

# Molecular Activation of Organic Bis-Chalcogen Compounds via Through-Space and Through-Bond Interactions between Chalcogen Atoms

Naomichi Furukawa and Kenji Kobayashi

Department of Chemistry and Tsukuba Advanced Research Alliance Center,  
University of Tsukuba, [REDACTED]

**Abstract:** Various types of bis-chalcogenides and their monooxides which have the two chalcogen atoms in close proximity can be activated photochemically or chemically to generate a reactive species such as o-quinodimethane or to promote dealkylation reactions. These molecular activations proceed via intramolecular through-space interaction between the two chalcogen atoms or the formation of  $\sigma$ -bonded dichalcogenadication. Intermolecular through-space and intramolecular through-bond interactions as new modes are also described.

## 1. Introduction

The formation of  $\sigma$ -bonded dichalcogenide dication (two-center two-electron bond) via through-space interaction or transannular interaction between two or more chalcogen atoms in juxtaposition in one molecule has attracted much attention in heteroatom chemistry (ref. 1). A simple molecular orbital representation of this bond formation is shown by the potential energy diagram (Figure 1). When the nonbonded electron pairs between two chalcogen atoms are in close proximity, the electrons would be accommodated in the bonding  $\sigma$  orbital and the antibonding  $\sigma^*$  orbital. Therefore, the removal (oxidation) of the two electrons in the antibonding  $\sigma^*$  orbital becomes more favorable by the bonding interaction between the two chalcogen atoms to produce the dichalcogenide dication (ref. 2). In fact, the oxidation potentials of such bis-chalcogenides are much lower than those of the corresponding mono-chalcogenides (ref. 3). We have found that the dichalcocogenadication salts having the 1,5-dichalcogenacyclooctane framework can be isolated as a stable form by a two-electron oxidation of bis-chalcogenides using 2 equiv of  $\text{NOBF}_4$  or by an acidification of the monooxides with trifluoromethanesulfonic anhydride ( $\text{Tf}_2\text{O}$ ), which have been characterized by the X-ray crystallographic analysis (ref. 4). These dication salts act as oxidizing agents or electrophiles depending on the added reagents.

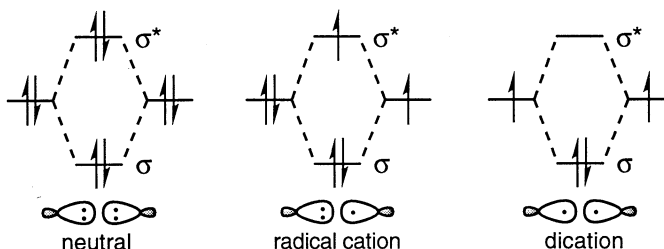


Figure 1. A molecular orbital representation of two-center two-electron bond.

However, the reactivities of dichalcogenadications and bis-chalcogenides having the two chalcogen atoms in juxtaposition still remain unexplored. By the rational molecular design, molecular activation of organic bis-chalcogen compounds via through-space interaction or the formation of the dichalcogenadications may occur to generate a reactive species or to produce a useful building block in organic synthesis. In this paper, we report our recent advance based on this strategy; photoreactions, dealkylations, and an oxygen migration reaction of bis-chalcogenides and their monooxides. We also describe a reaction via through-bond interaction that is in marked contrast to through-space interaction.

## 2. Photochemical Reactions via Through-Space Interaction between Chalcogen Atoms

### 2.1. Photogeneration of *o*-Quinodimethane by *peri*-Selenium Participation

We have found a new method for the generation of *o*-quinodimethane by the photoinitiated cleavage of the C-Se bond of an organoselenium compound (ref. 5). The cyclic bis-selenide containing both benzylic methylene groups and a naphthalene ring, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin (**1**), was designed as a precursor of *o*-quinodimethane. The cyclic bis-selenide **1** is stable in the dark. On the other hand, when a mixture of **1** and a dienophile (electron deficient olefins and acetylene) in  $\text{CHCl}_3$  at room temperature was exposed to scattered light in the laboratory for 48 h, the photodegradation of **1** cleanly proceeded to afford naphtho[1,8-*cd*]-1,2-diselenole (**3**) and the cycloadduct **4** in high yields as shown in Scheme 1. This result unambiguously indicates the generation of *o*-quinodimethane (**2**). This reaction was accelerated by the irradiation with 254 nm UV light, i.e., the cycloaddition was completed in 3 h. Several representative results obtained under the standard conditions are summarized in Table 1.

Scheme 1

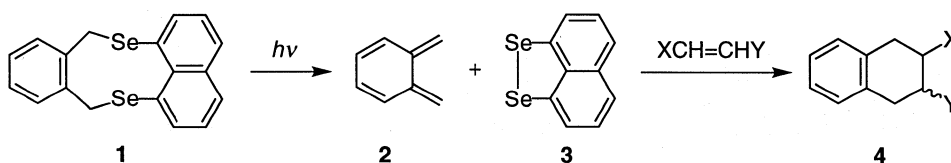
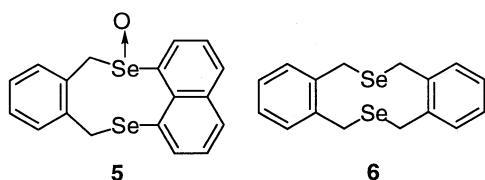


Table 1. Cycloadduct Formation of *o*-Quinodimethane Generated from **1** with Dienophile.

