Chapter 1

General Introduction

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I. Introduction

In the recent decades, organic chemistry has attracted attention in the industrial and biological point of view. Organic chemistry has traditionally been defined as the chemistry of compounds where the carbon atom is the principal element. Carbon is a second row element whose position in the periodic table is shown in Table 1. The unique ability of carbon atoms to bond together and to form stable compounds with atoms such as hydrogen, oxygen and nitrogen, is the basis for all biological life, which has been recognized since the mid-eighteenth century. Since then organic chemistry has developed into one of the most important fields in chemistry[1]. However, the discoveries of atoms with unusual bonding properties have attracted great interest causing the emergence of a new field called heteroatom chemistry.

Electronegativity of the elements Belonging to Groups 13 to 17.

Group / Row	13	14	15	16	17
2	B 2.0[a]	C 2.5	N 3.0	O 3.5	F 4.0
3	Al 1.5	Si 1.8	P 2.1	**S 2.5**	Cl 3.0
4	Ga 1.6	Ge 1.8	As 2.0	**Se 2.4**	Br 2.8
5	In 1.7	Sn 1.8	Sb 1.9	**Te 2.1**	I 2.5

[a] Electronegativity according to Pauling's value.

Table 1-1

Heteroatoms are defined as follows: 1) the elements except group 1 and 2 from the main group elements and those belonging from group 13 to group 17 and the third to six row in the periodic table; 2) elements whose electronegativities are more than 2.0 (value presented by Pauling) among those belonging from group 13 to 17 except typical main group elements of first and second rows, while other elements bearing the electronegativities less than 2.0 are regarded

as typical metals. Thus, heteroatom chemistry is focused on the study of organic compounds containing a variety of heteroatoms, where the atoms other than carbon are regarded as the central elements.

II. Chalcogen Elements

A. Comparison of Sulfur, Selenium and Tellurium

Although sulfur, selenium and tellurium belong to the same group in the periodic table, their chemistry differs markedly. This may be realized by a comparison of the elements as shown in Table 1-2.

Characteristic Chemical Properties of Sulfur, Selenium and Tellurium.

	S	Se	Te
Atomic Number	16	34	52
Atomic Weight	32.06	78.96	127.60
Electronegativity[a]	2.5	2.4	2.1
First Ionization Potential (eV)	10.36	9.75	9.01
Atomic Radius (Å)	1.020	1.163	1.356
Covalent Radius at Carbon (Å)	1.787	1.930	2.123
Covalent Radius at Oxygen (Å)	1.765	1.908	2.101
NMR Measurable Isotope	-	^{77}Se	^{125}Te

[a] Electronegativity according to Pauling's value.

**Table 1-2**

B. Organic Sulfur Compounds

Sulfur is widely distributed in nature and biologically the most important element among the chalcogens. A rich variety of organic sulfur compounds are found in living systems, and biochemically notable sulfur compounds are for example the essential amino acids cysteine and methionine and antibiotics such as pencillin and bacitracin. Therefore sulfur and organic sulfur compounds have been studied extensively since the eighteenth century[2]. Characteristic chemical properties of sulfur and organic sulfur compounds, among others, are: 1) the sulfur atom is capable of taking various oxidation states, 2) divalent as well as higher valent sulfur can stabilize adjacent carbanions, and 3) tricoordinated sulfur atoms can be attacked by nucleophiles to form pentacoordinated σ-sulfuranes as unstable intermediates.

1. Organic Sulfur Compounds in Synthesis

Three most important properties of organic sulfur compounds in organic syntheses are the formation of a C–C bond, the transformation of one functional group into another, and the protection of a functional group with an appropriate group which can be released readily. A sulfur atom in the organic compounds can provide effective clues to solve all of these problems.

For the formation of a C–C bond, nucleophilic substitution of a carbanion or electrophilic attack of carbenium ion on a carbon atom is frequently utilized. When a compound having either the sulfenyl group, sulfinyl group, or sulfonyl group is treated with strong bases such as butyl lithium, lithium diisopropylamide (LDA), or NaH, a carbanion can be readily generated at the carbon atom adjacent to these functional groups. In either nucleophilic substitution with alkyl halides or nucleophilic addition to carbonyl compounds or electrophilic olefins, carbanion thus formed reacts with suitable electrophiles to result in the formation of a C–C bond.

Another distinct feature of sulfur compounds is that many types of reactions are available for cleavage of a C–S bond. A variety of reactions have been developed for either the homolytic or the heterolytic dissociation of a C–S bond to produce a new functional group. For example, Raney nickel is a well-known desulfurization reagent for converting R-SR', to R-H[3], while pyrolysis of RCH_2CH_2SOAr gives an olefin $RCH=CH_2$ *via* an E_i process.[4] Therefore, a combination of these desulfurization reactions with the sulfur-assisted C–C bond formation described above realizes a wide range of methodology in organic syntheses using the sulfur compounds. In this result, for example, carbanions derived from 1,3-dithiane can be used for new homologation as depicted in the following process as shown in Scheme 1-1. 1,3-Dithianes are easily formed from the carbonyl compounds and 1,3-propanedithiol under the influence of Lewis acids and boron reagents.[5]

4
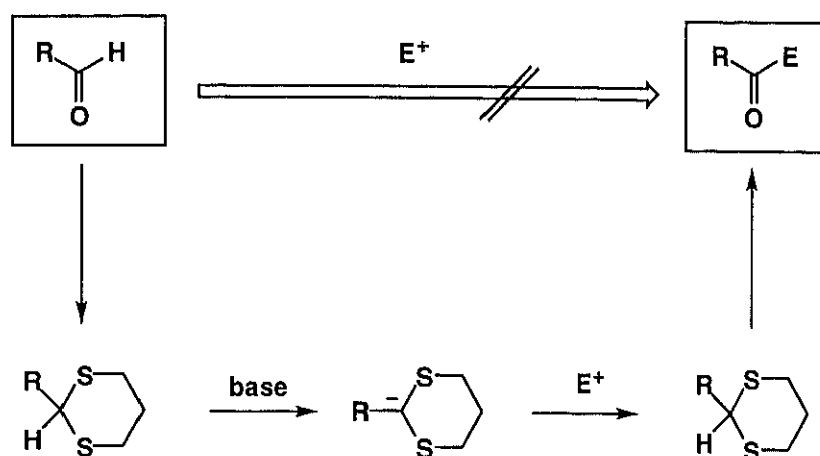
Scheme 1-1

The reaction of dithianes with n-butyl lithium in THF at low temperature leads to the anion. After the reaction with an electrophilic compound, the hydrolysis can generally be carried out in polar solvents such as acetone, alcohols and acetonitrile to release the corresponding carbonyl compounds. This method was introduced by Corey and Seebach, and is termed "Umpolung of the reactivity".[6] These compounds are employed on general concepts based on the facile conversion of sulfur functional groups to the better leaving groups, following by hydrolysis

2. Pummerer Rearrangement

The Pummerer rearrangement reaction has been widely studied and has received considerable attention as a synthetically useful process.[7] It is the reaction of sulfoxides in which the S→O bond is broken and a group containing oxygen or other electronegative substituent is incorporated α to sulfur. The overall result of the transformation is thus reduction at sulfur and oxidation at the α CH position. The mechanism of this reaction has been thoroughly investigated and is said to involve the preliminary formation of the acyloxy sulfonium ion **2**, which can be deportonated to give the ylide **3**. The cation **4**, which can be described as the thienium **4a** or the sulfur-stabilized carbocation **4b**, would be formed, and would undergo a nucleophilic addition to give the final product **5**.

(R³CO)₂O

R³CO₂⁻   3

+ R³CO₂H

1   2

4a   4b

5
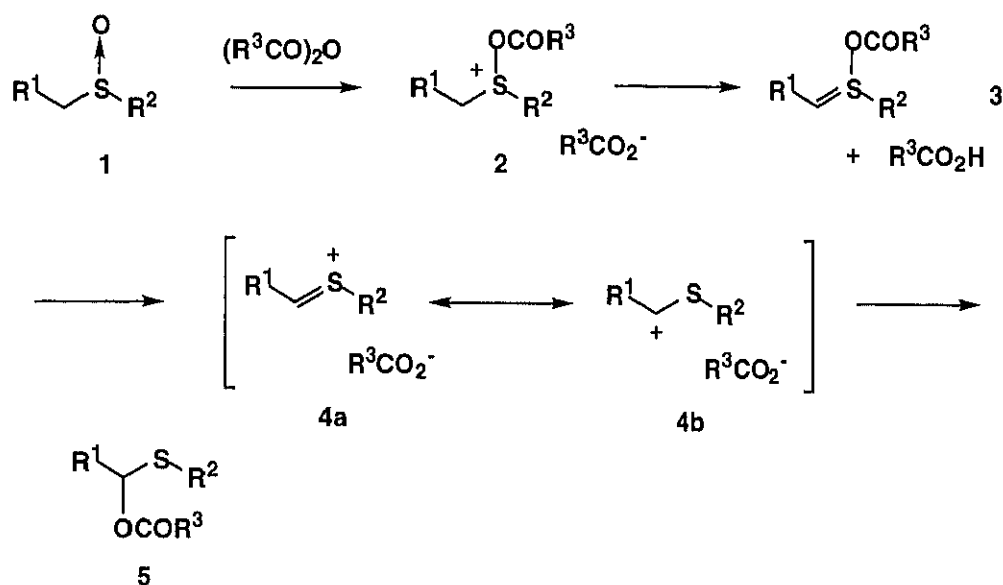
Scheme 1-2

Because the products from aliphatic sulfoxides can be readily hydrolyzed to carbonyl compounds, these reactions have been widely utilized in a variety of organic syntheses. On the other hand, similar reactions of the aromatic sulfoxides have not been extensively explored. Pummerer-type rearrangements of p-sulfinylphenols would be an effective method for the preparation of p-quinones *via* the O, S-acetals and would also be interesting from a mechanistic standpoint. King and Jung et al. have reported related studies on the reaction of acid anhydride with 3,5-dimethyl-4-(methylsulfinyl)phenol[8] and with 4-methyl-2-(arylsulfinyl) phenols.[9] The main products in these reactions were obtained through conjugated addition of nucleophiles to the sulfonium ions (like **8**), while the O,S-acetals (like **9**) were obtained in very low yield and only in very few cases.[9] Recently, Kita et al reported the isolation of the quinone mono O,S-acetals (like **9**) intermediates of the reaction with 1-ethoxyvinyl esters.[10]

(R²CO)₂O

6   7   8   9   10
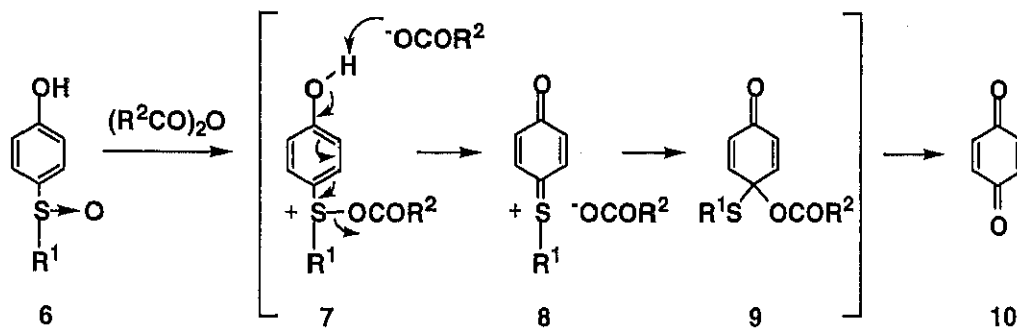
Scheme 1-3

3. Sulfenium Ion

Sulfenium ion species have generally been unstable and highly reactive as a strong electrophile reagent. Therefore, few of this species have been neither directly detected, nor isolated as a 'free' cation.

Most of the early work was performed using 2,4-dinitrobenzenesulfenyl chloride 11. Kharasch and co-workers[11] presented evidence for the ionic behavior of this sulfenyl chloride based on examination of 11 in solutions of 100% sulfuric acid or fuming sulfuric acid. The result of the study was in agreement with the following equilibrium.
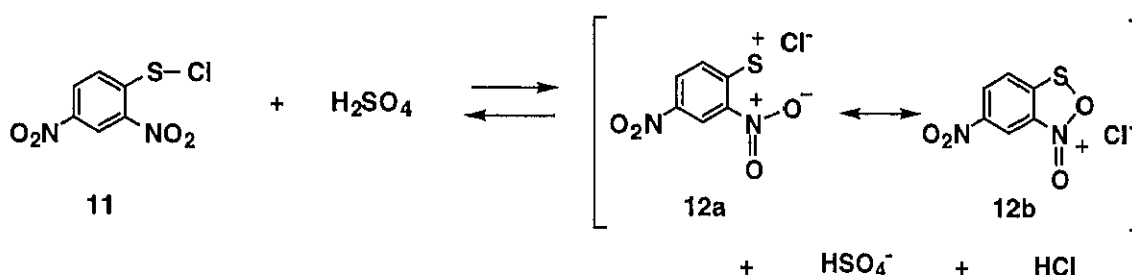
Scheme 1-4

The bright red color of the solutions was attributed to the sulfenium ion 12a, which was shown to migrate to the cathode; in addition, hydrogen chloride was evolved during the reaction. Spectroscopic examinations of the solution, with and without added bisulfate, showed a diminution of the color ascribed to 12a, when excess bisulfate was added.

