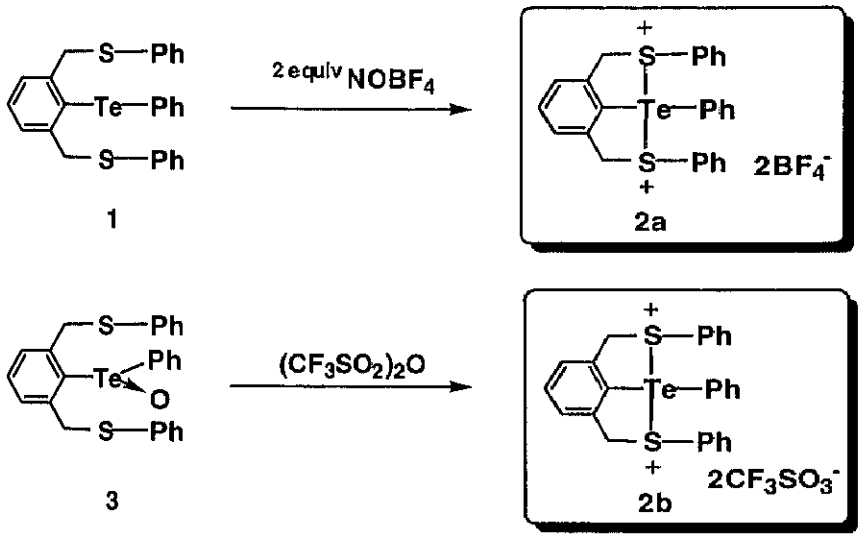
Chapter 4

Synthesis of Hypervalent Telluranes by Remote Oxidation through π–Conjugated System

CONTENTS

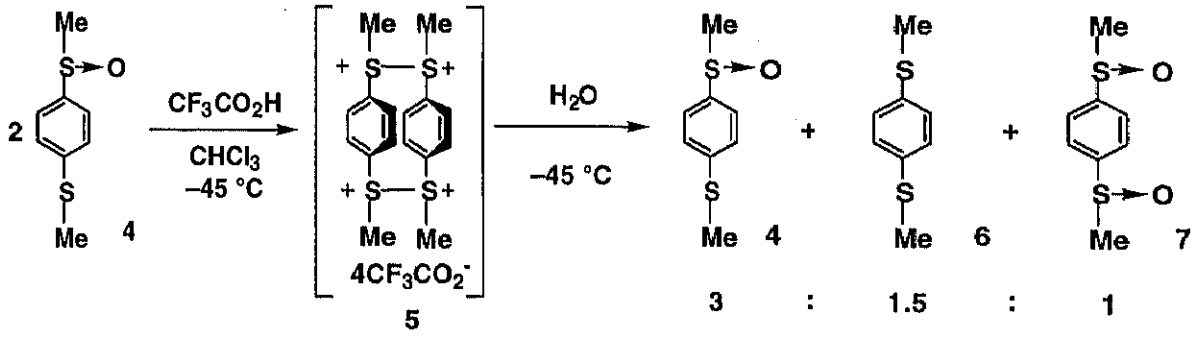
I. Introduction

Recently, some dicationic telluranes were synthesized by the reactions of tellurides or telluroxides having heteroatoms at the 2,6-positions on the benzene ring with oxidizing reagents such as $NOBF_4$ and $NOPF_6$, or $(CF_3SO_2)_2O$ as described in Chapter 2. In the case of these reactions, each central tellurium atom should be directly oxidized by oxidizing reagents to form the corresponding dicationic telluranes.[1)]



Scheme 4-1

Furthermore, it is reported that the remote oxygen migration occurred between the sulfur atoms in the monooxide of 1,4-bis(methylthio)benzene in the presence of CF_3CO_2H. This reaction has been proposed to proceed not *via* the corresponding quinoide type intermediate but *via* the bis(dithia dication) dimer.[2)]



Scheme 4-2

On the basis of these results, the author tried to react the tellurides connecting sulfinyl group at the 4-position of the tellurophenyl group with $(CF_3SO_2)_2O$ to obtain the corresponding dicationic telluranes. Apparently, the deoxygenation from the sulfinyl group is promoted by the

telluride group *via* the donation of electrons. Namely, the author proposes that this process proceeds via the new remote oxidation reaction involving electron transfer through π-conjugated bonds like the Domino effect. In this Chapter the synthesis and reaction mechanism of the dicationic telluranes obtained by the new remote oxidation reactions are described.

II. Remote Oxidation

The concept of the remote oxidation that proposed in this Chapter is quite new one. 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 remote position will be oxidized indirectly. The concept of the remote oxidation is illustrated in Figure 4-1.