Dienophile	Product <b>4</b>	Yield (%) of <b>4</b>	Yield (%) of <b>3</b>
		97	96
		94	97
		99	98
		87	84



The cyclic voltammogram of **1** in  $\text{CH}_3\text{CN}$  showed a reversible oxidation wave at +0.17 V vs  $\text{Ag}/0.01 \text{ M AgNO}_3$ . The oxidation potential of **1** is lower than those of 1,8-bis(benzylseleno)naphthalene (+0.46 V) and dibenzyl selenide (+0.98V), which are irreversible. The reaction of the selenoxide **5** with a dienophile did not proceed at all. These results suggest that the destabilization of **1** by transannular

lone pair-lone pair repulsion may facilitate the photochemical cleavage of the C-Se bond of **1** leading to **2** and **3**. The transannular selenium-selenium interaction of **1** promotes electron transfer from the selenide. The naphthalene unit in **1** is essential for the present reaction, because the bis-selenide **6** remained unchanged under the same conditions. The generation of **2** may be rationalized by a mechanism involving photoinduced electron transfer from **1** to the excited state, which undergoes the cleavage of the C-Se bond.

The diselenide **3** is the starting material for the synthesis of **1** and is recyclable after the present reaction which proceeds under the irradiation of room or sun light. Thus, the present reaction may be regarded as an economical and environmentally benign reaction.

## 2.2. Photochemical Reactions of Naphtho[1,8-*de*][1,3]dithiin Derivatives

The 1,8-dichalcogena naphthalene is a valuable scaffold for the generation of various active species or functional groups by changing the bridging group between the two chalcogen atoms. The naphtho[1,8-*de*][1,3]dithiin derivatives were designed as next target molecules. Although naphtho[1,8-*de*][1,3]dithiin (**7**) itself is the thermally and photochemically stable molecule, the 1-oxide (**8**) (ref. 6), 1-*N*-tosyl-sulfilimine (**9**) (ref. 7), and 1-bis(ethoxycarbonyl)methylide (**10**) (ref. 8) derivatives quantitatively produced the corresponding carbonyl compound, *N*-tosylaldimine, and olefin, respectively, with the complete recovery of naphtho[1,8-*cd*]-1,2-dithiole (**11**) on exposure to a high-pressure mercury lamp (400 W or 500 W) in benzene at room temperature under Ar (Scheme 2). Several representative results obtained here are summarized in Table 2. All reactions proceed cleanly and quantitatively in protic and aprotic solvents including ethanol, acetonitrile, THF, dichloromethane, chloroform, benzene, and hexane. The present reactions are tolerant to carbonyl, hydroxyl, olefinic, and heterocyclic functionalities.

Scheme 2

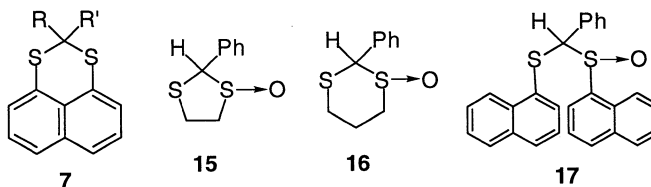
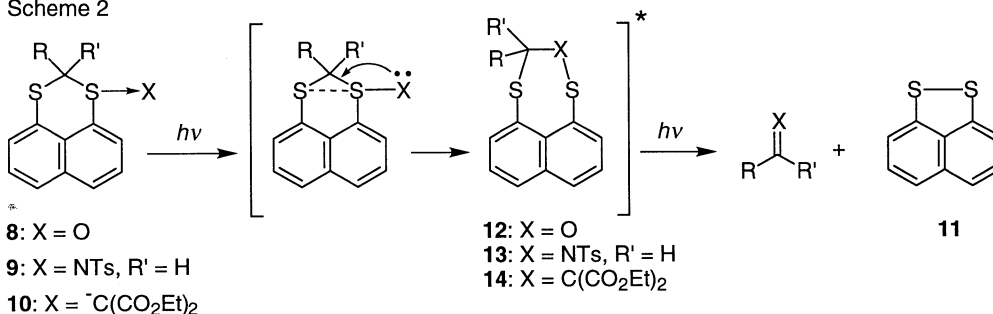
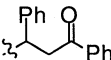


Table 2. Preparation of Carbonyl Compounds, Imines, and Olefins by Photolysis of **8**, **9**, and **10** <sup>a</sup>

<b>8</b>	R	R'	Yield (%) of Carbonyl	Yield (%) of <b>11</b>
	Ph	H	>99	>99
	PhCH=CH	H	>99	>99
	2-Furyl	H	>99	>99
	Ph	2-Pyridyl	>99	>99
	Ph		>99	>99
	Ph	PhCH(OH)-	82	91
<b>9</b>	R	R'	Yield (%) of Imine	Yield (%) of <b>11</b>
	Ph	H	>99	>99
	PhCH=CH	H	>99	>99
<b>10</b>	R	R'	Yield (%) of Olefin	Yield (%) of <b>11</b>
	Ph	H	>99	>99
	PhCH=CH	H <sup>b</sup>	>99	>99
	Ph	PhCH <sub>2</sub> <sup>b</sup>	>99	>99

<sup>a</sup> In benzene at room temperature under irradiation with 400W high-pressure Hg lamp ( $\lambda > 300$  nm) for **8** and **9**. In CH<sub>2</sub>Cl<sub>2</sub> at room temperature under irradiation with 500W high-pressure Hg lamp ( $\lambda = 313$  nm) for **10** and **14**. <sup>b</sup> Compounds **14** were used in place of **10**.