While it is quite possible that 2,4-dinitrobenzenesulfenyl chloride behaves as typical sulfenium ion precursor, the initial studies on this molecule certainly induced further mechanistic investigations are required to characterize the sulfenium ion. The cationic properties of sulfenyl halides are further substantiated by their reaction properties and products. Sulfuric acid solutions of 12a readily attacks benzene, giving 2,4-dinitrophenyl phenyl sulfide. In the absence of conditions which promote ionization, the sulfenyl chloride does not enter into this reaction. Other Friedel-Crafts catalysts such as aluminum chloride, boron trifluoride, and tin (IV) chloride also promote sulfenylation of an aromatic ring.

$$Ar-S-Cl \quad + \quad Ar'-H \quad \xrightarrow{AlCl_3} \quad Ar-S-Ar' \quad + \quad HCl$$

Scheme 1-5

The earliest attempts to cleanly generate a sulfenium ion under mild conditions were carried out by Kharasch. In the study of the chemistry of 2,4-dinitrobenzenesulfenyl chloride 11, it has been found that tertiary amines such as pyridine catalyze the reaction of 11 with alcohols. This

catalytic effect is presumably due to the intermediacy of a sulfenylpyridinium ion **14**.
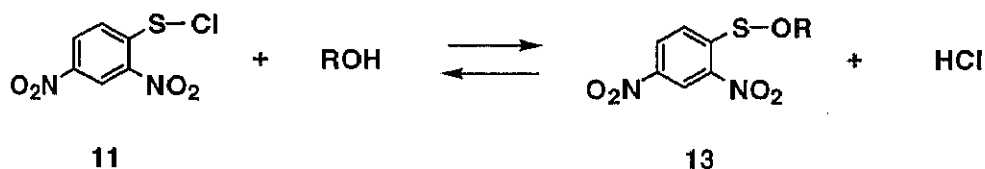
Scheme 1-6
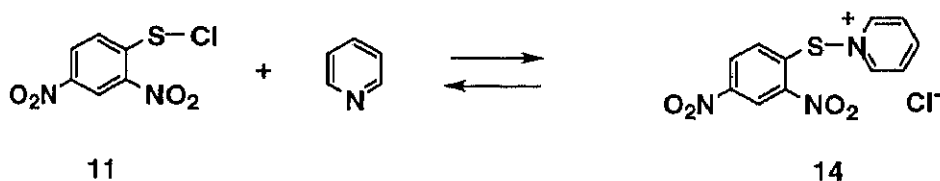
Scheme 1-7

When sterically hindered tertiary amines (i.e., N,N-dimethyl-2,4,6-trimethylaniline) are used, the catalytic effect disappears because it can not form an ammonium ion. While isolatable examples of sulfenylammonium ions have not yet been reported, their presence as intermediates in the above reactions seems to be reasonable.

The reaction of a sulfenyl halide with a silver salt was first reported in 1953[11]. When 2,4-dinitrobenzenesulfenyl chloride is treated with a silver perchlorate in cold 1,2-dichloromethane, the sulfenium perchlorate, with its characteristic color, is generated in solution along with silver chloride. While these were the mildest conditions for the generation of the sulfenium ion at the time, very little chemistry was described for this species. The formidable challenge of producing sulfenium ions under non-acidic conditions was taken up by Helmkamp and co-workers, who scrutinized the reactions of sulfenyl halides with silver salts.

$$\text{Ar}-\text{S}-\text{Br} \quad + \quad \text{Ag}^+ \quad \longrightarrow \quad \text{Ar}-\text{S}^+ \quad + \quad \text{AgBr}$$
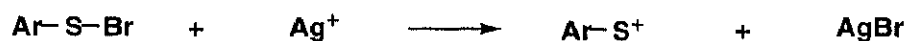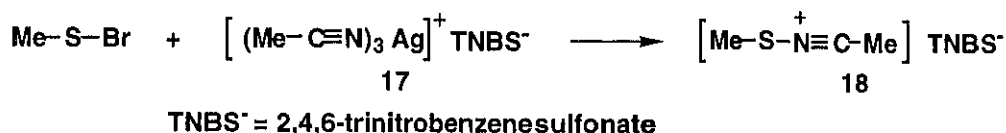
Scheme 1-8

These workers used silver 2,4,6-trinitrobenzenesulfonate to generate the sulfenium ion because of its solubility in organic solvents and of the non-nucleophilicity of the trinitrobenzenesulfonate anion. It was mechanistically of major interest to determine whether the cation was formed or not, and to differentiate between singlet and triplet ground states for the reactive form of the sulfenium ion. Both alkane- and arenesulfenyl halides were treated with silver trinitro-benzenesulfonate in nitromethane, dichloromethane and in acetonitrile to produce solutions of the corresponding sulfenyl 2,4,6-trinitrobenzenesulfonate. The nature of these species was investigated by conductivity measurements and by NMR studies. The conductivity

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of solutions of the sulfenium salt indicated an ionic species if the reactant silver ion was coordinated with acetonitrile, but not otherwise. It was concluded that in solvents other than acetonitrile, the sulfenyl product exists in a covalent form such as the *O*-alkylsulfenyl sulfonate **17** rather than an intimate ion pair.
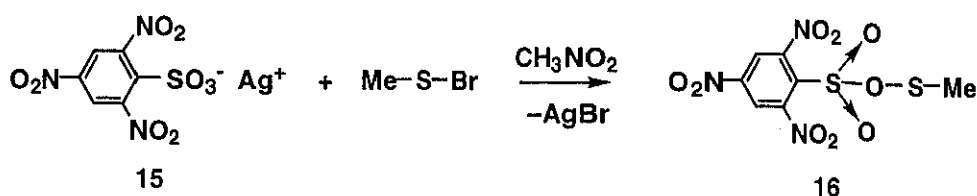
Scheme 1-9

The situation is significantly altered in acetonitrile solution which is thought to promote the formation of silver-complexed acetonitrile salts. These species are then responsible for the formation of a thionitrilium salt **17**. In this system, the solvent thus acts as a transfer agent for the sulfenium ion.

TNBS⁻ = 2,4,6-trinitrobenzenesulfonate

Scheme 1-10

The above conclusions have been largely substantiated by NMR data of the various solutions. In nitromethane, the spectra show very sharp lines for the solvent, trinitrobenzenesulfonate and methanesulfenium protons. These qualitative observations suggest that the sulfur atom exists in the singlet state, since a paramagnetic species should give rise to line broadening. In acetonitrile solutions, the acetonitrile protons are shifted about 0.2 ppm downfield, while the chemical shift for the methyl protons of the methanesulfenium ion appears at 2.8 ppm. The latter information indicates that a formal positive charge on the sulfur atom is unlikely and gives further evidence for a nitrilium species. Olah[14] has found that protons α to s protonated sulfur atom of a thiol or a sulfide are more deshielded (about 3.0 ppm) than those observed in the methanesulfenium solutions. Thus, it appears that sulfenium ions exist in solution, although complexed or associated with solvent molecules. The intervention of solvents such as acetonitrile, or even the formation of the covalently bonded species, does not inhibit or preclude further reactions of sulfenium species. This can be evidenced by the trapping of these sulfur cations by a number of nucleophilic species.

C. Organic Selenium Compounds

Selenium is one of the ten essential elements for mammal, birds and fish, but nevertheless it has been studied less than sulfur. However, the chemical and physical characteristics of organoselenium compounds resemble those of the corresponding organosulfur compounds, and the main features of the chemistry of selenium are well established[15].

Selenium can be prepared with either an amorphous or crystalline structure. Crystalline monoclinic selenium is deep red; crystalline hexagonal selenium, the most stable variety, is a metallic gray. Elemental selenium is relatively nontoxic and is considered to be an essential trace element. However, hydrogen selenide (H_2Se) and other selenium compounds are extremely toxic, and resemble arsenic in their physiological reactions. Hydrogen selenide in a concentration of 1.5 ppm is intolerable to man. Selenium occurs in some soils in amounts sufficient to produce serious effects on animals feeding on plants such as locoweed (an American plant) grown in such soils.

1. ^{77}Se NMR Spectroscopy

The ^{77}Se isotope has a natural abundance of 7.5% and a nuclear spin of 1/2. This nucleus has a medium sensitivity which is about three times greater than that of the ^{13}C nucleus. Therefore, the structural determination of selenium compounds is more easily undertaken as compared to the sulfur analogues for which only one NMR active isotope (^{33}S) has a very low receptivity and complicated by a large quadrupole moment. The structure of organic selenium compounds and the course of reactions can be elucidated by measuring ^{77}Se NMR spectroscopy.

The resonance frequency of ^{77}Se NMR is equal to 19.071 MHz in a magnetic induction where the resonance of ^1H is measured at 100 MHz. Chemical shifts are given in ppm downfield from dimethyl selenide (MeSeMe) which is adopted as a reference. The chemical shifts appear in a range of 2500 ppm for organic selenium compounds and are sometimes affected to a certain extent by solvents and temperature. The ^{77}Se chemical shifts relative to Me_2Se are summarized in the Figure 1-1. Selenium chemical shifts are generally assumed to be dominated by the paramagnetic term and a decrease of electron density at the selenium atom leads to a decreasing shielding. Therefore, tetravalent and hexavalent selenium derivatives tend to have chemical shifts in the lower field region. The sensitivity to the changes of the electronic surroundings for δ ^{77}Se seems to be about six times greater than that for δ ^{13}C.
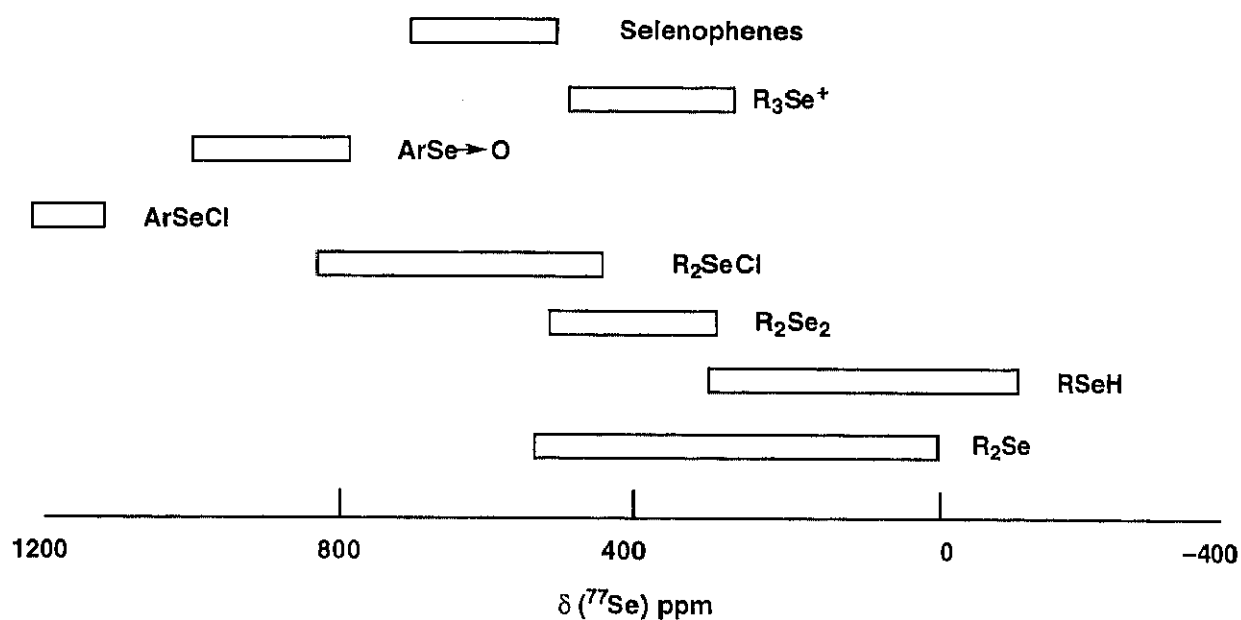
Figure 1-1

2. Pharmacological Aspects of Organic Selenium Compounds

Selenium is essential to mammals and higher plants in small amounts. It may help protest against free radical oxidants and against some heavy metals. And selenium deficiency syndrome was recognized in animals and human, and selenium was found to be an important element in human nutrition.[16]

Recently, an organic compound, 2-phenyl-1, 2-benzoisoselenazole-3 (2H)-one (ebselen) 19,[17] was reported to have anti inflammatory activity in various inflammatory models with very low toxicity. Ebselen itself exhibited glutathione peroxidase-like activity *in vitro* and antioxidant activity independent of exogenous glutathione.

