Chapter 5

Oxidation of Dichalcogenides with Neighboring Four Methylthiomethyl Groups

CONTENTS

I. Introduction

In general, studies on the oxidation of dichalcogenide are classified into two classes according to their method. The first one is the oxidation with peroxy acids and second one is electrochemical oxidation. There are many reports about the oxidation of disulfide, but there are a few reports about the oxidation of diselenides or ditellurides, because the oxidation of them usually gives polymeric products.

The oxidation of disulfide with peroxy acids is considered to proceed *via* various stable intermediates as shown in Scheme 5-1. When the sulfide is unsymmertrical, oxidation with peroxy acids usually affords two regioisomeric thiosulfinic S-esters (thiosulfinate) as the initial oxidation products, of which the ratio depends on the electron density of the sulfur atom. However, when the electron-rich sulfur atom is substituted by a bulky group, the ratio is known to be controlled by the steric effect instead of the electronic effect.[1]
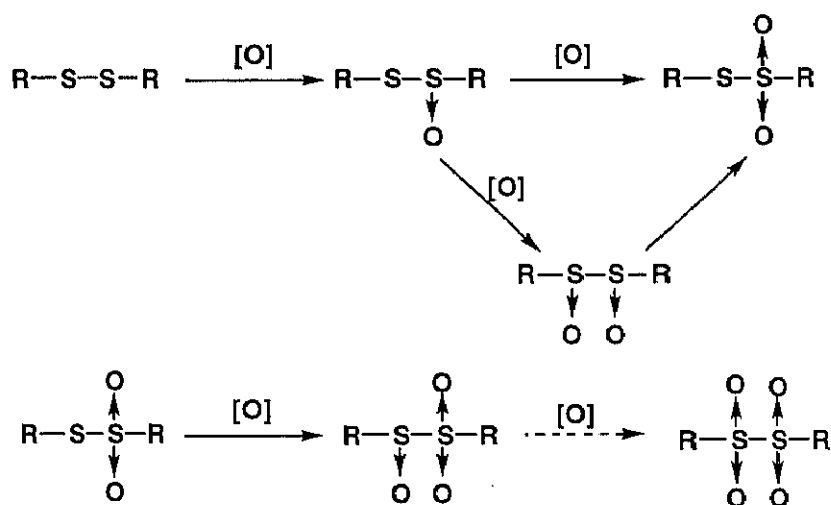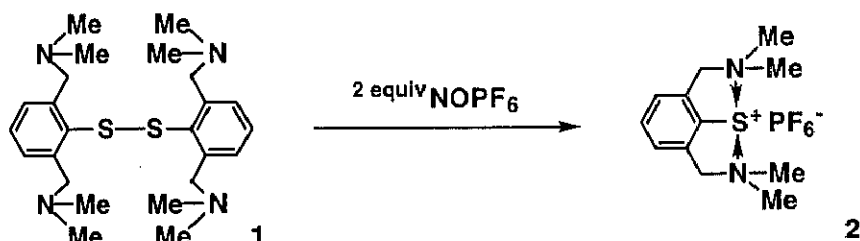

Scheme 5-1

The electrochemical oxidation of organic disulfides, mainly diaryl disulfides, has been extensively investigated during the last decades. Literatures in the field give sometimes contradicted. Some authors believe that the oxidation process proceeds by a one electron transfer mechanism,[2] possibly leading to oligomers, while other authors believe that a two electron transfer process is operative.[3] However, the anodic reaction can be understood as a symmertrical splitting of the –S–S– bond[4] and the postulated intermediate Ar–S+ (sulfenium ion) can react with nucleophiles (alkenes) to give products as shown in Scheme 5-2.
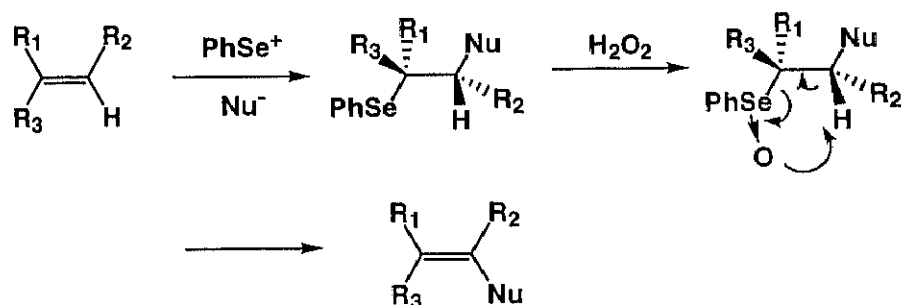