The following features are noteworthy in the present reactions. (1) In marked contrast to the reaction of **8**, five- and six-membered 1,3-dithia derivatives **15** and **16** were unreactive under the same conditions. Although 1-naphthylidithioacetal monooxide **17** underwent photodecomposition, the products obtained were a mixture of intractable compounds. These results show that the 1,8-dithia naphthalene unit is essential for the present reactions. (2) The present reactions are the intramolecular process which was confirmed by the crossover experiments. (3) The structure of **9** (R = CH<sub>3</sub>, R' = H) was determined by the X-ray crystallographic analysis, showing that the S...S distance of 2.856 Å is much shorter than the sum of the van der Waals radii (3.70 Å) of the two sulfur atoms. This suggests the existence of the lone pair-lone pair interaction between the two sulfur atoms at the 1,8-positions of naphthalene. (4) The consumption of the substrates **8**, **9**, and **10** and the formation of the products and **11** were unaffected by the addition of benzophenone as a triplet sensitizer, respectively, indicating that the present reactions may proceed through an excited singlet state, probably the lowest excited singlet (S<sub>1</sub>) state. (5) In all cases, the intermediates **12**, **13**, and **14** (Scheme 2) were detected by the <sup>1</sup>H NMR during the course of the reactions and can be isolated. Furthermore, the structures of **13** (R = Ph, R' = H) and **14** (R = Ph, R' = H) were determined by the X-ray crystallographic analysis, showing that the S...S distances are 3.108 and 3.132 Å, respectively (Figure 2). (6) The effect of light intensity on photolysis of the substrates was studied in order to elucidate whether the present reactions are a one-, two-, or multi-photon process. The loss of the substrates was proportional to the first power of the 313 nm light, respectively, whereas the formation of the products was proportional to the square of the intensity, respectively. These results indicate that the consumption of the substrates as well as the intermediates proceeds by a one-photon process to give the intermediates and products, respectively.

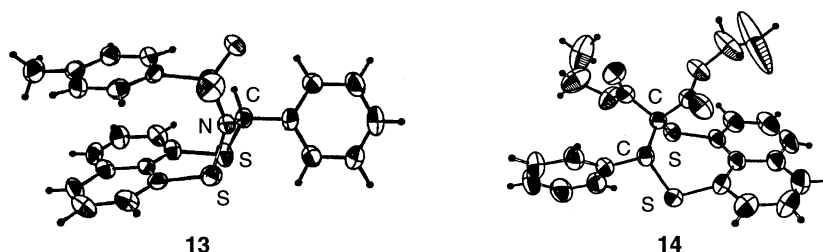
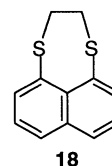


Figure 2. X-ray crystal structures of **13** and **14** ( $R = \text{Ph}$ ,  $R' = \text{H}$ , respectively).

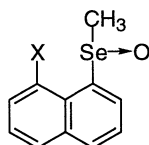
In the primary photochemical step, the intermediates **12**, **13**, and **14** may be formed by a radical or concerted rearrangement of the sulfinyl oxygen, the *N*-tosyl group, and the sulfonium ylide carbon to the 2-carbon atom, respectively, via the  $\text{S}\cdots\text{S}$  through-space interaction. Thereafter, the intermediates should be converted into the corresponding products and **11** via the  $\text{S}\cdots\text{S}$  through-space interaction in the secondary photochemical step (Scheme 2). The ab initio calculation of model compound **18** (the CIS method to the  $S_1$  state with the STO-3G\* basis set) indicates that the excitation to the  $S_1$  state causes a bonding interaction between the two sulfur atoms, making the second step photochemical reaction possible (ref. 8b).



### 3. Dealkylation Reactions via Through-Space Interaction between Chalcogen Atoms

#### 3.1. Se-Demethylation Induced by *peri*-Substituent Participation

In the reaction of methyl phenyl selenoxide with acetic anhydride, the Pummerer reaction proceeds to give  $\alpha$ -acetoxymethyl phenyl selenide. However, the reactions of 8-substituted-1-(methylseleno)naphthalenes (**19**,  $X = \text{SeCH}_3$ ; **25**,  $X = \text{N}(\text{CH}_3)_2$ ) are not the case; the Se-demethylation occurs via through-space interaction.

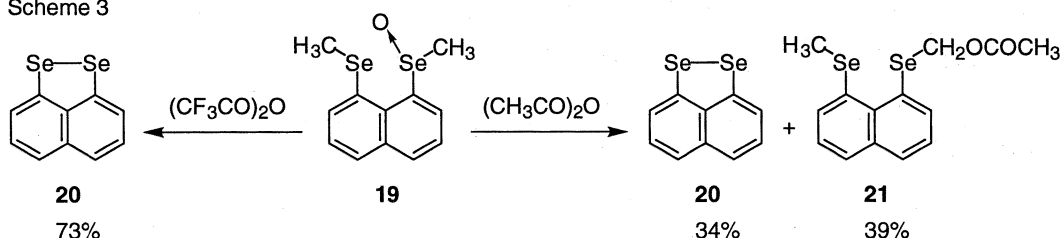


**19**:  $X = \text{SeCH}_3$ , **25**:  $X = \text{N}(\text{CH}_3)_2$

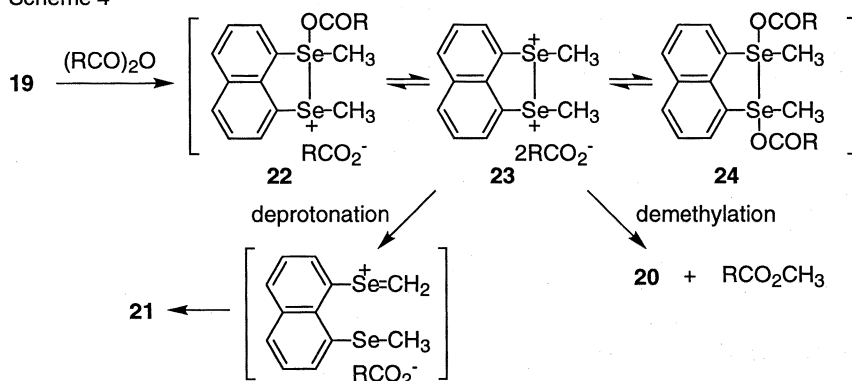
1,8-Bis(methylseleno)naphthalene 1-oxide (**19**) was treated with 1 equiv of acetic anhydride in benzene at room temperature for 3 h under Ar to afford naphtho[1,8-*cd*]-1,2-diselenole (**20**) (34%) as the demethylated product as well as the  $\alpha$ -acetoxylated selenide **21** (39%) as the Pummerer reaction product. When trifluoroacetic anhydride was used in place of acetic anhydride, the selenide **20** (73%) was produced without the formation of the Pummerer reaction product (Scheme 3) (ref. 9).