Glutathione peroxidase is a selenoenzyme which catalyzes the reduction of H_2O_2 and other hydroperoxide. Glutathione (GSH) is utilized as a cofactor, supplying the electrons for the following reductive reaction (eq. 1).

$$ROOH + 2GSH \rightarrow ROH + H_2O + GSSG \quad (eq.1)$$

The mechanism by which Ebselen catalyzes the reduction of peroxides has been the subject of several studies.[18] Fisher and Dereu[19] proposed that at high peroxide concentrations, Ebselen is first oxidized to its seleninamide [R(Se=O)NR'$_2$], which then reacts with 1 equiv of thiol to form the corresponding thioseleninate [RSe(=O)SR']. The further reaction of the latter species with a second equivalent of the thiol then regenerates the original selenamide 19, via a selenenic acid (RSeOH), along with 1 mol of the disulfide (Scheme 2, path A). Under

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conditions of excess thiol, which represents a more realistic scenario in vivo, 19 reacts directly with the thiol to afford a selenenyl sulfide (RSeSR') intermediate that disproportionates to the corresponding diselenide and disulfide in the slow step. Further oxidation of the diselenide then regenerates the original selenamide via a selenenic anhydride (RSeOSeR) (Scheme 2, path B). Peptidic nitrogen atoms may function similarly in the formation of cyclic selenamide species in the natural enzyme glutathione peroxidase.
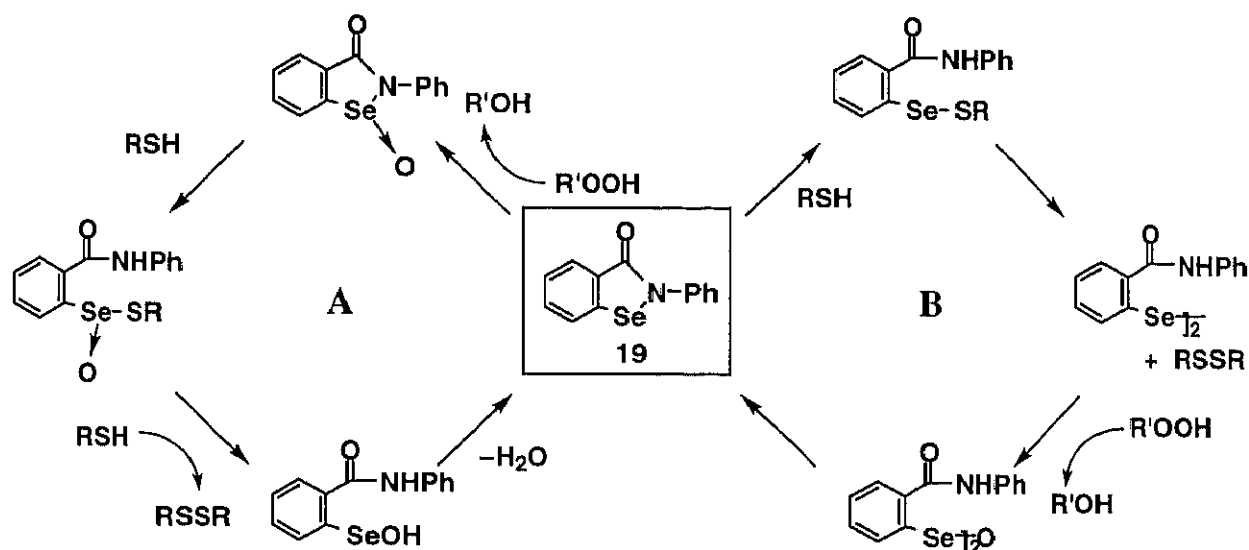
Scheme 1-11

D. Organic Tellurium Compounds

Tellurium is the second heaviest element of the chalcogens, whose crystalline has a silvery-white appearance, and exhibits a metallic luster when pure. And its abundance is as rare as gold. This may be the reason that the element has been studied less intensively than sulfur and selenium. Though, recently, studies on organotellurium compounds have increased and many interesting results, especially regarding hypervalent compounds, have accumulated.[20] Characteristic chemical properties of tellurium and organic tellurium compounds, among others, are: 1) the tellurium atom possesses almost metallic character, 2) the tellurium atom has several oxidation states, 3) hypervalent organotellurium compounds are the most stable among the hypervalent chalcogen compounds.

1. ^{125}Te NMR Spectroscopy

Tellurium has two NMR detectable isotopes, ^{123}Te and ^{125}Te. However, the ^{123}Te isotope is not useful for NMR, except for the measurement of $J(^{123}$Te$-^{125}$Te), because of its low natural abundance of 0.87%. The ^{125}Te isotope has a natural abundance of 6.99% and a nuclear spin of 1/2, and this isotope is commonly used for NMR. ^{125}Te spectroscopy has been employed to

characterize organic tellurium compounds and solves the special problems concerning the structures and conformations of the molecules bearing tellurium in solution.

The resonance frequency of [125]Te NMR is equal to 26.17 MHz in a magnetic induction where the resonance of ^{1}H is measured at 100 MHz. Chemical shifts are given in ppm downfield from dimethyl telluride (MeTeMe) which is adopted as a reference. The chemical shifts appear in a range of 3500 ppm for organic tellurium compounds and are sometimes affected to a certain extent by solvents and temperature. The [125]Te chemical shifts relative to Me_2Te are summarized in the Figure 1-2.

R_2TeBr_2

F_5TeOX

R_3Te^+

Tellurophenes

$ArTeX_3$

TeX_6^{2-}

R_2Te_2

TeX_4

R_2Te

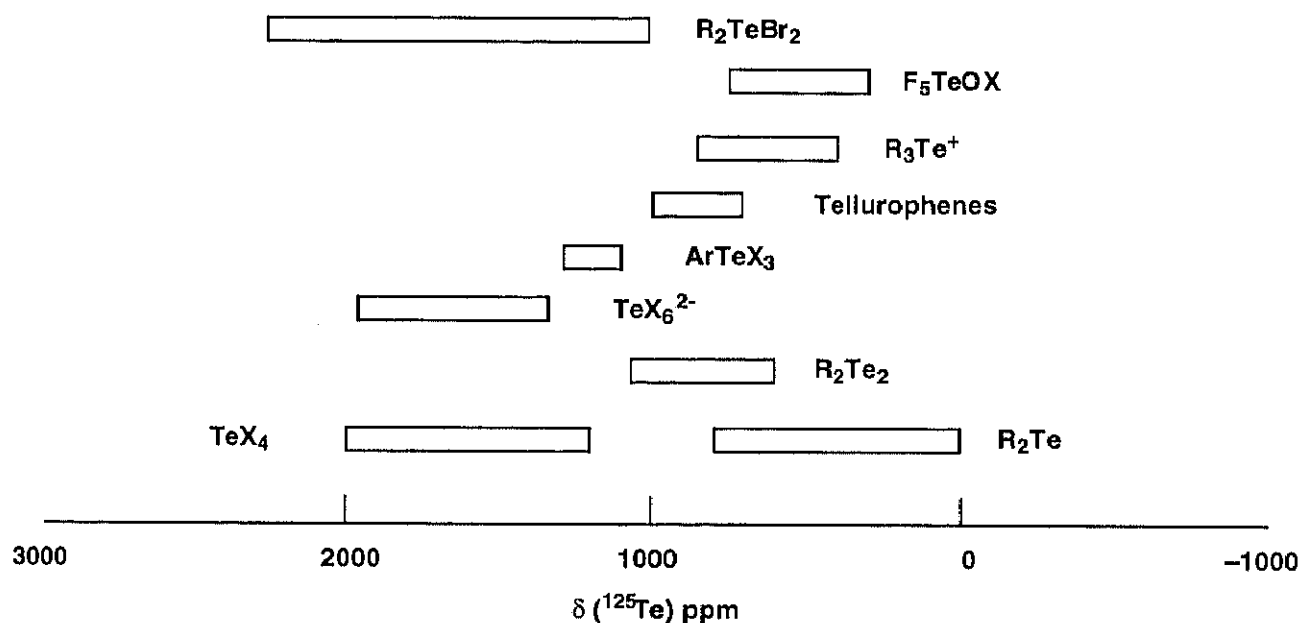3000   2000   1000   0   −1000

δ ([125]Te) ppm

Figure 1-2

In some studies, the chemical shifts are shown to correlate with the oxidation states of the tellurium atom and electronegativity of the ligands.[21] For example, Zumbulyadis and Gysling reported that the increase in oxidation states causes the low field shift of the [125]Te NMR chemical shift. On the other hand, Gassmann and Detty et al. did not observe this tendency when they observed the [125]Te NMR spectra of telluropyranes and related compounds. In recent paper, Koizumi et al. reported the relationship between the structure of organotellurium compounds and the [125]Te NMR chemical shifts.[22] In the paper it is reported that the [125]Te NMR chemical shift of organotellurium compounds is sensitive to the type and size of the substituents (aromatic, aliphatic) and the oxidation states of the tellurium atom.

II. Intramolecular Interaction

A. Intramolecular Reaction

Intramolecular reactions as dealt with in this work, usually proceed much faster than their intermolecular counterparts (Figure 1-3). This is probably the reason for the evolution of enzyme catalyzed reactions in biological systems, since fast conversions of metabolites often are required.[23]
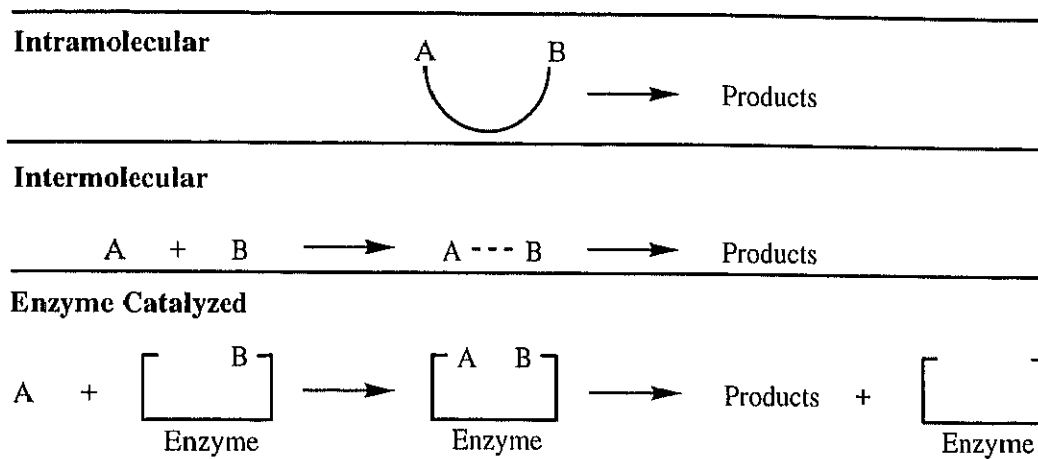

Figure 1-3

Generally, prior to the actual reaction the enzyme and substrates are brought together by weak chemical interactions (hydrogen bondings, hydrophobic interactions and van der Waal forces), so that the reacting groups on the enzyme and substrates are in close proximity. This results in a much faster reaction rate between the substrates compared to that without the presence of the enzyme (Scheme 1). This phenomenon called enzyme catalysis can be investigated by using intramolecular reactions as models, since intramolecular reactions between covalently linked reactants somewhat resemble the enzyme catalyzed reactions.[24]

Some suggestions to explain the rate difference between intra- and intermolecular reactions are: 1) the proximity effect, 2) the entropic effect and 3) substrate anchoring.

B. Intramolecular Coordination

Intramolecular coordination plays a crucial role in defining the molecular structure of compounds with spatially suitably fitted functionalities, secondary and tertiary structures of biologically important macromolecules, and modes of packing of molecules in a crystal. Special attention has been given to intramolecular noncovalent attractive interactions existing between di- and tetracoordinated sulfur, selenium, and tellurium atoms from one side and oxygen or nitrogen atoms from another side.[25] When occurring within a molecule, interactions of this

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kind strongly affect the reactivity and enhance the stability of the chalcogen containing compounds. These interactions are also responsible for the high biological activity of selenium, in particular selenoproteins and nucleoside analogues.[26]

A peculiar feature of the chalcogen-oxygen and chalcogen-nitrogen bonds is the strong dependence of their strengths and lengths on the nature of chalcogen, its valence state, and the electronegativity of the attached substituent. By varying these factors in a series of compounds with similar geometry it is possible to cover wide ranges of chalcogen-oxygen or chalcogen-nitrogen intramolecular distances, from those approaching values characteristic of covalent bonds to those close to van der Waals contacts. This trend is illustrated by data of X-ray structural analysis for compounds with five-membered chelate rings formed by the intramolecular coordination (Figure 1-4).[27]
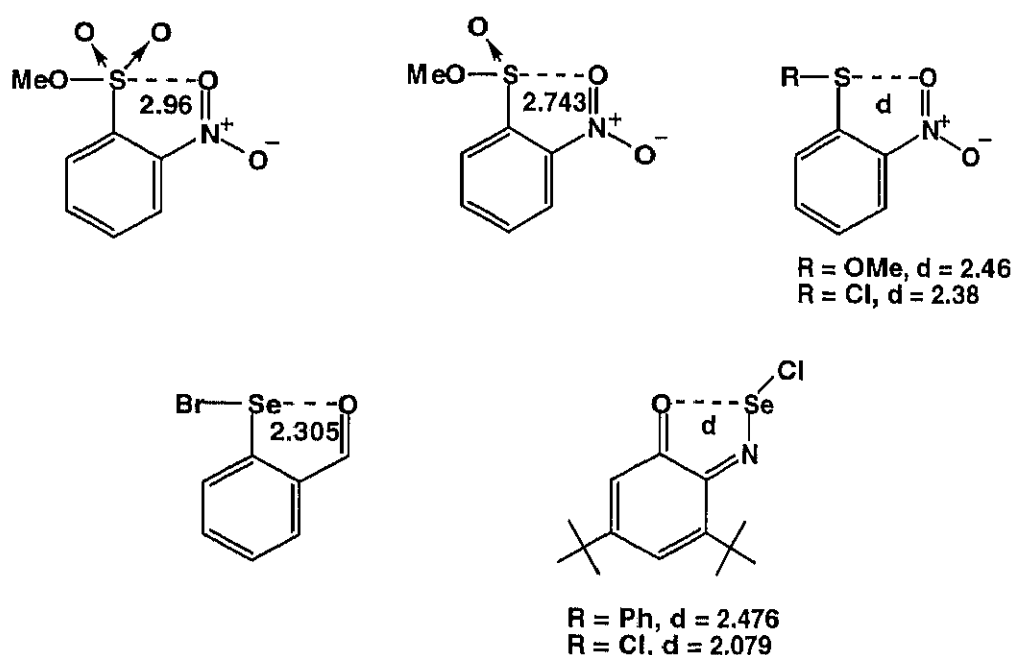

