d) N. Furukawa, Bull. Chem. Soc. Jpn. 70 (1997) 2571.

[3] (a) H. Fujihara, N. Furukawa, in; C. Chatagilialoglu, K.-D. Asmus (Eds.), Sulfur-Centered Reactive Intermediates in Chemistry and Biology, NATO-ASI Series, Life Sciences, Plenum, London, 1990, p. 193. (b) N. Furukawa, S. Sato, Top. Curr. Chem. 205 (1999) 89. (c) N. Furukawa, S. Sato, in: K.-y. Akiba (Ed.), Chemistry of Hypervalent Compounds, vol. 1, VCH, New York, 1999, p. 241 (Chapter 8).

[4] (a) H. Fujihara, A. Kawada, N. Furukawa, J. Org. Chem. 52 (1987) 4254. (b) R.S. Glass, S.W. Andruski, J.L. Broeker, H. Firouzabadi, L.K. Steffen, G.S. Wilson, J. Am. Chem. Soc. 111 (1989) 4036. (c) H. Fujihara, R. Akaishi, N. Furukawa, Tetrahedron 49 (1993) 1605 and references therein. (d) H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, N. Furukawa, Tetrahedron Lett. 32 (1991) 4537.

[5] (a) H. Fujihara, J.-J. Chiu, N. Furukawa, J. Am. Chem. Soc. 110 (1988) 1280. (b) T. Nakahodo, O. Takahashi, E. Horn, N. Furukawa, Chem. Commun. (1997) 1767.

[6] H. Shima, R. Kobayashi, T. Nabeshima, N. Furukawa, Tetrahedron Lett. 37 (1996) 667.

[7] H. Shima, R. Kobayashi, N. Furukawa, unpublished results.

[8] D.N. Kevill, S.W. Anderson, J. Am. Chem. Soc. 108 (1986) 1579.

[9] (a) G.A. Olah, Carbocations and Electrophilic Reactions, Wiley, New York, 1974. (b) G.A. Olah, Top. Curr. Chem. 80 (1979) 21. (c) G.K.S. Prakash, T. Rawdah, G.A. Olah, Angew. Chem. Int. Ed. Engl. 22 (1983) 390.

[10] K. Kobayashi, M. Goto, R. Kobayashi, H. Shima, E. Koyama, N. Furukawa, unpublished results.

[11] H. Naka, T. Maruyama, S. Sato, N. Furukawa, Tetrahedron Lett. 40 (1999) 345.

[12] H. Naka, M. Shindo, T. Maruyama, S. Sato, N. Furukawa, Chem. Lett. (1999) 723.

[13] A.B. Bergholdt, K. Kobayashi, E. Horn, O. Takahashi, S. Sato, N. Furukawa, J. Am. Chem. Soc. 120 (1998) 1230.

[14] (a) H. Fujihara, J.-J. Chiu, N. Furukawa, J. Chem. Soc. Chem. Commun. (1986) 1359. (b) H. Fujihara, H. Mima, T. Erata, N. Furukawa, J. Am. Chem. Soc. 114 (1992) 3117. (c) H. Fujihara, Y. Higuchi, H. Mima, N. Furukawa, Chem. Lett. (1994) 619. (d) H. Fujihara, T. Nakahodo, N. Furukawa, J. Chem. Soc. Chem. Commun. (1996) 311.

[15] K. Kobayashi, S. Sato, E. Hom, N. Furukawa, Angew. Chem. Int. Ed. Engl. 39 (2000) 1318.

[16] K. Kobayashi, S. Sato, E. Hom, N. Furukawa, Tetrahedron Lett. 39 (1998) 2593.

[17] (a) A.J. Parker, N. Kharasch, Chem. Rev. 59 (1959) 583. (b) A. Senning (Ed.), Topics in Sulfur Chemistry, Georg Thieme, Stuttgart, 1976.

[18] H. Fujihara, H. Mima, N. Furukawa, J. Am. Chem. Soc. 117 (1995) 10153.

[19] K. Kobayashi, E. Koyama, K. Namatame, T. Kitaura, C. Kono, M. Goto, T. Obinata, N. Furukawa, J. Org. Chem. 64 (1999) 3190.

[20] (a) R. Tanikaga, K. Nakayama, K. Tanaka, A. Kaji, Chem. Lett. (1977) 395. (b) V.G. Nenajdenko, N.E. Shewhenko, E.S. Balenkova, Tetrahedron 54 (1998) 5353.

[21] K. Kobayashi, T. Obinata, N. Furukawa, Chem. Lett. (1997) 1175.