This unusual reaction of **19** under mild conditions may be ascribed to the interaction between the two-selenium atoms. The proton-decoupled  $^{77}\text{Se}$  NMR spectrum of **19** shows the satellite peak due to the  $^{77}\text{Se}$ - $^{77}\text{Se}$  coupling of  $J_{\text{Se-Se}} = 203$  Hz. A mechanism shown in Scheme 4 seems to be plausible. The reaction of **19** with acid anhydrides leads to the selenonium cation which is stabilized by *peri*-selenium participation to form the selenonio selenurane **22**, diselena dication **23**, or bis-selenurane **24** as an intermediate. The Pummerer reaction could proceed via addition of a carboxylate anion to the alkylidene selenonium ion generated from the deprotonation of **22**, **23**, or **24** by a carboxylate anion. Alternatively, the demethylation may occur in either the substitution by a carboxylate anion on the methyl carbon atoms of **22** or **23**, or the ligand coupling reaction in **24**. Since the  $\text{CF}_3\text{CO}_2^-$  ion is much weaker base as compared to the  $\text{CH}_3\text{CO}_2^-$  ion, it would be reasonable that the demethylation is predominant in the reaction of **19** with  $(\text{CF}_3\text{CO})_2\text{O}$ .

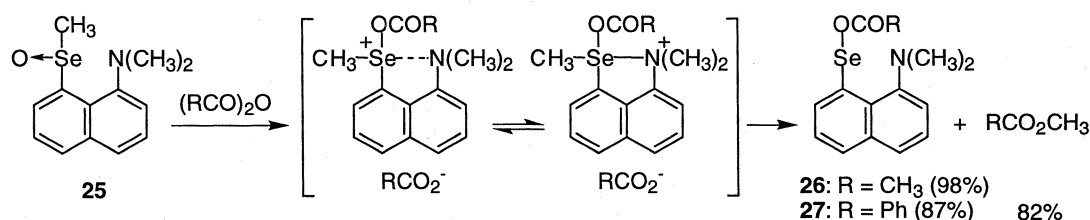
Scheme 3



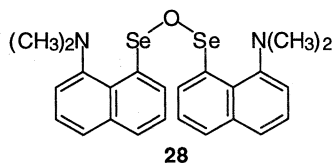
Scheme 4



Scheme 5



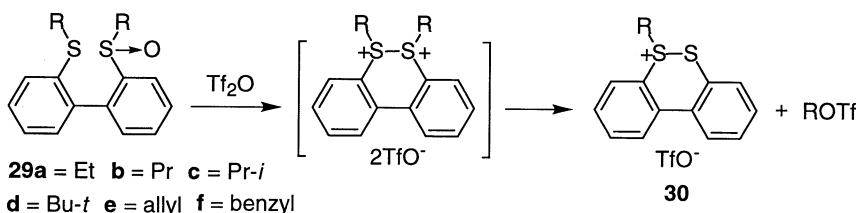
The reaction of 8-dimethylamino-1-methylselenonaphthalene 1-oxide (**25**) with 2 equiv of acetic anhydride in benzene at room temperature under Ar afforded the Se-demethylated product, the selenoperacetate **26** in quantitative yield. Similar treatment of **25** with 2 equiv of benzoic anhydride in chloroform gave the selenoperbenzoate **27** (87%) and  $\text{PhCO}_2\text{CH}_3$  (82%) (Scheme 5) (ref. 10). None of the Pummerer rearranged product was obtained in these reactions. The reaction of **25** with acid anhydrides leads to the cationic species stabilized by *peri*-nitrogen or the selenazonaphthalene as an intermediate. Subsequently, a carboxylate anion could attack on the carbon atom of the Se-methyl group of the intermediate (Scheme 5). The selenoperacetate **26** was hydrolyzed by aqueous NaOH to afford the stable selenenic anhydride **28**.



### 3.2. Dealkylation of 2,2'-Bis(alkylchalcogeno)biphenyl Derivatives and Their Oxides via Dichalcogenadications

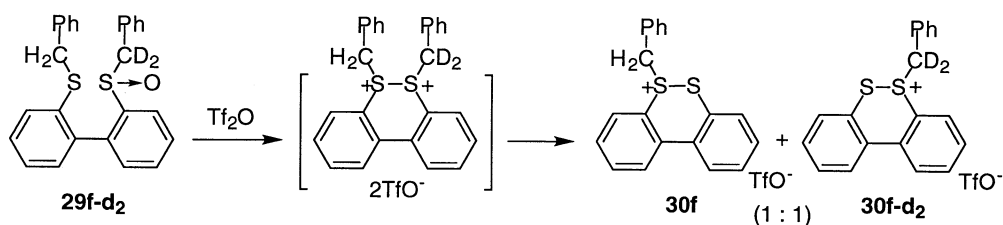
By treatment with triflic anhydride ( $\text{ Tf}_2\text{O}$ ), the monooxides of cyclic bis-sulfides having some rigid structure such as 1,5-dithiacyclooctane and dibenzodithiocin are readily converted into the stable, isolable dithiadication at room temperature (ref. 4a). On the other hand, other dithiadication generated from acyclic system having a flexible structure have not been studied well because of their instability. We have found the facile dealkylation of the monooxide of 2,2'-bis(alkylthio)biphenyl with  $\text{ Tf}_2\text{O}$  via the formation of dithiadication to give the corresponding thiasulfonium salt (ref. 11).