Scheme 5-2

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As described in Chapter 3, if the resulting sulfenium ion is stabilized by two neighboring nitrogen atoms, it is possible to isolate the corresponding sulfenium ion. The disulfide **1** reacts with 2 equivalents of one electron oxidizing reagent to form the sulfenium ion **2** quantitatively.
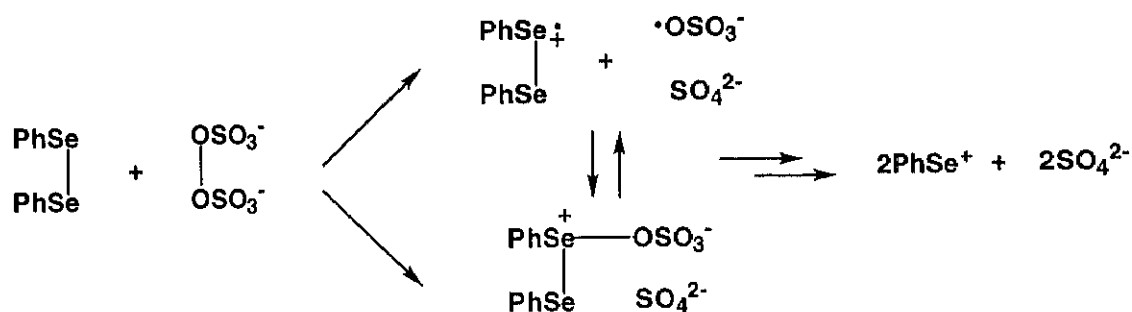

Scheme 5-3

On the other hand, the oxidation of diselenide is investigated in view of organic synthesis. Most useful reaction involving organoselenium reagent is the trans-addition reaction to the carbon-carbon double bonds.[5] They are highly stereospecific, and subsequent oxidation leads to regioselective and stereospecific elimination (syn elimination) of the selenoxide to yield carbon-carbon double bond.[6]

Scheme 5-4

The production of the electrophilic phenylselenenium ion can be effected by electrochemical oxidation of diphenyl diselenide, in which the use of halide anions is required as mediators.[7] In a recent paper, chemical preparation of phenylselenenium ion is reported.[8] It is generated by the peroxydisulfate ion oxidation of diphenyl diselenide, which occurs according to the scheme 5-5.

Scheme 5-5

The oxidation of ditelluride is less investigated compared with diselenide or disulfide. It is only reported that the dispropotionation reaction of diphenyl ditelluride gives benzenetellurinic anhydride,[9] although it is not strictly oxidation reaction of the ditelluride. As shown in Scheme 5-6, diphenyl ditelluride reacts rapidly with sodium hydroxide to give the dispropotionated product. In the presence of oxygen the reaction gives after neutralization as the only reaction product benzenetellurinic anhydride. Under these conditions benzenetellurolate was oxidized to the ditelluride, which is again transformed to the benzenetellurinate. As a result of the reaction, diphenyl ditelluride is oxidized to benzenetellurinic anhydride by oxygen.

$$2 \ Ar-Te-Te-Ar \xrightarrow[\text{THF}]{\text{NaOH}} 3 \ Ar-Te^- + Ar-TeO_2^-$$

Scheme 5-6

The oxidation of diphenyl ditelluride by tetrachlorinated orthobenzoquninone to give $[(Cl_4C_6O_2)TeC_6H_5]_2O$ as shown in Scheme 5-7.[10] However the mechanism of the reaction has not been elucidated yet and the source of the oxygen atom in the final product is also an unknown problem.