Figure 1-4

Tellurium, especially, is the element easy to form intramolecular coordination. Tellurium compounds (in oxidation states II and IV), because of the presence of lone pair of electrons and also vacant 5d orbitals, can function as both electron donors and electron acceptors depending on the partner. Compounds of the type RTeX and R_nTeX_{n-4} (where X is a halide) act as good acceptors. Examples of the organotellurium compounds containing intramolecular coordination are shown in Figure 1-5.[25b), 28]
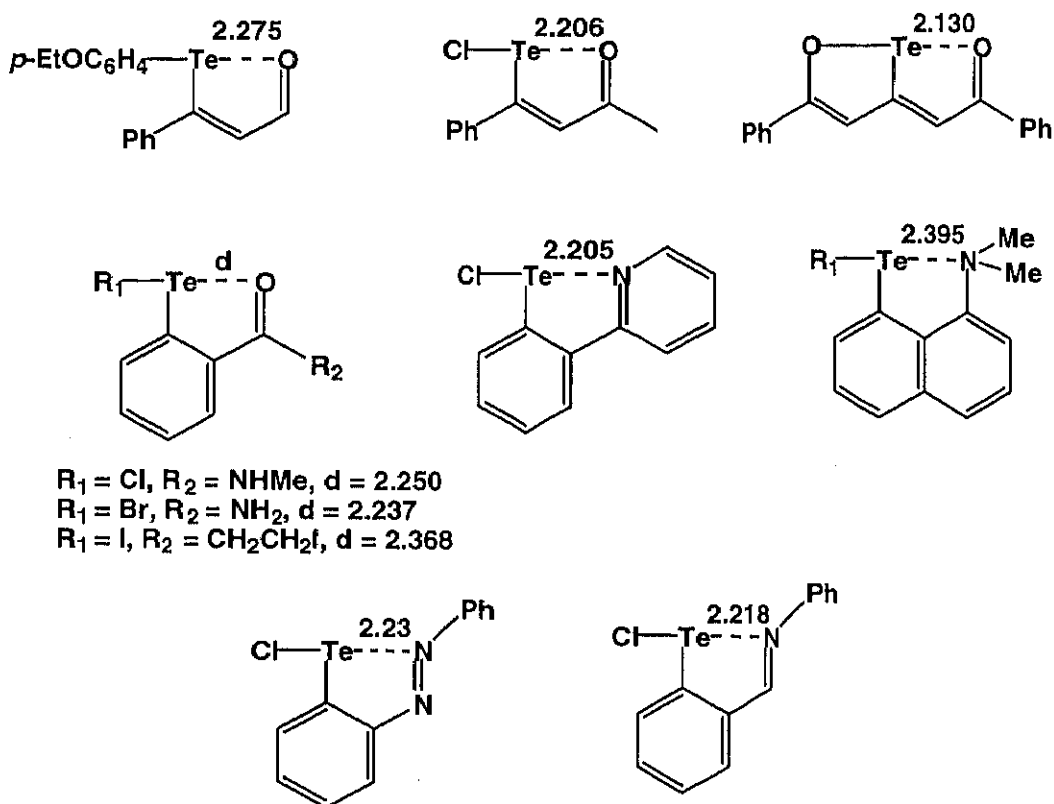
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Figure 1-5

R₁ values listed in figure:

R₁ = Cl, R₂ = NHMe, d = 2.250
R₁ = Br, R₂ = NH₂, d = 2.237
R₁ = I, R₂ = CH₂CH₂I, d = 2.368

III. The Octet Rule and Hypervalent Bond

A. Octet Rule and Duodecet Rule

In describing the electronic structures of molecules, the Lewis octet rule has special historical and practical significance. For most compounds, Lewis dot pictures are used to establish whether atoms have an octet of electrons (two for hydrogen, helium and lithium). These numbers represent the filled s and p levels and reflect the unique stability of the inert gas electron configurations. The octet rule is a excellent basic rule to use in predicting stable combinations of elements, recognizing that electronic configurations equivalent to those of the inert gases have unusual stability. In practice, this rule works in over 95 % of the compounds, but it is true that it dose not work all of them. Very electronegative atoms like fluorine and chlorine can react with larger atoms of group 15, 16, 17 and 18 to give compounds in which there appear to be more than 8 electrons associated with the central atom.

For the third and subsequent periods, it is recognized that there are many exceptions to the octet rule. For example, elements of the third period form species such as SiF_6^{2-}, PF_6^-, SF_6 and ClF_5, each of which have six electron pairs in the valence shell of the central atom. Apparently, the valence shells of third period elements can accommodate a maximum of six pairs of electrons,

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especially when they are bonded to highly electronegative ligands. From these facts, Robinson[29] suggested that it is more relevant to use a duodecet rule for the period 3 and 4 elements rather the octet rule which is only valid for period 2 elements just as the corresponding rule for 1 elements is a duet rule.

B. Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

The valence shell electron pair repulsion (VSEPR) model[30] – also known as the Gillespie–Nyholm rules has for many years provided a useful basis for understanding and rationalizing molecular geometry, and because of its simplicity it has gained widespread acceptance as a pedagogical tool. In its original formulation the model was based on the concept that valence shell electron pairs behave as if they repel each other and thus keep as far apart as possible. But in recent years more emphasis has been placed on the space occupied by valence shell electron pair, called the domain of the electron pair, and on the relative sizes and shapes of these domains.[31] This reformulated version of the model is simpler to apply, and it shows more clearly that the Pauli principle provides the physical basis of the model.

C. Hypervalency

Musher[32] originally defined hypervalent molecules as those formed by the non-metals of groups 15-18 of the periodic table by expanding their valence-shell from the normal octet to decet or dodecet, thus producing multivalent compounds or hypervalent compounds. Hence, in a hypervalent molecule the octet rule is not obeyed, since there are more than four pairs of electrons in the outer shell. Consequently, hypervalent compounds are interesting not only for their unusual bonding properties, but also for their important roles as intermediates in nucleophilic and electrophilic substitution reactions. Hypervalency is a well-known phenomenon for many of the heteroatoms. However, only hypervalent molecules with a central chalcogen atom will be discussed here.

The theoretical description of the hypervalent bond is still controversial, since the two models that have been proposed, individually, seem to be inadequate. However, the molecular orbital model proposed by Musher[32] and Rundle[33] gives a qualitatively satisfactory explanation for the hypervalent bond, and in general agrees well with experimental data. Therefore, this model will be used to describe hypervalency. Comprehensively, the second model is a valence bond model in which the atomic d-orbitals participate in the bonding, so that sp^3d hybridization of the central atom's atomic orbitals allows five bonds to be built. This can explain the fact that hypervalency is observed more frequently for third-row atoms than for second-row atoms, because the proximity of the 3d/(3s3p) orbitals ensures that the sp^3d hybridization is not too costly in energy. On the contrary, hybridization of this type should be very unfavorable for second-row atoms.

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According to Musher[32] and Rundle[33] the molecular geometry around the hypervalent atom is trigonal bipyramidal (TBP configuration). The hypervalent atom which is placed in the center and surrounded by two apical and three equatorial ligands, forms two different types of chemical bonds i.e. the three-center-four-electron bond and three sp^2 hybridized bonds. The two most electronegative ligands prefer to occupy the apical positions (L_{ap}), while the three electropositive ligands take the equatorial positions (L_{eq}). Therefore, lone-pair electrons always occupy an equatorial site (Figure 1-6).

Apical Bond; three-center four-electron bond

Equatorial Bond; sp^2 hybrid orbital bond

X   = Central Atom
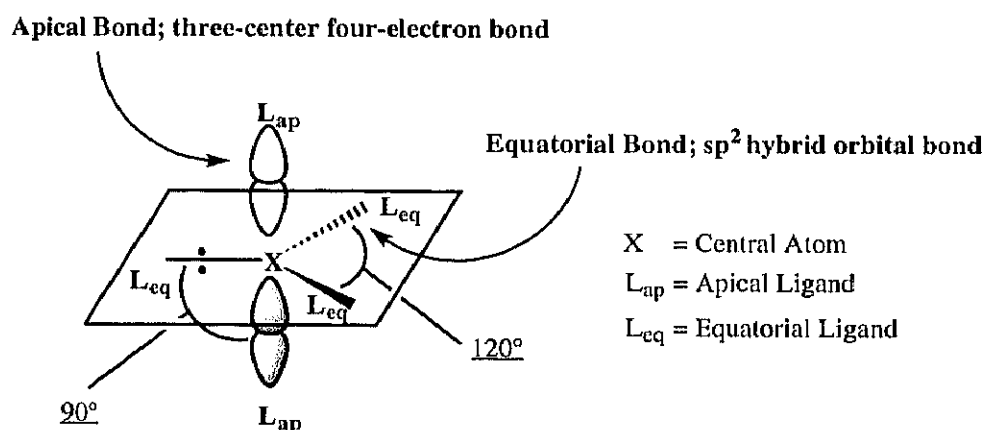L_{ap} = Apical Ligand
L_{eq} = Equatorial Ligand

Figure 1-6

In the ideal TBP structure as shown in Figure 1-6, the atoms that make up the hypervalent bond are colinear (180°) and the bond angle between the two equatorial ligands is 120°. However, in general when the hypervalent compound has a lone-pair as equatorial ligand, the repulsive force between the lone-pair and the bonding electrons will be relatively large causing smaller angles between the axial ligands (<180°) and between the equatorial ligands (<120°). This fact has been verified by X-ray crystallographic analysis of many hypervalent compounds. The molecular orbital model for the three-center-four-electron bond is shown in Figure 1-7.
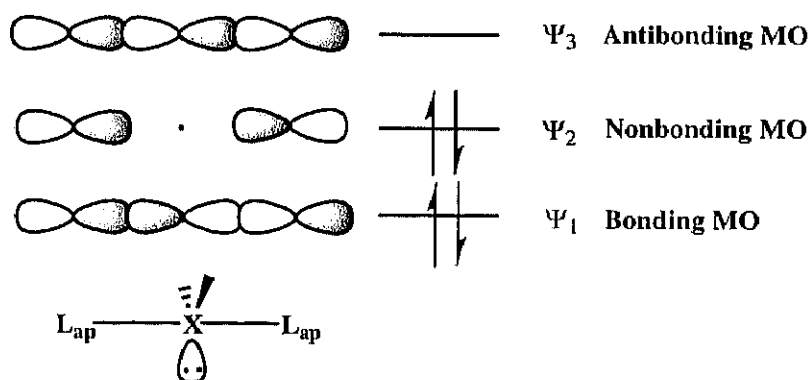

Ψ_3 Antibonding MO

Ψ_2 Nonbonding MO

Ψ_1 Bonding MO

L_{ap}————X————L_{ap}

Figure 1-7

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The hypervalent bond is formed by the overlapping of two p-atomic orbitals supplied from the apical ligands and one p-orbital from the central atom. Two electrons of the four bonding electrons occupy the lowest bonding orbital (Ψ_1) and the other two electrons take the non-bonding orbital (Ψ_2). This allows for a net binding stabilization, since the two filled molecular orbitals have bonding (Ψ_1) and approximately non-bonding (Ψ_2) character, while the anti-bonding (Ψ_3) molecular orbital remains empty.

Several important generalizations can be made from this model. For example the two electrons in the approximately non-bonding hypervalent molecular orbital (Ψ_2) are associated with the apical ligands, and hence a more negative charge is expected for the apical positions. Therefore, more electronegative substituents have preference for the apical sites, which indeed is observed experimentally. In addition, the symmetry of the Ψ_2 molecular hypervalent orbital forbids contributions from the central atom p_z orbital and results in relatively greater positive charge on the central atom. Thus, hypervalent species with large differences in electronegativity between the apical ligands and the central atom are favored. Because the two apical bonds only have two electrons in a bonding molecular orbital, the expected σ-bond order of one-half predicts that the apical bonds will be long and weak. Therefore, generally, hypervalent compounds are unstable and tend to resume the normal valency by decomposition or ligand coupling[34].
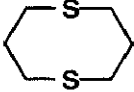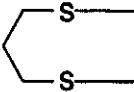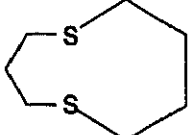
V. Transannular Interaction

Since Leonard's early work[35] transannular interactions have been well known phenomena for seven or eight membered cyclic compounds bearing two heteroatoms arranged appropriately in space. In 1-p-tolyl-1-azacyclooctan-5-one **22**, a transannular interaction between the amino nitrogen and the carbonyl group was observed as evidenced by the reduced C=O stretching frequency in the infrared spectrum. Upon protonation of the compound 1-methyl-1-azacyclooctan-5-one **23**, the transannular interaction could be converted into a σ-bond via a transannular reaction, since protonation occurred on the oxygen with the concomitant formation of a C-N bond resulting in the disappearance of the C=O stretch (Scheme 1-12).