Scheme 6

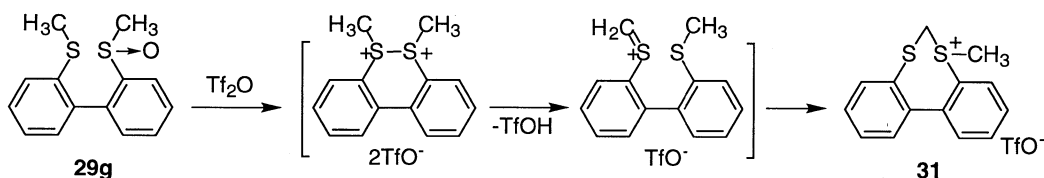


The reaction of the monooxide of 2,2'-bis(alkylthio)biphenyl (**29a**, R = Et; **29b**, R = Pr; **29c**, R = Pr-*i*; **29d**, R = Bu-*t*; **29e**, R = allyl; **29f**, R = benzyl) with 1 equiv of  $\text{ Tf}_2\text{O}$  in  $\text{ CHCl}_3$  or  $\text{ CH}_3\text{CN}$  at -45 °C to room temperature gave the thiasulfonium salt (**30**) as the dealkylated product in quantitative yield together with alkyl triflate (Scheme 6). For **29a** and **29b**, the dithiadication as an intermediate was observed by  $^1\text{H}$  NMR spectroscopy during the course of the reaction in  $\text{ CD}_3\text{CN}$  at -45 °C. For example, in the  $^1\text{H}$  NMR spectrum, the two sets of peaks showing the unsymmetrical structure in **29a** due to the diastereomers immediately disappear by adding  $\text{ Tf}_2\text{O}$  and in its place a new set of peaks having a highly symmetrical structure appears at  $\delta$  1.43 (t,  $J$  = 7.2 Hz, 3H) and 3.80-3.95 (m, 2H). The  $^{13}\text{C}$  NMR spectrum under the same conditions shows a similar result. This species generated *in situ* was treated with 2 equiv of thiophenol or  $\text{ H}_2\text{O}$  at the same temperature to give the reduced bis-sulfide and diphenyl disulfide or **29a** in quantitative yield, respectively. These results unambiguously indicate the generation of the dithiadication as an intermediate, which is gradually decomposed to the thiasulfonium salt **30a** and ethyl triflate. For **29c-f**, dithiadication were not detected due to their high instability. The reaction of the deuterium-labeled **29f-d**, afforded a 1:1 mixture of **30f** and **30f-d** (Scheme 7), suggesting that the present reaction proceeds through the formation of dithiadication.

Scheme 7



Scheme 8



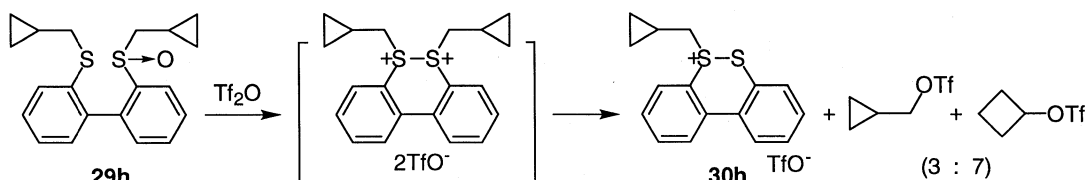
The reactivity of monooxide of 2,2'-bis(methylthio)biphenyl (**29g**) is the only exception, which was converted into the cyclic methylsulfonium salt **31** in 80% yield. The formation of **31** may proceed

through a dithiadication followed by its deprotonation and, subsequently, nucleophilic addition by the neighboring sulfide sulfur atom on the carbon atom of the resulted methyldiene sulfonium group (Scheme 8). The isotope effect ( $k_H/k_D$ ) in the step of proton abstraction was 7.7.

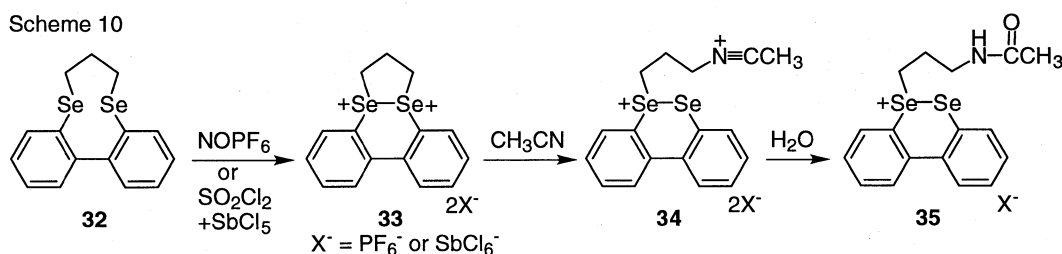
The study on intramolecular competitive reaction by use of the substrate having two kinds of alkyl groups reveals the relative reactivity of alkyl groups on the sulfur atoms of the dithiadications, which decreases in the order Me >> Et, Pr > benzyl group for the deprotonation and benzyl >> Et > Pr >> Me group for the dealkylation reaction.