Scheme 5-7

In this Chapter, the oxidation of the dichalcogenides with neighboring four methylthio groups is described systematically.
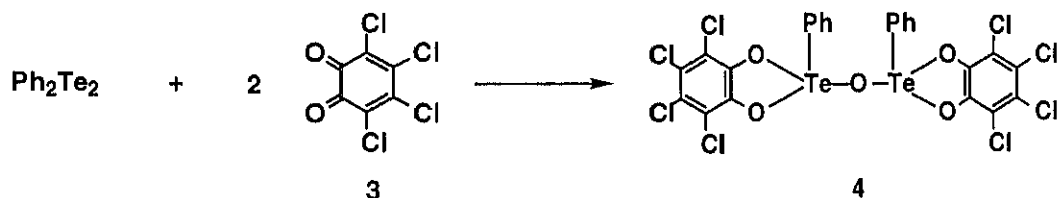
II. Synthesis of the Dichalcogenides

The dichalcogenides, having four methylthiomethyl groups at the ortho position of the chalcogen atoms, were synthesized as shown in Scheme 5-8. 2,6-Bis(methylthiomethyl)-bromo benzene 5 was lithiated by t-BuLi, and then reacted with an elemental sulfur to produce the corresponding disulfide 6. The diselenide 7 and the ditelluride 8 were also synthesized from 2,6-bis(methylthiomethyl)-bromobenzene 5 with a selenium or a tellurium powder as shown in the Scheme.
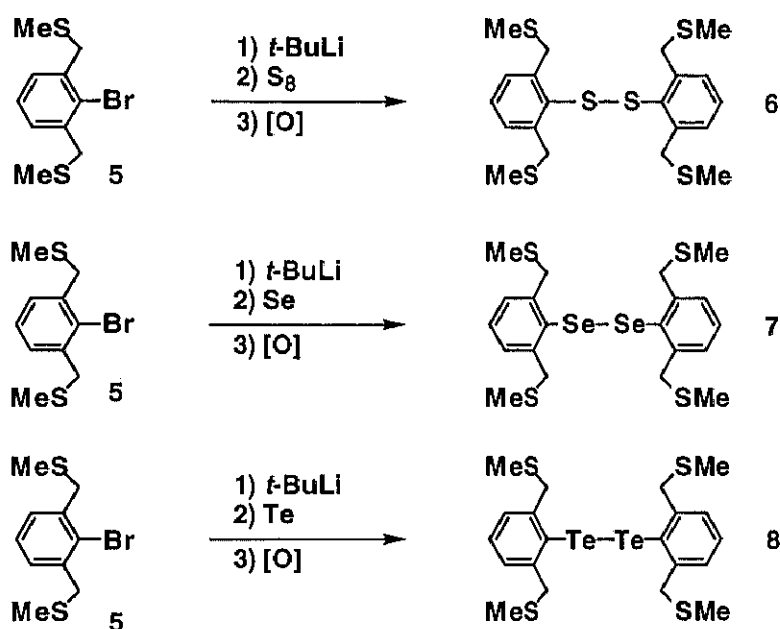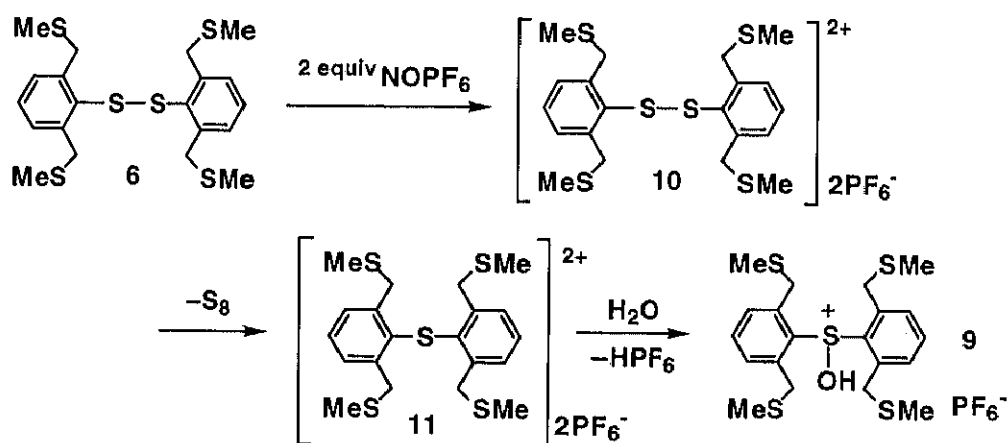