Transannular Interaction   Transannular Reaction
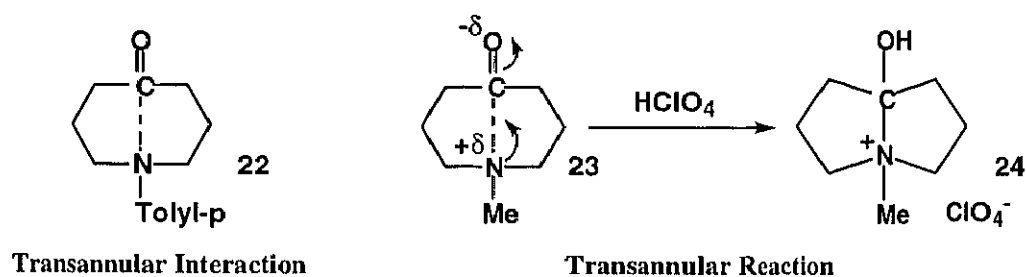
Scheme 1-12

Further evidence for the transannular interaction between the tertiary amine and the carbonyl group in **23** was obtained by dipole moment and optical rotatory dispersion measurements and ^{13}C and ^{17}O NMR analysis.[36]

Another intensively investigated compound where considerable transannular interaction exists is the bis-sulfide, 1,5-dithiacyclooctane **25**. The conformational characteristics of this compound is that the two sulfur atoms are on the same side of the eight membered ring in the boat-chair form as well as in the chair-chair form. Therefore an attractive force between the two sulfur atoms exists even in the neutral state, which is apparent from the relatively low ionization potential (8.30 eV) and electrochemical oxidation potential (0.34 volt) of **25** compared to those of 1,4-dithiacycloheptane **26** and 1,5-dithiacyclononane **27** (Table 1-3).[37]

	25	**26**	**27**
Ionization Potential (eV):	8.30	8.68	8.36
Oxidation Potential [a] (mV):	340	840	420

[a] mV vs. Ag/Ag$^+$

Table 1-3

Furthermore, when **25** is converted into the partially mono charged compounds such as the monosulfoxide **28**[38] and the monosulfilimine **29**[39] an enhanced transannular interaction is observed, since X-ray crystallographic analysis shows that the distances between the two sulfur atoms in the molecules are shorter than that of the neutral compound **25** (Table 1-4).
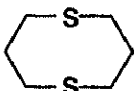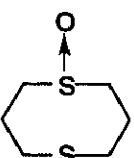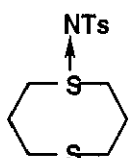
|	**25**	**28**	**29**
S-S Bond Distance (Å):	3.58	3.14	3.14

Table 1-4

Thus, transannular or intramolecular interactions between two functional groups is a major feature in medium sized cyclic compounds, which could be used to generate dications or

hypervalent compounds via transannular reactions, resulting in new bond types and functional group combinations with new functionalities.

A. σ-Bonded Dications

Generation of the σ-bonded dication can be obtained by the oxidation of the appropriate parent compound using methods such as pulse radiolysis[40] and electrochemical oxidation[41] or by the treatment with oxidizing agents such as nitrosyl tetrafluoroborate $(NOBF_4)$[42], nitrosyl hexafluorophosphate $(NOPF_6)$[43], concd sulfuric acid[44] and trifluoromethanesulfonic anhydride $((CF_3SO_2)_2O)$[45]. Only electrochemical oxidation and treatment with oxidizing agents will be viewed here.

Formation of the σ-bonded dication of **25** by transannular interaction was first reported by Musker et al.[46] who oxidized **25** using the one electron oxidant $NOBF_4$. The treatment of **25** with one equivalent of $NOBF_4$ produced a cation radical **30** which was stable in solution for several days, and further oxidation afforded the isolable dication tetrafluoroborate salt **31** (Scheme 1-12). The structure of the salt **31** was assigned on the basis of UV, ^{13}C NMR and elemental analysis.
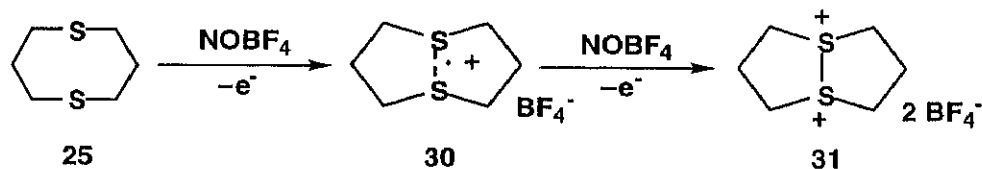
Scheme 1-12

Schematic view of orbital interactions and electronic configurations

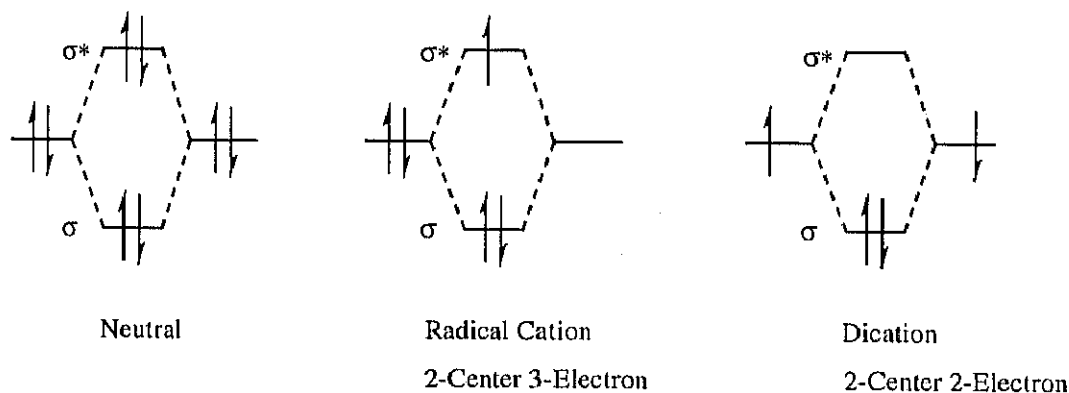| Neutral	Radical Cation	Dication
	2-Center 3-Electron	2-Center 2-Electron

Figure 1-8

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Furthermore, as mentioned in the precedent section, cyclic voltammetry studies of **25**, related cyclic dithioethers and analogous monothioethers[47] revealed remarkably low peak potentials for the cyclic compounds compared to those of the analogous monothioethers. The lowest peak potential observed was that of **25**, 0.34 volt (Ep vs. Ag/0.1 M Ag$^+$) which was 0.80 volt lower than that of the corresponding monothioether analog, heptamethylene sulfide. The large difference in the oxidation potentials indirectly showed the significance of the transannular interaction between the two sulfur atoms. In addition, the mesocyclic dithioethers exhibited reversible redox behavior, and detailed analysis of the current-voltage curves of **25**, unexpectedly revealed that oxidation of the cation radical to the dication proceeded more easily than that of the parent compound. Asmus et al.[40] suggested the electronic structures depicted in Figure 1-8 to explain this behavior. In the cation radical the odd electron is in an antibonding orbital (σ^*). Removal of this electron for the formation of the dication is energetically favorable, although the repulsive Coulombic interaction between the positively charged sulfur atoms increases.

Furukawa et al. also investigated the formation of the dication of **25**, but took a different approach, since the oxidations were carried out on the corresponding sulfoxide **28**. In the reaction of the sulfoxide **28** with concd sulfuric acid-d$_2$ (D_2SO_4) they detected the dication **31b** by ^{1}H and ^{13}C NMR spectroscopy[44] (Scheme 1-13).
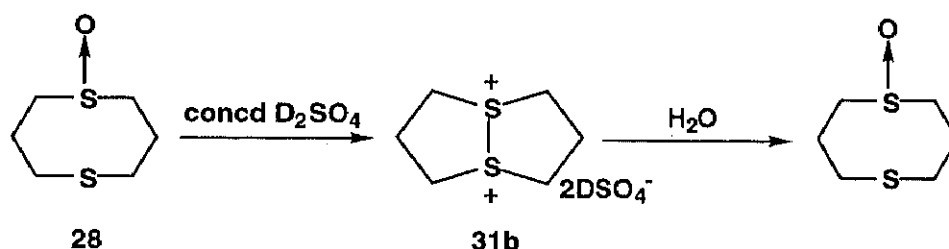
Scheme 1-13

The ^{1}H NMR spectrum of the D_2SO_4 solution showed broad signals at δ 2.10-3.32 and 3.40-4.32 in a 1:2 ratio, thus in agreement with the spectrum previously reported by Musker et al. It was assumed that the intermediate in the reaction mainly was the dithia dication in equilibrium with a low concentration of the cation radical of **25**. Hydrolysis of the solution gave the starting material **28**, indirectly confirming the formation of the dication **31b**.

Direct evidence for the σ-bonded dication of **25** was presented by Furukawa et al.[45], since they were able to successfully carry out an X-ray crystallographic analysis of the dication salt, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) **31c** (Figure 1-8).
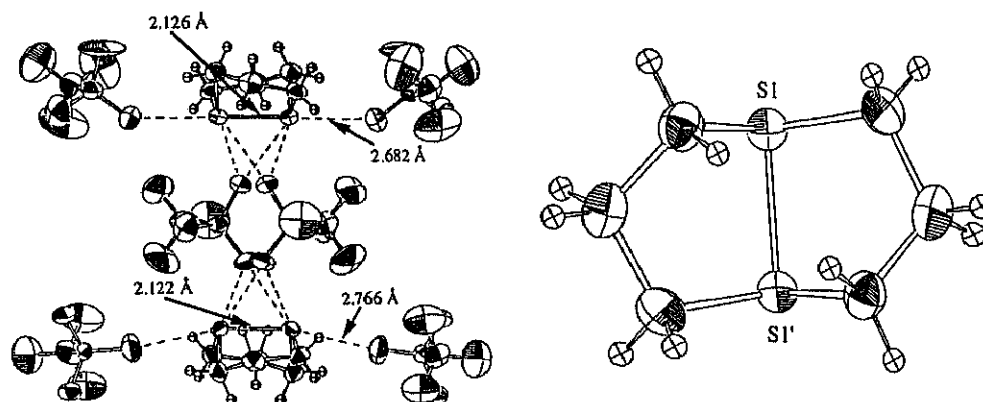
ORTEP view of the dication 31c [45)]

Figure 1-8

The dication **31c** was obtained from the reaction of sulfoxide **28** with ((CF$_3$SO$_2$)$_2$O), a reaction which proceeded via the initial formation of the trifluoromethanesulfonyloxysulfonium cation **32** which subsequently was converted to the dication **31c** by intramolecular nucleophilic displacement of the trifluoromethanesulfonate ion (CF$_3$SO$_3^-$) by the second sulfur atom as shown in Scheme 1-14.
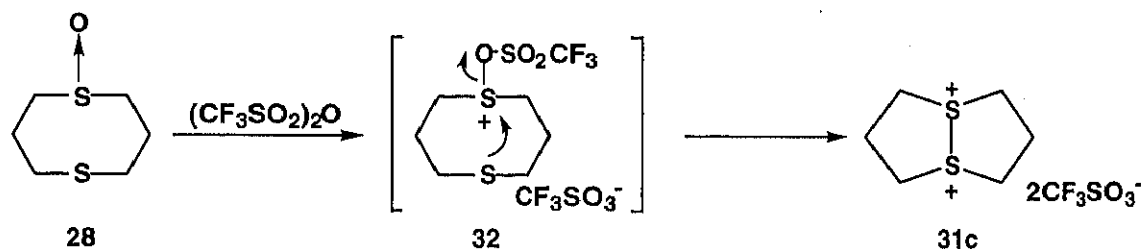
Scheme 1-14

The crystal structure of **31c** confirmed the precedent results, and clearly showed the σ-bond between the two sulfur atoms. According to the X-ray results of 31c, the S(1)–S(2) length is 2.12 , which is only slightly longer than the normal S-S single bond (2.08Å) of disulfides. The bond angle of ∠C–S–C is 104.1° and that of ∠S–S–C is 92.7°. It is interesting to note that a very strong interaction is observed between the sulfur atom (S$^+$) of the dication and the oxygen atom of the triflate counter anion. The S–O (TfO) distance is 2.682Å, which is markedly shorter than the sum of van der Waals radii of sulfur and oxygen atoms (3.35Å). The angles of ∠S$^+$–S$^+$···O is 176.3°. A nearly collinear interaction of O···S$^+$–S$^+$···O is observed with a central two fold symmetry. The optimized transannular S–S distance is 3.307Å for 1,5-DTCO **25** and 2.140Å for **31**, as postulated by an *ab initio* RHF MO calculation based on the STO-3-

Similarly, the 1,5-diselenacyclooctane dication **33** was prepared from the bis-selenide with two equivalents of $NOBF_4$ or $NOPF_6$. The X-ray crystallographic analysis of BF_4^- salts of **33** revealed that the Se^+–Se^+ distance is 2.38Å, which is roughly identical to the normal Se–Se single bond (Figure 1-9). The distances between the fluorine atoms of BF_4^- and the Se^+ atom are in the range 2.68-3.25Å, which is also within the van der Waals contact of Se$\cdots$F (3.37 Å).