Thus, the dithiadication having a flexible structure is highly reactive to result in the facile dealkylation reaction. It is noteworthy that the triflate anion which possesses a very weak nucleophilicity acts as a nucleophile. The kinetic study using the dithiadications generated *in situ* from **29a** and **29b** showed that both dealkylation reactions obey good first-order kinetics with respect to the dithiadication including two molecules of triflate anion and that the activation parameters are  $E_{act} = 21.5 \pm 1.1$  and  $25.2 \pm 0.6$  kcal/mol,  $\Delta H^\ddagger_{298} = 21.0 \pm 1.1$  and  $24.8 \pm 0.5$  kcal/mol, and  $\Delta S^\ddagger_{298} = 14.8 \pm 4.5$  and  $30.4 \pm 2.1$  eu, respectively. The large positive  $\Delta S^\ddagger_{298}$  values in both cases suggest that the transition state for the dealkylation should be "loose" where the C-S(+) bond is weakened and lengthened, indicating a  $S_N1$  process. Further evidence for a  $S_N1$  process in the present dealkylation reaction arises from the reaction of the monooxide of 2,2'-bis(cyclopropylmethylthio)biphenyl (**29h**) (Scheme 9). When the reaction of **29h** with  $Tf_2O$  was carried out at  $-90^\circ C$  in  $CD_2Cl_2$ , the  $^1H$  NMR spectrum showed the formation of cyclopropylmethyl and cyclobutyl triflates in the ratio of 3:7 as well as cyclopropylmethyl thiasulfonium salt **30h**, although the corresponding dithiadication was not detected at all. The important fact is that the ratio of cyclopropylmethyl and cyclobutyl triflates obtained here remains unchanged below  $-40^\circ C$ . This result strongly supports that the cyclobutyl triflate is not formed by an isomerization of cyclopropylmethyl triflate, but formed in the initial dealkylation step from the dithiadication and indicates the large  $S_N1$  character in the present reaction.

Scheme 9



Scheme 10



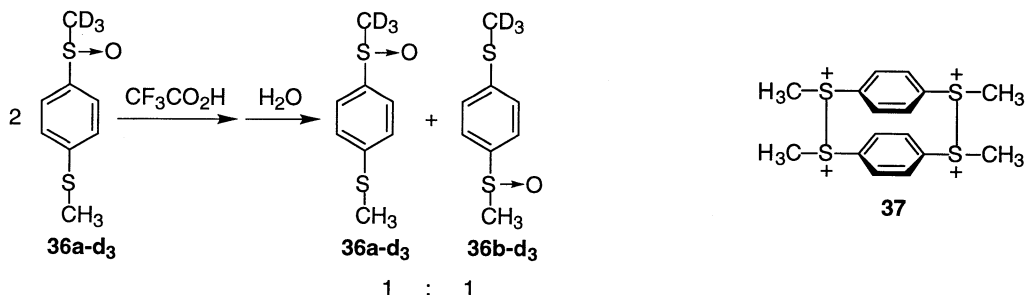
The diselenadication **33** is formed and can be isolated in the reaction of the bis-selenide **32** with 2 equiv of  $NOPF_6$  or with a combination of 1 equiv of  $SO_2Cl_2$  and 2 equiv of  $SbCl_5$  in  $CH_3CN$  at  $-45^\circ C$ . The dication **33** is stable in  $CH_3CN$  at below  $-20^\circ C$ , whereas at more than  $0^\circ C$  it is gradually decomposed to the selenaselenonium salt **34** formed by the addition reaction of  $CH_3CN$ , which is hydrolyzed by  $H_2O$  to give the amide **35** (Scheme 10) (ref. 12). This result also suggests that the dealkylation by  $CH_3CN$  bearing no nucleophilicity proceeds via a  $S_N1$  process.

#### 4. Bis(dithiadication) Dimer via Intermolecular Two-Point Interaction

The monooxide of bis-sulfide, the two sulfur atoms of which are separated intramolecularly not to contact each other, can allow intermolecular through-space interaction by multi-point interaction. The

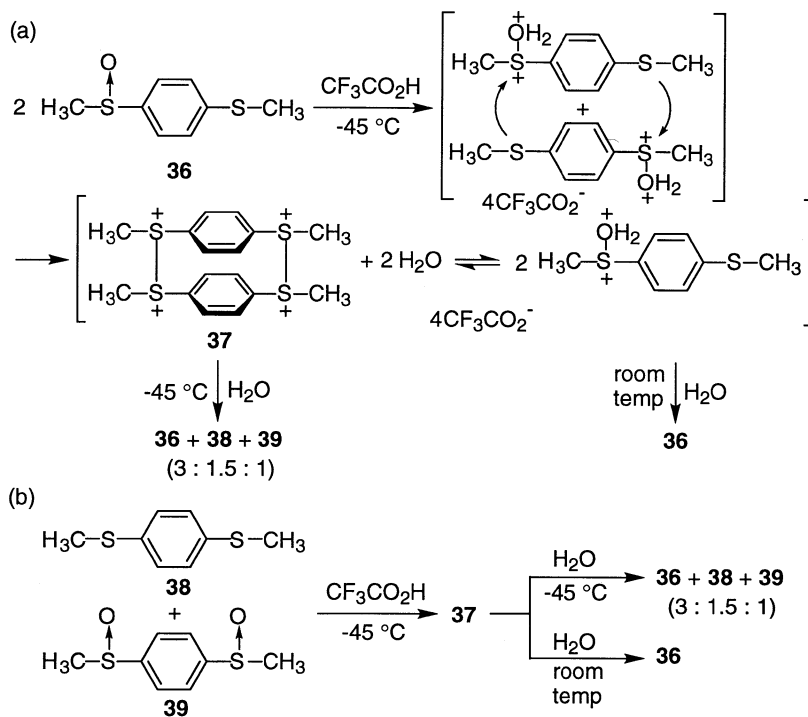
oxygen migration reaction of the monooxide of 1,4-bis(methylthio)benzene (**36**) mediated by  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CHCl}_3$  proceeds via the bis(dithiadication) dimer **37** formed by intermolecular through-space interaction (ref. 13).