Scheme 5-8

II. Oxidation of the Dichalcogenides

The disulfide 6 was treated with two equivalents of $NOPF_6$ to oxidize the sulfur atoms. By adding the solution of $NOPF_6$, an elemental sulfur was produced as a precipitate immediately. This result means that the desulfurization has occurred by the oxidation of the disulfide. The resulting crystals were identified by ^1H and ^{13}C NMR. In the ^1H NMR spectrum of the crystals, only two singlet signals, due to the methyl and benzyl group, were observed in aliphatic area. Furthermore those signals were shifted down field from δ 1.96 to 2.39 and from δ 3.59 to 4.34 respectively compared with those of the disulfide 6. These downfield-shifts indicate the notion that the sulfur atom should be positively charged species. The ^{13}C NMR spectrum of the crystals also suggested a symmetric structure. Finally the structure of the resulting crystals was clarified to be the hydroxysulfonium salt 9.

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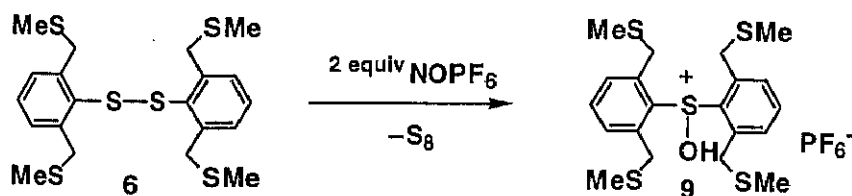
Scheme 5-9

The reaction is considered to proceed via the mechanism shown in Scheme 5-10. The mechanism of the present reaction may proceed initially by the two-electron oxidation of the disulfide followed by adding the solution of NOPF$_6$. Subsequently the hydroxysulfonium salt **9** should be produced *via* the desulfurization and the hydrolysis.
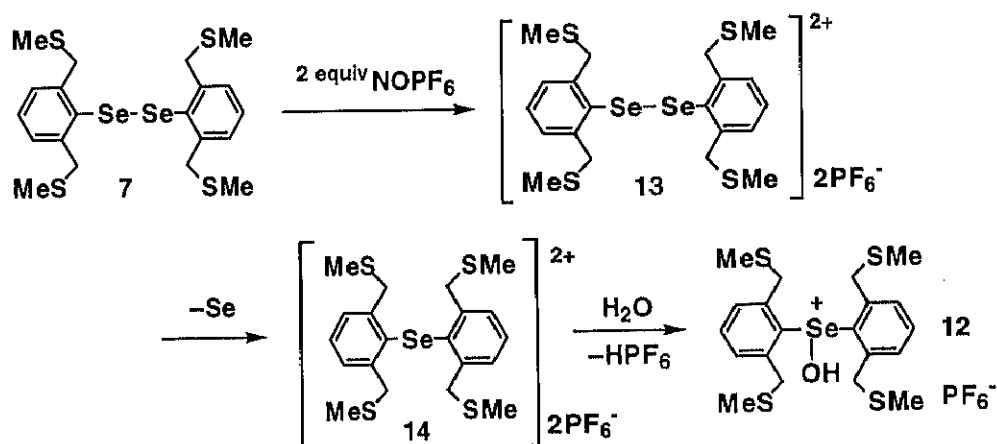

Scheme 5-10

The diselenide **7** was also treated with two equivalents of NOPF$_6$ to oxidize the selenium atom. In the reaction, elemental selenium was formed as a precipitate by adding the solution of NOPF$_6$. This result indicates the notion that one of the two selenium atoms should be released by the oxidation as the case of the corresponding disulfide **6**. Removal of the solvent also gave colorless crystals, which were identified by ^{1}H, ^{13}C and ^{77}Se NMR. The ^{1}H and ^{13}C NMR spectrum of the crystals showed almost the same pattern as the case of the oxidation of the disulfide. And the ^{77}Se NMR signal of the crystals was appeared at δ 821.7 as a singlet peak and no other peak was observed. This chemical shift of the ^{77}Se NMR indicates the cationic selenium of the product. Finally the structure of the crystals is predicted to be the hydroxyselenonium salt **12**.
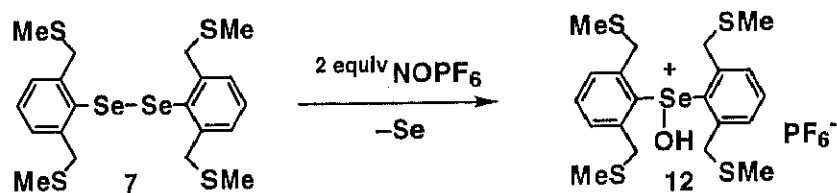
Scheme 5-11