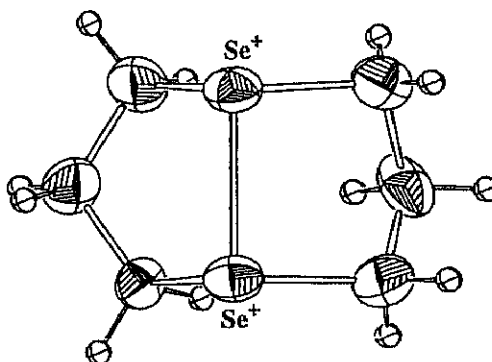**ORTEP view of the dication 33[43]**

Figure 1-9

On the basis of the results obtained from the investigations on the framework of compound **25**, several other sterically congested dications derived from dibenzothiocin[50], 1,9-disubstituted dibenzothiophenes[51], o,o'-dithiasubstituted biphenyls, 1,8-dithiasubstituted naphthalenes, dithio peri-bridged dinaphthalene dinaphtho[1,8-b,c]-1,5-dithiocin and the corresponding selenium compounds[52] were synthesized, and their structures were determined by spectroscopic methods (Figure 1-10). It is noted that in all new frameworks employed the chalcogen atoms are attached to aromatic rings, which could effect the stability of the dications i.e. delocalization of the positive charges versus electron withdrawing effect. However, an explanation concerning the stability of these compounds has not yet been found.

In summary, the results show that when a cation or a radical is produced on one of the chalcogen atoms, the second chalcogen atom interacts to enhance the stability and thus resulting in the formation of the dication.
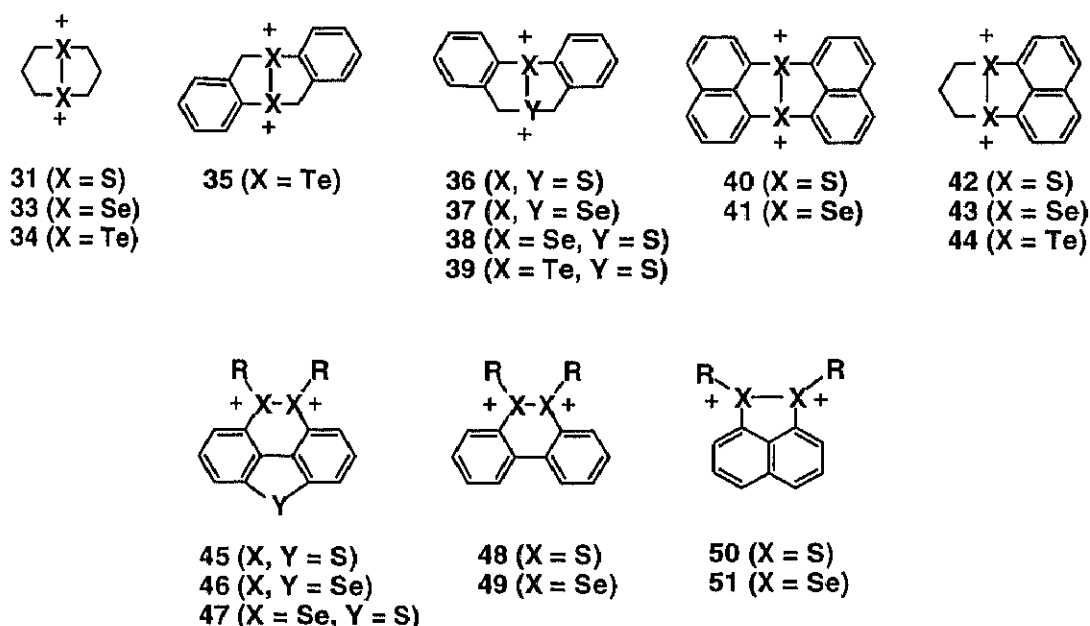
31 (X = S) 35 (X = Te) 36 (X, Y = S) 40 (X = S) 42 (X = S)
33 (X = Se)   37 (X, Y = Se) 41 (X = Se) 43 (X = Se)
34 (X = Te)   38 (X = Se, Y = S)   44 (X = Te)
                           39 (X = Te, Y = S)

45 (X, Y = S) 48 (X = S) 50 (X = S)
46 (X, Y = Se) 49 (X = Se) 51 (X = Se)
47 (X = Se, Y = S)

Figure 1-10

B. Hypervalent Dications

Accumulation of transannular or through-space interaction among more than three chalcogen atoms creates a new dication species as shown in Scheme 1-15. In this model, the chalcogen dications derived from the tris-sulfides or their monooxides are connected by a central hypervalent atom and the atoms of the cationic center serve as electropositive ligands.


X = S, Se, Te
Y = BF$_4$, TfO
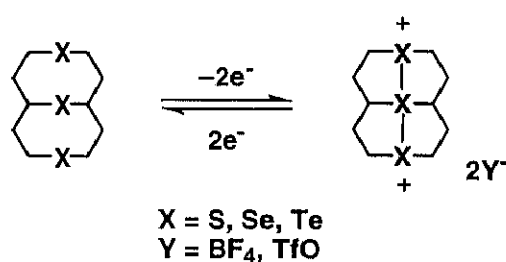
Scheme 1-15

The preparation of these new hypervalent bonded compounds is carried out by one of two methods. The first is the oxidation process using one electron oxidants such as NOBF$_4$, whereas the second method is the treatment of monooxide with concd H$_2$SO$_4$ or acid anhydrides.[52] 2,6-Bis(methylthiomethyl)phenyl phenyl sulfide 56 and related sulfides were prepared.

The sulfoxides 52 were dissolved in concd D$_2$SO$_4$. Their measured ^{1}H NMR spectra indicate the formation of dication 53 via through-space interactions between the three sulfur

25

atoms. On treatment of a D_2SO_4 solution of 53 with H_2O, the three products 54, 55 and 56 were obtained in 1 : 6 : 1 ratio as shown in Scheme 1-16. Selenides behave similarly to the sulfides.[53)
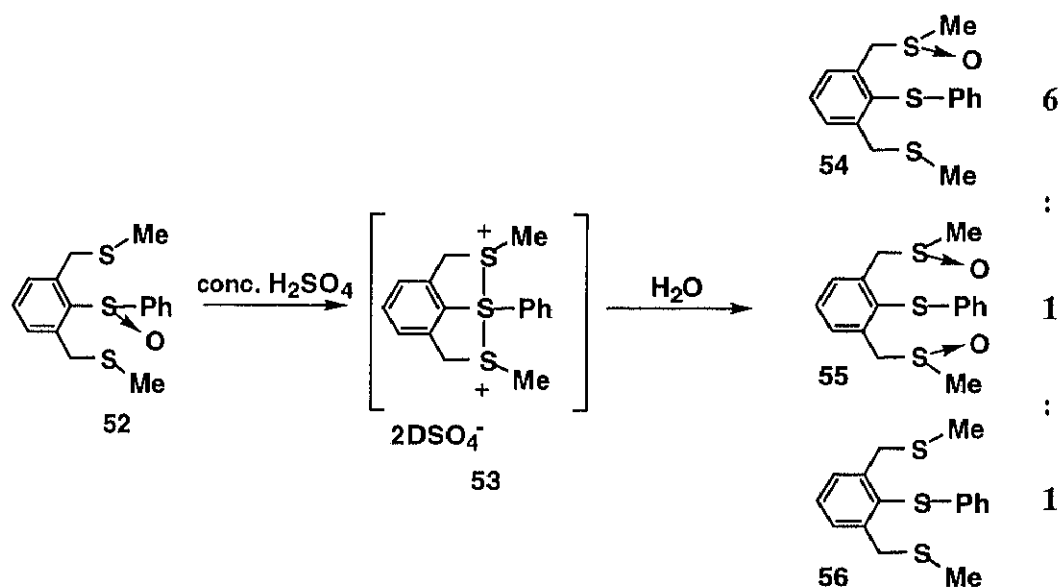
Scheme 1-16

In the rigid cyclic tris-sulfide, 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin 57, formation of a hypervalent dication $2DSO_4^-$ salt via transannular bond formation between the three sulfur atoms was observed, in the reaction of the tris-sulfide 57 and its sulfoxides, 58 and 59 with concd D_2SO_4 (Scheme 1-17).
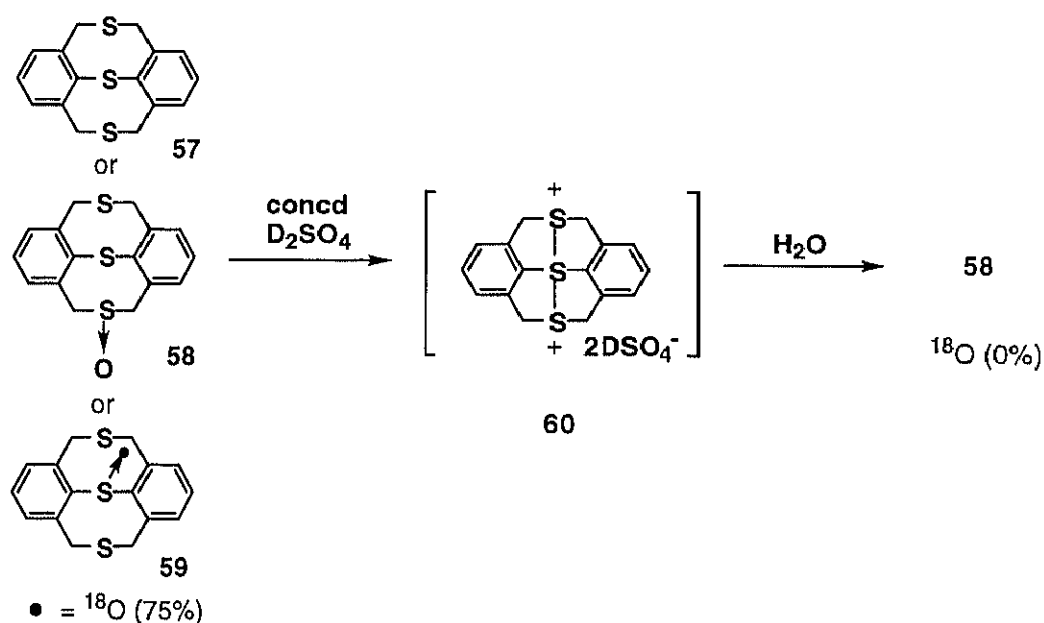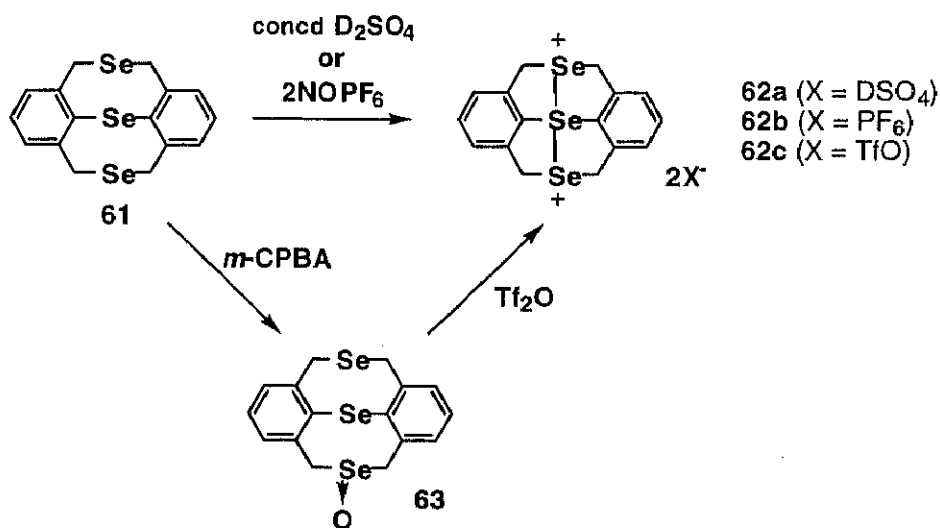

Scheme 1-17

The reaction that was followed by ^{1}H and ^{13}C NMR spectroscopy showed that the characteristic AB quartet set of the chair-chair conformation of the neutral compound **57** disappeared and new AB quartet peaks appeared. Moreover, in the ^{13}C NMR spectrum, two signals due to the corresponding methylene carbon atoms of **58** coalesced into one signal in D_2SO_4. These results clearly indicated that a conformational change of the chair-chair to the boat-boat form took place, to give the dication salt **60** by transannular bond formation between the three sulfur atoms. In addition, when the concd D_2SO_4 solutions of **57-59** were hydrolyzed, only sulfoxide **58** was obtained, and ^{18}O tracer experiments showed that an oxygen-exchange reaction took place. This also suggested the formation of the dication salt **60**, since initial formation of the dication salt **60** followed by a water molecule attack on the central arylic sulfur atom, could account for these results. The reaction is a new type of oxygen-transfer reaction, because normally in acid-catalyzed oxygen transfer reactions, oxygen migration from sulfoxides to sulfides usually takes place solely from the arylic sulfur atom to the alkyl sulfur atom.[55]

The unusual behavior of the dication salt **60** compared with other acyclic systems can be explained in terms of the rigidness of the dication. Under the given reaction conditions a sulfurane structure is formed to give a hypervalent bond, which is orthogonal to the π-orbitals of the two phenyl rings. Therefore, the positive charge on the central sulfur atom cannot be stabilized by resonance with the two phenyl rings, and hence, the positive charge is preferentially concentrated on the central arylic sulfur atom rather than the benzylic sulfur atoms. Thus, the aryl sulfur atom is attacked by water. These findings are in agreement with the hypervalent bond theory proposed by Musher and Rundle, despite the fact that the hypervalent dication salts and neutral hypervalent compounds are different. The positive charges in the dication salt **60** should then be distributed over the entire hypervalent bond, but with the main positive charge located on the central sulfur atom. The formula for the hypervalent dication salt **60** as depicted in Scheme 1–17 should therefore be considered in the way that two positive charges exist in the molecule.