Scheme 11



The reaction of deuterium-labeled *para*-substituted **36a-d<sub>3</sub>** with  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CHCl}_3$  at room temperature gave a 1:1 mixture of **36a-d<sub>3</sub>** and **36b-d<sub>3</sub>** (Scheme 11). In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a mixture of **36** and  $\text{CF}_3\text{CO}_2\text{H}$  in  $\text{CDCl}_3$  at  $-45^\circ\text{C}$ , a new species **37** having a highly symmetrical structure was observed as a main component, which the  $^1\text{H}$  NMR spectrum exhibits two singlet peaks at  $\delta$  3.07 and 8.02. We have proposed a bis(dithiadication) dimer as **37**, although the question of whether it is a through-space or through-bond interaction always accompanies this type of reaction.

Scheme 12



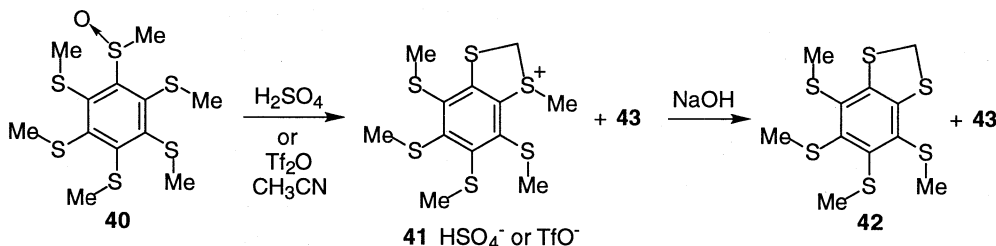
The existence of **37** as an intermediate in the present reaction is supported by the following. (1) There is a reaction mixture temperature dependent equilibrium between **37** and the protonated **36**. At lower temperature **37** is dominant. (2) Quenching the reaction mixture containing **37** as the main component with H<sub>2</sub>O at -45 °C afforded the bis-sulfide **38** and the bis-sulfoxide **39** as well as **36** in the ratio of **36**:**38**:**39** = 3:1.5:1 (Scheme 12a). If a *para*-quinoid type dication is formed via through-bond interaction at -45 °C, **36** should be the sole product. This is not the case. The formation of **38** and **39** as well as **36** strongly suggests the existence of the bis(dithiadication) dimer **37**. The double protonations of the oxygen atom of the sulfinyl group followed by the sulfur-oxygen bond breakage due to the nucleophilic attack by the sulfide sulfur atom of the other substrate may produce the intermediate **37** and two molecules of H<sub>2</sub>O. The nucleophilic attack by H<sub>2</sub>O on the sulfur atoms of **37** from the reverse side would give **36**, while the nucleophilic attack from the same side would afford **38** and **39**. (3) The reaction of **38** with **39** under the same conditions gave **37** at -45 °C that was quenched with H<sub>2</sub>O to produce **36**, **38** and **39** in the same ratio as that for the reaction of **36** (Scheme 12b). Quenching at room temperature afforded only **36**. In the reaction of **38** or **39** itself under the same conditions, the substrates remained unchanged, respectively. (4) The deuterium-labeled monooxide of 1,3-bis(methylthio)benzene which cannot conjugate via through-bond interaction also underwent the oxygen migration. (5) In marked contrast, a 1:1 mixture of trideuteriomethyl phenyl sulfoxide and methyl phenyl sulfide under the same conditions at room temperature did not undergo an oxygen transfer at all. Thus, the multi-point interaction between intermolecular sulfur atoms is undoubtedly the important factor in the present oxygen migration reactions.

## 5. $\pi$ -Delocalized Benzene Dication of Hexakis(methylthio)benzene via Through-Bond Interaction

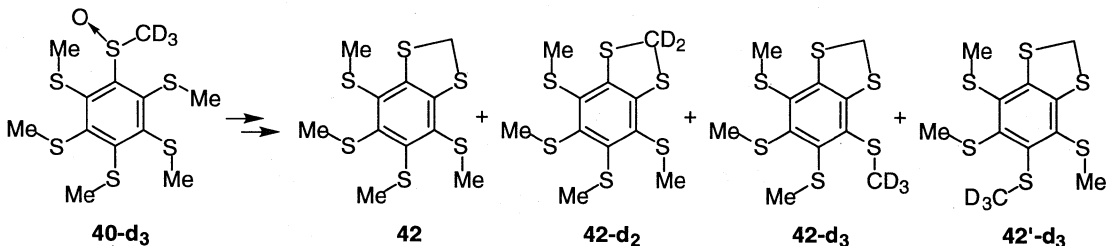
We have extended the studies described in Sections 3-2 and 4 to the monooxide of hexakis(methylthio)benzene (**40**) and have found the formation of cyclic sulfonium salt **41** via through-bond interaction (ref. 14).

The reaction of **40** in conc. H<sub>2</sub>SO<sub>4</sub> at room temperature followed by quenching the mixture with aqueous NaOH gave the cyclic sulfide **42** (29%), hexakis(methylthio)benzene (**43**) (28%), and **40** (10%) (Scheme 13). The reaction of **40** with 1 equiv of Tf<sub>2</sub>O in CH<sub>3</sub>CN at -40 °C to room temperature followed by the same quenching afforded **42** (35%) and **43** (34%). In both cases, the formation of cyclic sulfonium salt **41** before quenching was confirmed by the <sup>1</sup>H NMR and FAB-Mass spectroscopies.