The mechanism of the reaction is predicted as shown in Scheme 5-12. This reaction mechanism is almost the same as the case of the oxidation of the disulfide **6**. Initially two-electron oxidation of the diselenide **7** should give the corresponding dication **13**, and the elimination of the elemental selenium and the hydrolysis of the resulting dication should give the hydroxyselenonium salt **12**.
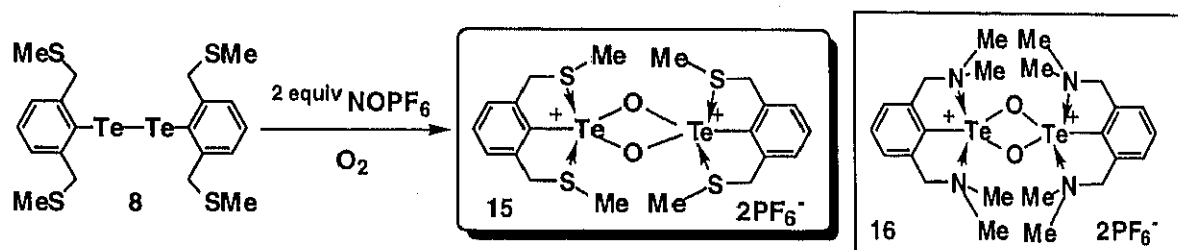
Scheme 5-12

The oxidation of the ditelluride **8** was also carried out by using two equivalents of $NOPF_6$. In this reaction no elemental tellurium was eliminated by the oxidation and the pale yellow solution was obtained. After removal of the solvents, the residue was analyzed by ^1H, ^{13}C and ^{125}Te NMR. The ^1H and ^{13}C NMR spectrum of the residue showed complex signals and could not be identified. And the ^{125}Te NMR signal of it appeared at δ 1265.8 as a singlet and no other peak was observed. This chemical shift of ^{125}Te NMR indicates the symmetric and cationic tellurium atoms. However the purification of the product at anhydrous condition was difficult. The crude product was treated at open air conditions. Recrystallization of the crude product from acetonitrile gave pale yellow crystals, which were also analyzed by ^1H, ^{13}C and ^{125}Te NMR.

In the ^1H NMR spectrum of the crystals, two singlet peaks assigned to methyl groups were observed in a 1 : 1 ratio, and two sets of AB quartet signals of benzylic methylene protons were also observed in a 1 : 1 ratio. These AB quartet signals of benzylic methylene protons indicate

the existence of the interaction between the sulfur atom and the tellurium atom. And aromatic protons were appeared as two sets of a triplet and a doublet signal and each signals were observed in a 1 : 2 ratio. Furthermore the ^{125}Te NMR spectrum of the crystals showed two singlet peaks at δ 1406.3 and 1427.2 in a 1 : 1 ratio. This chemical shifts of the ^{125}Te NMR due to the unsymmetrical two cationic tellurium atoms. In order to identify the existence of interaction between the two tellurium atoms, the satellite peaks of each two peaks were tried to detect. However no satellite peak could be observed at each peaks because of the broadness of the peak. Even in the variable temperature NMR, the satellite peak could not be observed at all.