The tris-selenide analog **61**, 1,11-(methanoselenomethano)-5H,7H-dibenzo[b,g][1,5] diselenocin, was synthesized and similar transannular bond formation was observed on treatment with concd D_2SO_4, oxidation with two equivalents $NOPF_6$[56], or treatment with Tf_2O via monoselenoxide of the tris-selenide.[57] New evidence for the formation of a dication salt **62** was presented, because the reaction as shown in Scheme 1–18 could be monitored by ^{77}Se NMR.

Scheme 1-18

61 in deuturated chloroform (CDCl$_3$) showed two peaks at δ 366 ppm (-SeCH$_2$Ar) and δ 209 ppm (-SeAr), which changed dramatically to δ 535 ppm (-SeCH$_2$Ar) and δ 830 ppm (-SeAr) in concd D$_2$SO$_4$. Also, clear satellite peaks were observed, thus indicating the formation of **62a**, which is a new selenurane bearing two apical selenonio ligands. Again, there seems to be agreement with the hypervalent bond theory, since the largest downfield shift in the [77]Se spectrum was observed for the arylic selenium atom, which therefore should be the most deshielded and positive of the three selenium atoms.

Recently, the structure of the dication **62c** was determined by X-ray analysis.[57] The ORTEP view of the structure is shown in Figure 1-11. It is seen that the bond angles Se(1)-Se(2)-Se(3) and C(1)-Se(2)-C(7) are 170.6° and 96°, respectively, hence in agreement with the theory of the hypervalent bond structure.
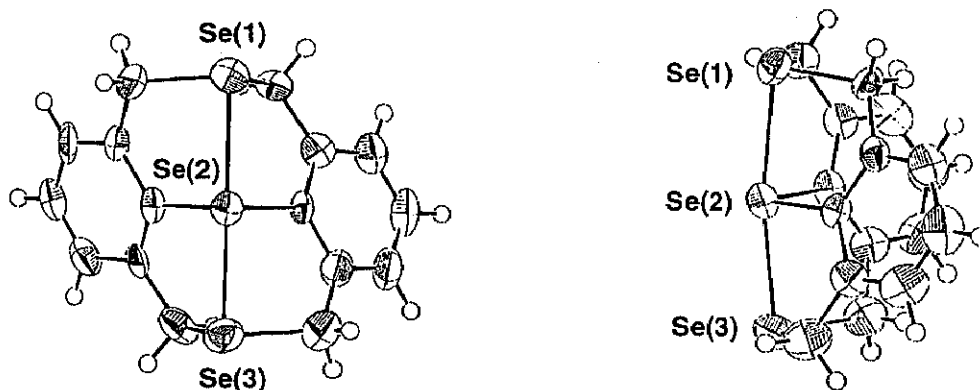
ORTEP view of the dication 62c
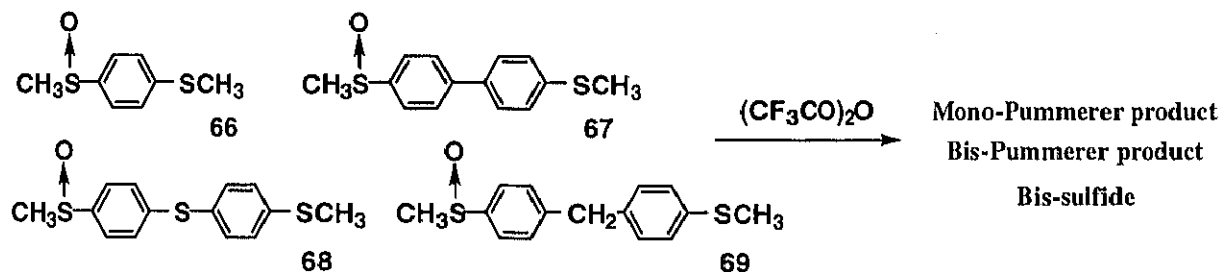

Figure 1-11

28

VII. Intermolecular Interaction

Despite the large body of information on σ-bonded dichalcogen dications formed by intramolecular reactions through transannular effects,[46a] bond formation by intermolecular reactions has received much less attention. Musker et al. pointed out that the radical cation prepared from 1,5-dithiacyclooctane and one equivalent of nitrosyl tetrafluoroborate ($NOBF_4$) would be dimerized in the solid state to form an intermolecular dithia dication.[42], [58]

Recently, Nenajdenko and co-workers reported the preparation and reactivity of a dithia dication, which is generated from the combination of dimethyl sulfoxide, triflic anhydride, and dimethyl sulfide (Scheme 1-19)[59]. Such a formation of dithia dicatoin by an intermolecular interaction would be worth pursuing from the viewpoint of molecular assembly, as well as organosulfur conducting materials.
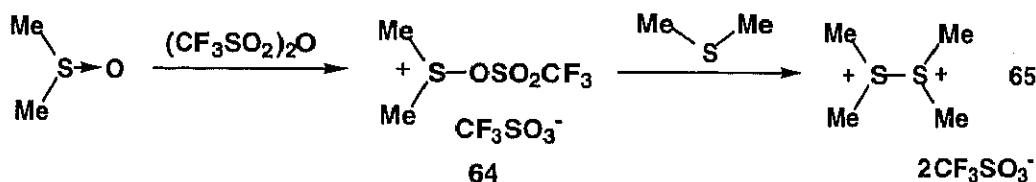
Scheme 1-19

As a new type of sulfur-sulfur intermolecular interaction, Furukawa et al., reported the remote Pummerer reaction *via* intermolecular through-space interaction between sulfonium and sulfenyl sulfur atoms.[60] It is much more favorable than an intramolecular through-bond interaction and abstraction of an α-proton of the sulfonium group leading to the Pummerer product. The reaction of the monosulfoxides with $(CF_3CO)_2O$ in CH_2Cl_2 gave a mixture of the corresponding mono- Pummerer product, the bis-Pummerer product and the bis-sulfide in an n:1:1 ration ($n \geq 2$). The 1:1 formation of the bis-Pummerer product and the bis-sulfide indicates an intermolecular interaction between sulfur atom. A dithia dication dimer **B** and/or a bis(dithia dication) cyclic dimer **C** are proposed as intermediates of the reactions.
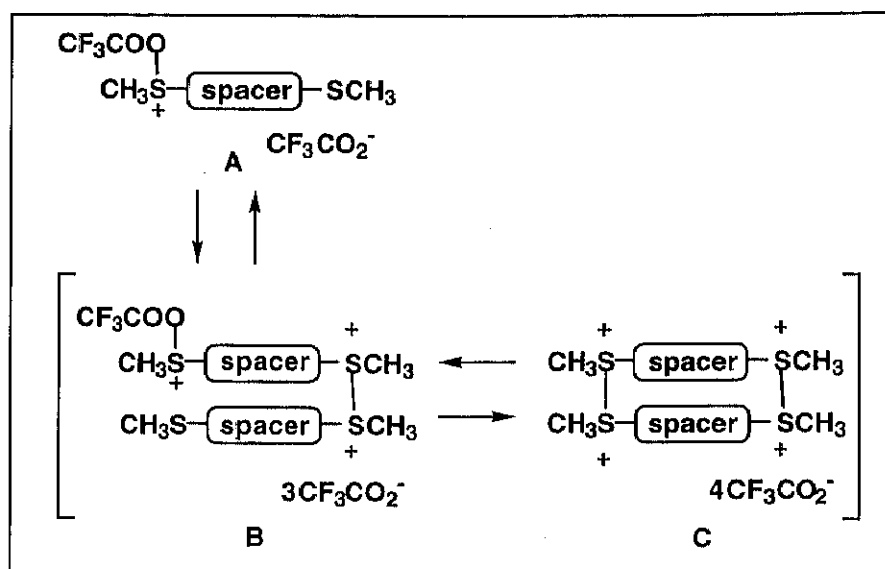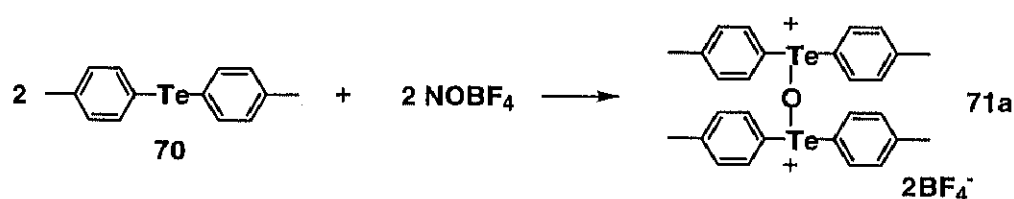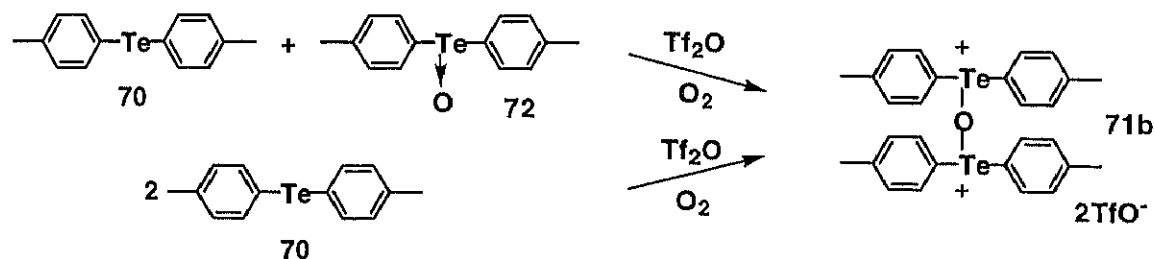

Scheme 1-20

Figure 1-12

As part of aim to synthesize an intermolecularly formed ditellurium dication and multi-telluirum dications,[61] bis[diaryltellurium(iv)] oxide dication was produced by insertion of the oxygen atom of nitrogen monoxide or an O_2 molecule between the two tellurium atoms by various chemical oxidations of diaryl tellurides (Scheme 1-21).[62] Treatment of bis(4-methylphenyl) telluride **70** with one equivalent of NOBF$_4$ afforded bis[bis(4-methylphenyl) tellurium(iv)] oxide bis(tetrafluoroborate) **71a** in quantitative yield as shown in Scheme 1-21.

Scheme 1-21

The similar dicationic bis[diaryltellurium(iv)] oxide ditriflate **71b** was quantitatively obtained by the reaction of a 1:1 mixture of **70** and **72** with one equivalent of triflic anhydride (Tf$_2$O) under an O_2 atmosphere (Scheme 1-22). Treatment of **70** with 0.5 equivalents of Tf$_2$O under the same conditions also afforded **71b** in quantitative yield.

Scheme 1-22

IX. π-Conjugated Oligomers[63]

The number of π-conjugated polymers investigated as advanced materials for electronic and photonic applications has developed rapidly, and has caused an ever increasing interest from both academic and industrial research laboratories.   The inherent synthetic flexibility, potential ease of processing, and the possibility of tailoring characteristic properties to accomplish a desired function makes them promising candidates for manifold applications in materials science. Thus, they are used as laser dyes, scintillators, light-emitting diodes, piezoelectric and pyroelectric materials, photoconductors, and are investigated for optical data storage, optical switching and signal processing, as well as in nonlinear optical applications.

Monodisperse π-conjugated oligomers are considered to act as molecular wires in molecular scale electronics and nanotechnological devices.   A variety of spectacular molecular architecture has resulted from the efforts aimed at the construction of such wires.   With the progress in synthetic organic methodology and the increasing availability of advanced analytical methods for the purification and characterization of very large molecules, monodisperse linear π-conjugated oligomers have recently reached the 10 nm length mark[64], which is about the current resolution limit for microstructure manufacturing by state-of-the-art lithographic techniques. This achievement in organic synthesis has greatly stimulated the interest in the experimental and theoretical study of molecular scale mesoscopic devices.