Scheme 13



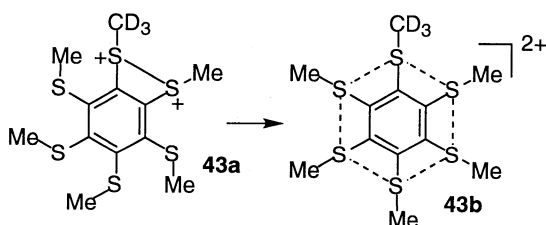
Scheme 14



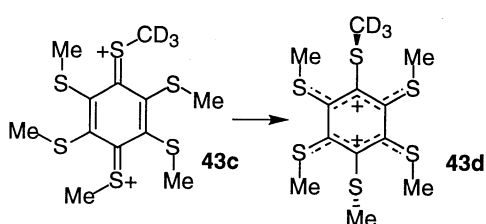
The reactions of the deuterium-labeled monosulfoxide **40-d<sub>3</sub>** gave a mixture of **42**, **42-d<sub>2</sub>**, **42-d<sub>3</sub>**, and **42'-d<sub>3</sub>** in the ratio of 0.74:0.26:1:1 under both reaction conditions, which were evaluated by the <sup>1</sup>H NMR and EI-Mass spectroscopies (Scheme 14). The equal distribution of the deuterated-methyl group obtained here may be interpreted as follows. At first, addition of two protons of H<sub>2</sub>SO<sub>4</sub> or Tf<sub>2</sub>O to the sulfinyl oxygen atom occurs. Subsequently, a nucleophilic substitution by the neighboring sulfide sulfur atom via through-space interaction gives a four-membered ring  $\sigma$ -bonded dithiadication **43a**. The  $\sigma$ -delocalization of **43a**, i.e., **43b**, would result in the equal distribution of the deuterated-methyl group (Path A) (Scheme 15). Another possibility may be attributed to through-bond interaction to give a *para*-quinoid dithiadication **43c** that is converted into a more stable anti-quinoid benzene dication **43d** (ref. 15),  $\pi$ -delocalization of which results in the distribution of the deuterated-methyl group (Path B). Preliminary ab initio calculation using the RHF method with the 3-21G<sup>(\*)</sup> basis set, which was calculated by replacing the methyl group with a proton, indicates that the anti-quinoid benzene dication **43d** having a C<sub>2h</sub> chair conformation is relatively 23.8 and 56.6 kcal/mol more stable than **43c** and **43b**, respectively.

Scheme 15

(Path A)



(Path B)



## 6. Conclusion

The designed bis-chalcogenide compounds having two chalcogen atoms in close proximity attached on the naphthalene scaffold can be photochemically activated via through-space interaction between the chalcogen atoms to generate a reactive species or to produce useful organic functionalities. The formation of dichalcogenadication having flexible structures results in the highly reactive species, alkyl cation. The molecular activation methods presented here will open a way to new reaction chemistry as well as heteroatom chemistry. The present study of the alteration in intermolecular through-space or intramolecular through-bond interaction between the chalcogen atoms according to the structure of substrates may also open up new fields; the former will be applicable to supramolecular chemistry, whereas the latter will have relation to material science such as electron-conductivity.

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## References and Notes

- (1) (a) Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200-206. (b) Furukawa, N. *Bull. Chem. Soc. Jpn.* in press.
- (2) (a) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436-442. (b) Glass, R. S.; Andruski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4036-4045.
- (3) For example, (a) reference 2b. (b) Fujihara, H.; Yabe, M.; Chiu, J.-J.; Furukawa, N. *Tetrahedron Lett.* **1991**, *32*, 4345-4348.

- (4) (a) Fujihara, H.; Akaishi, R.; Furukawa, N. *Tetrahedron* **1993**, *49*, 1605-1618 and references cited therein. (b) Fujihara, H.; Ninoi, T.; Akaishi, R.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1991**, *32*, 4537-4540.
- (5) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, *58*, 5291-5292.
- (6) (a) Fujii, T. Ph D thesis, University of Tsukuba, **1996**. (b) Furukawa, N.; Fujii, T.; Kimura, T.; Fujihara, H. *Chem. Lett.* **1994**, 1007-1010.
- (7) (a) Fujii, T.; Kimura, T.; Furukawa, N. *Tetrahedron Lett.* **1995**, *36*, 1075-1078. (b) Fujii, T.; Kimura, T.; Furukawa, N. *Tetrahedron Lett.* **1995**, *36*, 4813-4816.
- (8) (a) Fujii, T.; Sakuragi, H.; Furukawa, N. *Tetrahedron Lett.* **1995**, *36*, 8039-8042. (b) Fujii, T.; Takahashi, O.; Furukawa, N. *J. Org. Chem.* **1996**, *61*, 6233-6239.
- (9) Fujihara, H.; Saito, R.; Yabe, M.; Furukawa, N. *Chem. Lett.* **1992**, 1437-1440.
- (10) Fujihara, H.; Tanaka, H.; Furukawa, N. *J. Chem. Soc. Perkin Trans. 2* **1995**, 2375-2377.
- (11) (a) Shima, H. Ph D thesis, University of Tsukuba, **1997**. (b) Shima, H.; Kobayashi, R.; Nabeshima, T.; Furukawa, N. *Tetrahedron Lett.* **1996**, *37*, 667-670.
- (12) Goto, M.; Koyama, E.; Kobayashi, R.; Shima, H.; Kobayashi, K.; Furukawa, N. unpublished results.
- (13) Kobayashi, K.; Obinata, T.; Furukawa, N. submitted for publication.
- (14) Kobayashi, K.; Namatame, K.; Takahashi, O.; Furukawa, N. unpublished results.
- (15) For benzene dication, see: Olah, G. A.; Shamma, T.; Burrichter, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3407-3408 and references cited therein.

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