The elemental analysis of the crystals is consistent with the molecular formula of the dication of the telluride **8** with one molar of O_2. Finally the structure of the crystals is suggested to be the dication **15**, in which two oxygen atoms and two tellurium atom makes four-membered ring. This structure is almost the same structure as the tellurenium monoxide dimer **16** as described in Chapter 3.
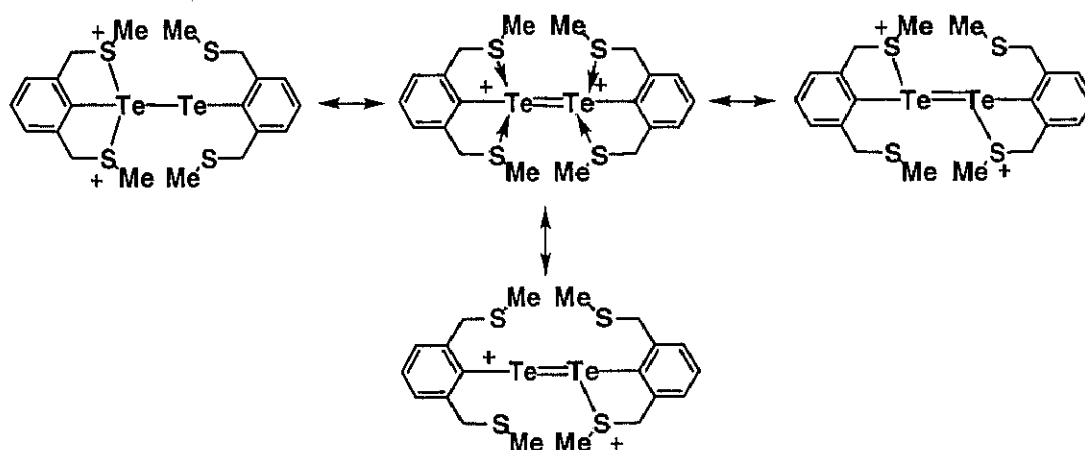

Scheme 5-13

The reaction is considered to proceed via the mechanism shown in Scheme 5-14. The oxidation of the ditelluride **8** should give the dicationic ditelluride **17**. The structure of the dicationic ditelluride **17** should be represented by the structure containing Te-Te double bond as shown in the scheme. This dicationic ditelluride should have high reactivity because of the Te-Te double bond. So the dicationic ditelluride **17** should react with one equivalent of oxygen to form the dication **15**.
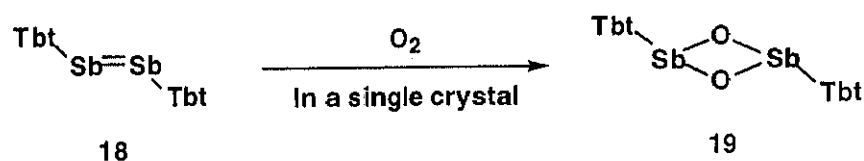

Scheme 5-14

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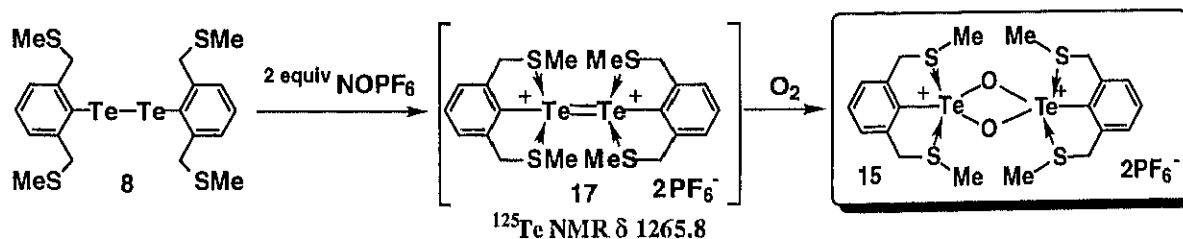
The dicationic ditelluride **17**, predicted as a intermediate in the reaction, has four neighboring sulfur atoms arranged suitably for coordinating the tellurium atom. By coordinating with the sulfur atom to the each tellurium atoms, it is possible to consider the equilibrium as shown in Scheme 5-15. This equilibrium should stabilize the dicationic ditelluride by dispersing positive charges to the four sulfur atoms.

Scheme 5-15

The dicationic ditelluride **17** was only observed by the [125]Te NMR, in which the signal was appeared at 1265.8 as one singlet peak. The X-ray structural analysis of the dicationic ditelluride **17** has not been succeeded yet, so the existence of the Te-Te double bond could not be identified.

Recently an Sb-Sb double bond compound, distibene, was synthesized and characterized.[11] The X-ray crystallographic analysis of the distibene **18** clearly indicated its double bond character. Interestingly the single crystal of the distibene **18** reacted with oxygen to produce the oxygen bridged compound **19** without any destruction of the crystal state (Scheme 5-16).

Tbt = 2, 4, 6-tris[bis(trimethylsilyl)methyl]phenyl

Scheme 5-16

It is interesting to compare this distibene with the dicationic ditelluride **17** because the distibene **18** is isoelectronic structure as the dicationic ditelluride **17**. These two chemical species react with oxygen molecules to form the corresponding oxygen bridged structure, suggesting the possibility for the existence of the dicationic ditelluride **17**.