The tremendous advances in the chemistry and physics of poly(p-phenylenevinylene) (PPV) over recent years have stimulated further interest in related types of structures, such as the poly(p-phenylene-ethynylene) (PPE) polymers **73**, or the poly(p-phenylene-butadiynylene)s **74** (Figure 1-13)[65].   PPEs exhibit large photoluminescence efficiencies both in solution and in the solid state as a consequence of their high degree of rigidity, and their extremely stiff, linear backbone enables maximum orientation, which is an important feature for the preparation of oriented films or blends.
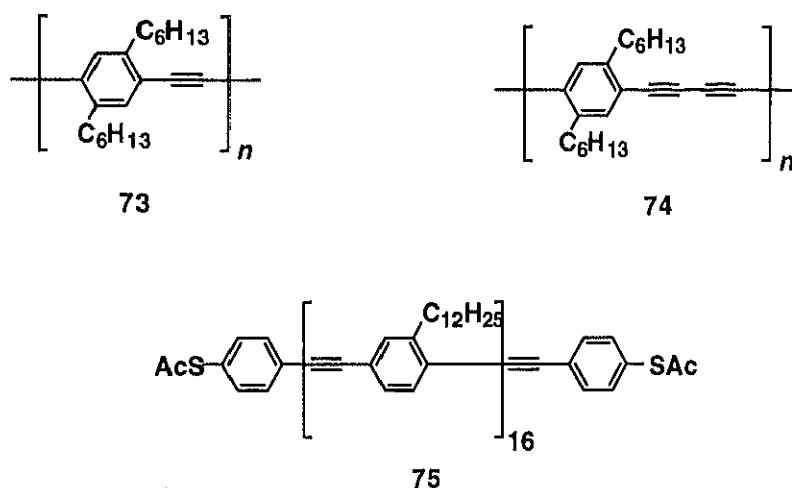

73   **74**

75

Figure 1-13

31

In an attempt to span the lithographically-derived probe gaps between two gold electrodes with a single molecule or with small packets of molecules, Tour and co-workers synthesized the 128 Å long oligo(p-phenyleneethynylene) rod.[66] Thioacetyl groups were introduced into 75[67] to generate sites for adhesion to the gold surfaces, which undergo cleavage to the desired thiol end groups under mildly basic conditions. An iterative convergent/divergent synthesis for hexyl- and isopentoxy-substituted PEEs was presented by Ziener and Godt.[68] This efficient strategy, which afforded gram quantities of octamer, takes advantage of the selectivity of the Pd-catalyzed alkyne–aryl cross-coupling for aryl iodides overbromides and the possibility for converting an aryl bromide into an iodide by a halogen–metal exchange.

Allara, Tour, Weiss, and co-workers self-assembled a small number of short poly(p-phenyleneethynylene) oligomers into an insulating monolayer film of nonconjugated alkylthiols on a gold surface, from which the molecular "wires" protruded by about 7 Å. By searching the surface of the layer with a scanning tunneling microscopy (STM) probe tip, a significantly enhanced current flow was found for the conjugated molecules relative to the insulating monolayer. In a different experimental set-up using the mechanically controllable break junction, Tour and co-workers measured the conductance of a junction containing a single benzene-1,4-dithiol molecule.

VIII. Introduction to the Thesis

In the context of this brief general introduction, the results obtained in this work will be discussed and presented in the following chapter. This work has concentrated on the flexible acyclic framework with three heteroatoms arranged liner configuration as shown in Figure 1-14.
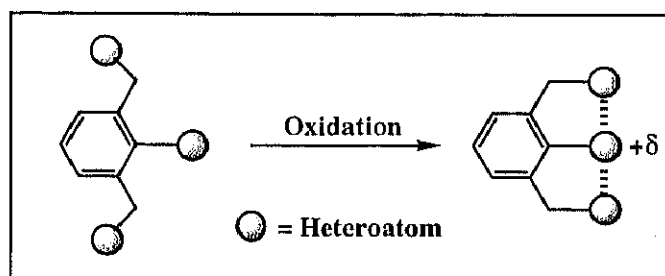

Figure 1-14

By using this framework, some cationic chalcogen species with unusual valent were synthesized as described in Chapters 2, 3, and 5. In Chapter 4, the new concept of oxidation, "remote oxidation", is proposed and investigated in the synthesis of the dicationic telluranes.

This thesis presents the following results in organic heteroatom chemistry, which are described in each chapter as following manner.

In Chapter 2, the chemical properties and preparation of a new type of dicationic σ-telluranes (λ⁴-tellane), [10–Te–4]²⁺ salts from the new flexible acyclic tris-chalcogenides via transannular bond formation are described. And the X-ray structure determinations reveal that two apical amino- and selenonio ligands bond to the central tellurium atom via transannular bond formation.
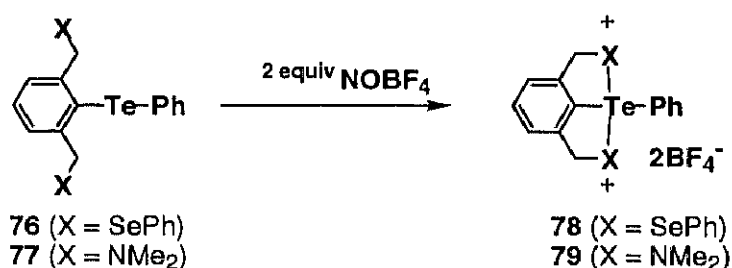
Scheme 1-23

In order to understand the charge distribution in the dicationic tellurane, on the basis of the crystal structure, an *ab initio* calculation was carried out using the RHF method and 3-21G(*) basis set. Surprisingly, the result revealed that the positive charges in the tellurane are distributed exclusively over the atoms that make up the hypervalent bond, concluding that the +Se-Te-Se+ hypervalent bonding system is electron rich with positively charged atoms.

In Chapter 3, the preparation of the sulfenium ion and the tellurenium monoxide dimer is described. This is the first isolation of the sulfenium ion stabilized by the neighboring two nitrogen atoms. The solid state structure of the sulfenium ion was determined by X-ray crystallographic analysis, and the structure of the tellurenium monoxide dimer was also determined.
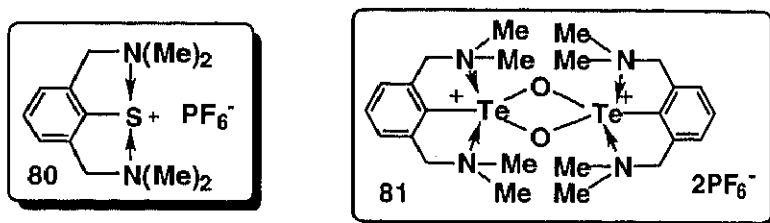

Figure 1-15

In Chapter 4, the "remote" oxidation of the tellurides is described. The word "remote" means that when the certain position of the molecule will be oxidized, the intramolecular electron shift will be caused through π-conjugated system and then the other position will be oxidized indirectly. The concept of the remote oxidation is illustrated in Figure 1-16.
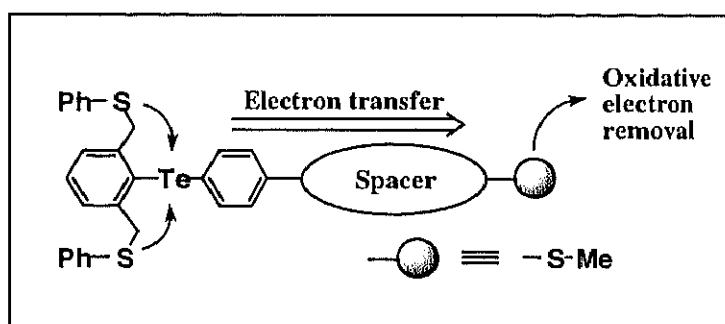
Figure 1-16

The telluride having methylsulfinyl group on treatment with trifluoromethanesulfonic anhydride gave the corresponding dicationic tellurane, quantitatively. These results indicate that the present reaction proceeds by the electron transfer through the benzene ring and the conformational change of methylthiophenyl group after the removal of oxygen on the sulfur atom. This reaction can be considered as the remote reaction for the synthesis of dicationic tellurane and may proceed via the dicationic species of quinone type (Scheme 1-24).

34
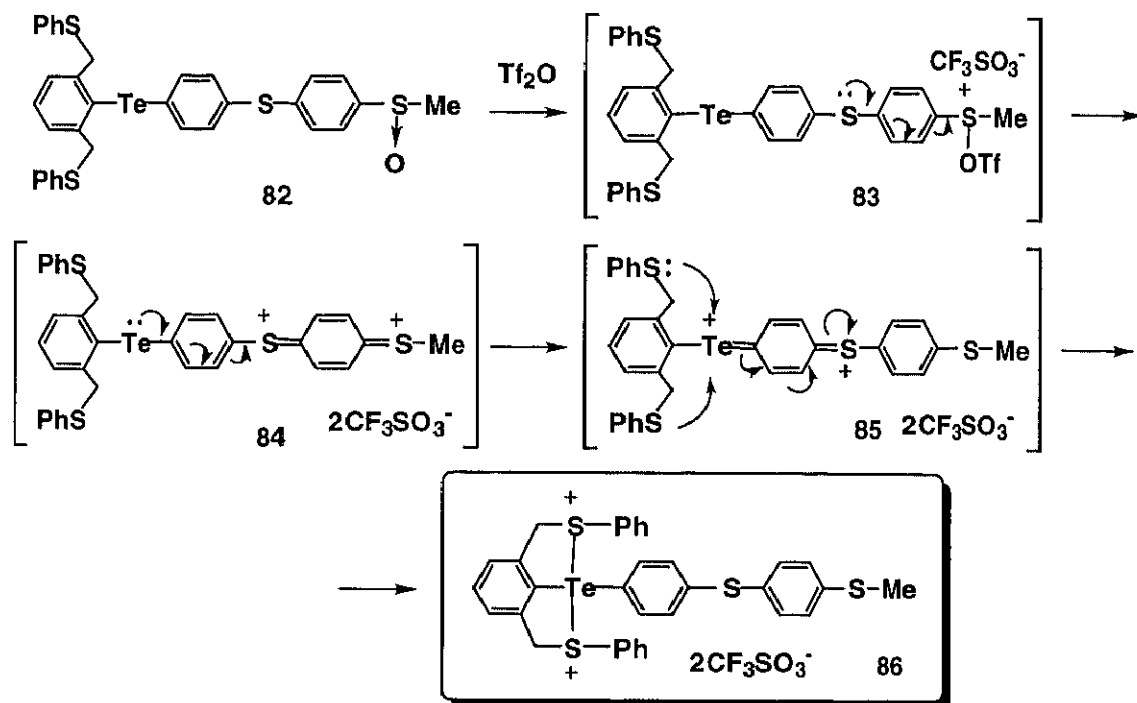
Scheme 1-24

In Chapter 5, the oxidation of the dichalcogenides having neighboring four sulfur atoms is described. The oxidation of the corresponding diaryl ditelluride gave the oxygen bridged dication, while the oxidation of the corresponding disulfide or the diselenide only gave the hyrdoxysulfonium salt or the hydroxyselenonium salt respectively (Scheme 1-25).

^{125}Te NMR δ 1265.8
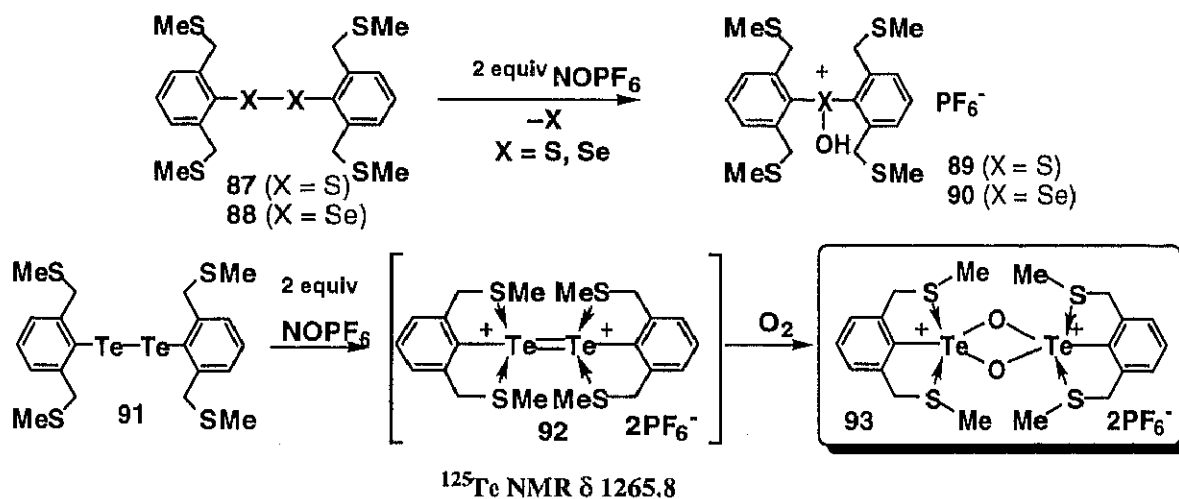
Scheme 1-25

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