IV. Conclusion

In conclusion, the oxygen bridged dication **15** was prepared by the oxidation of the ditelluride **8** having neighboring four sulfur atoms. This dication **15** should be produced via the corresponding dicationic ditelluride **17** having a Te-Te double bond. However the oxidation of the disulfide **6** or the diselenide **7** only gave the hyrdoxysulfonium salt **9** or the hydroxyselenonium salt **12** respectively and neither the dicationic disulfide nor the diselenide could be observed.

Expermental

General procedure. All NMR spectra were obtained with a JEOL LMN-EX-270 or a Bruker ARX-400 spectrometer. Each chemical shift was determined by two dimensional shift correlation (^{1}H–^{1}H–COSY) spectra. Mass spectra were taken with a Shimazu QP-2000 and a JEOL JMX SX102 mass spectrometer, and IR spectra with a JASCO FT/IR-300F spectrometer. All solvents and reagents were dried and purified according to standard methods. Elemental analyses were carried out by the Chemical Analytical Center at the University of Tsukuba.

Synthesis of the disulfide 6

t-BuLi (6.0 mL, 9.24 mmol, 1.54 M in n-hexane) was added to a dry THF (100 mL) solution of 2,6-bis(methythiomethyl)phenyl bromide 5 (1.64 g, 5.92 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then elemental sulfur (600 mg, 18.8 mmol) was added to the solution. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-$CHCl_3$, 4 : 1) to give a pale yellow oil, the disulfide 6 (429 mg) in 64% yield.
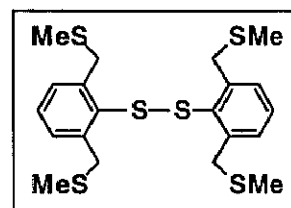
Disulfide 6

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 1.96 (s, 12H), 3.59 (s, 8H), 7.27–7.28 (m, 6H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 15.5, 36.9, 128.9, 129.7, 134.8, 143.8; MS (m/z) 229 (M^+/2).

Synthesis of the diselenide 7

t-BuLi (7.0 mL, 10.8 mmol, 1.54 M in n-hexane) was added to a dry THF (100 mL) solution of 2,6-bis(methythiomethyl)phenyl bromide 5 (2.01 g, 7.23 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then selenium powder (870 mg, 11.0 mmol) was added to the solution. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-$CHCl_3$, 4 : 1) to give a pale yellow oil, the diselenide 7 (890 mg) in 48% yield.
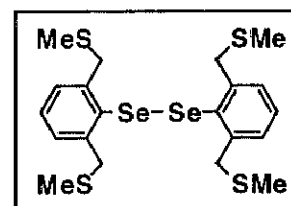
Diselenide 7

^{1}H NMR (400 MHz, CDCl$_3$, room temperature) δ 1.86 (s, 12H), 3.54 (s, 8H), 7.14–7.15 (m, 6H, Ar-H). ^{13}C NMR (100 MHz, CDCl$_3$, room temperature) δ 15.4, 36.8, 128.5, 133.1, 142.0, 144.2; ^{77}Se NMR (76 MHz, CDCl$_3$, room temperature) δ 358.9; MS (m/z) 277 (M$^+$/2).

Synthesis of the ditelluride 8

t-BuLi (5.0 mL, 7.7 mmol, 1.54 M in *n*-hexane) was added to a dry THF (100 mL) solution of 2,6-bis(methythiomethyl)phenyl bromide 5 (1.45 g, 5.24 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then tellurium powder (805 mg, 6.29 mmol) was added to the solution. The resulting mixture

was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, *n*-hexane-CHCl$_3$, 4 : 1) to give a pale yellow oil, the ditelluride 8 (163 mg) in 10% yield.
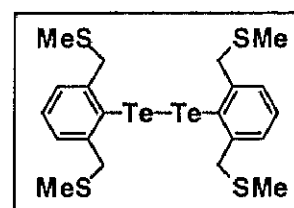
Ditelluride 8

^{1}H NMR (400 MHz, CDCl$_3$, room temperature) δ 1.92 (s, 12H), 3.78 (s, 8H), 7.17–7.20 (m, 6H, Ar-H). ^{13}C NMR (100 MHz, CDCl$_3$, room temperature) δ 15.3, 45.6, 118.9, 127.2, 128.9, 145.8; ^{125}Te NMR (126 MHz, CDCl$_3$, room temperature) δ 274.2; MS (m/z) 327 (M$^+$/2).

Oxidation of the disulfide 6

An anhydrous CH$_3$CN (10 mL) solution of NOPF$_6$ (130 mg, 0.74 mmol) was added dropwise to a solution of the disulfide 6 (139 mg, 0.30 mmol) in anhydrous CH$_2$Cl$_2$ (20mL) at –78 °C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH$_2$Cl$_2$ and CH$_3$CN gave colorless crystals of the hydroxysulfonium salt 9 (144 mg) in 51% yield.

Hydoxysulfonium salt 9

mp 98-112 °C (decomp.); ^{1}H NMR (400 MHz, CD$_3$CN, room temperature) δ 2.39 (s, 12H), 4.34 (s, 8H), 7.41–7.46 (m, 6H, Ar-H); ^{13}C NMR (100 MHz, CD$_3$CN, room temperature) δ 15.3, 45.6, 118.9, 127.2, 128.9, 145.8.
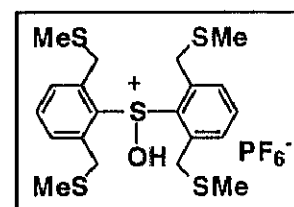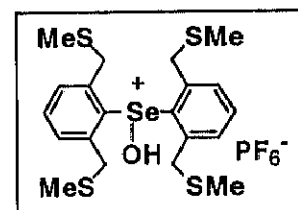
Oxidation of the diselenide 7

An anhydrous CH_3CN (10 mL) solution of $NOPF_6$ (116 mg, 0.66 mmol) was added dropwise to a solution of the disulfide 7 (152 mg, 0.28 mmol) in anhydrous CH_2Cl_2 (20mL) at -78 °C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH_2Cl_2 and CH_3CN gave colorless crystals of the hydroxyselenonium salt 12 (170 mg) in 56% yield.

Hydroxyselenonium salt 12

mp 90-98 °C (decomp.); ^1H NMR (400 MHz, CD_3CN, room temperature) δ 2.44 (s, 12H), 4.38 (s, 8H), 7.44–7.46 (m, 6H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN, room temperature) δ 19.5, 128.8, 128.8, 131.8, 137.3; ^{77}Se NMR (76 MHz, CD_3CN, room temperature) δ 821.7.


Oxidation of the ditelluride 8

An anhydrous CH_3CN (10 mL) solution of $NOPF_6$ (175 mg, 0.63 mmol) was added dropwise to a solution of the ditelluride 8 (163 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (20mL) at -78 °C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH_2Cl_2 and CH_3CN gave pale yellow crystals of the dication 15 (120 mg) in 48% yield.

Dication 15

mp 177-182 °C (decomp.); ^1H NMR (400 MHz, CD_3CN, -40°C) δ 1.93 (s, 6H), 2.00 (s, 6H), 4.12 and 4.24 (ABq, $J=$ 16.8 Hz, 4H), 4.20 and 4.63 (ABq, $J=$ 16.5 Hz, 4H), 7.25 (d, $J=$ 7.5 Hz, 2H, Ar-H), 7.37 (t, $J=$ 7.5 Hz, 1H, Ar-H), 7.61 (d, $J=$ 7.5 Hz, 2H, Ar-H), 7.73 (t, $J=$ 7.5 Hz, 1H, Ar-H); ^{13}C

NMR (100 MHz, CD_3CN, room temperature) δ 13.7, 14.7, 38.6, 129.4, 130.6, 130.8, 1331.1, 133.2, 138.1, 145.2, 147.2; ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 1406.3, 1427.2; Anal. Calcd for $C_{20}H_{26}F_{12}O_2P_2S_4Te_2$: C, 24.72; H, 2.70; Found: C, 25.04; H, 2.94.
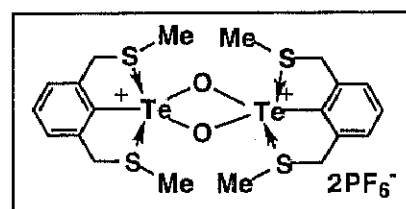
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