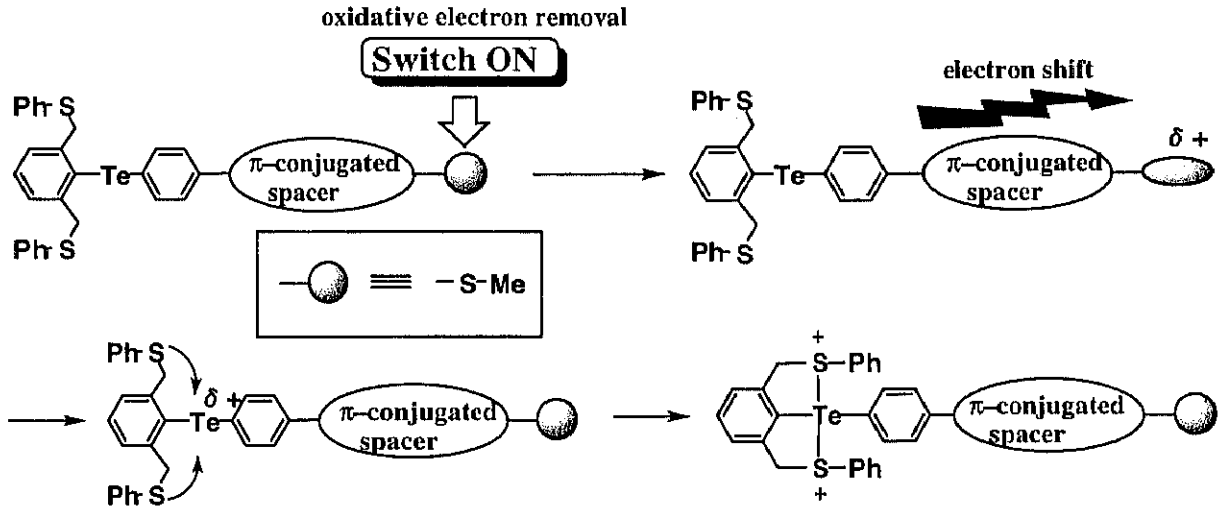
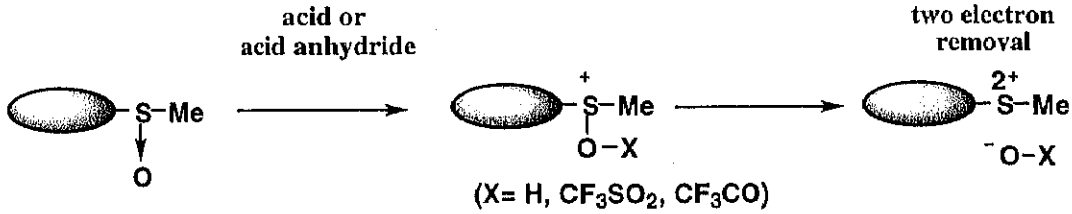


Figure 4-1

In order to oxidize the end of the molecules selectively, the following method was used. Sulfoxides are the oxidized species of sulfides, and they are known to be stable and easy to prepare. As shown in Scheme 4-3, acid or acid anhydrides react with sulfoxides to make deoxygenation. As a result, it is possible to remove two electrons from the sulfur atom. In this reaction, acid or acid anhydrides are used as initiators to make cationic sulfur atoms. This method was applied to produce various dication species as described in Chapter 1.



Scheme 4-3

III. Synthesis of the Tellurides

The tellurides, shown in Figure 4-2, were synthesized as substrates. There are three positions (A, B and C) possible to introduce the sulfinyl group to 2,6-bis[(phenylthio)methyl] phenyl phenyl telluride. However, for synthetic difficulty, the telluride introduced the sulfinyl group to the C position was not obtained in spite of many trials. The tellurium atom and the sulfinyl group are connected with π-conjugated spacer at the para position in the case of the tellurides **8** and **9**. The telluride **8** has a benzene spacer and the telluride **9** has a diphenyl sulfide spacer. It is possible to suppose many tellurides as substrates, in which the tellurium atom and the methylsulfinyl group should be connected with a π-conjugated spacer such as thiophene, 4-phenyleneethynyene, 4-phenylene and so on. However it is difficult to introduce these π-conjugated spacers into the telluride, so many proposed substrates could not be synthesized.

In order to confirm the necessity of the π-conjugated spacer, the telluride **11**, having no π-conjugated spacer between the tellurium atom and the sulfinyl group, was also synthesized. Furthermore the telluride **10** introduced methylsulfinyl group to the B position was also synthesized.

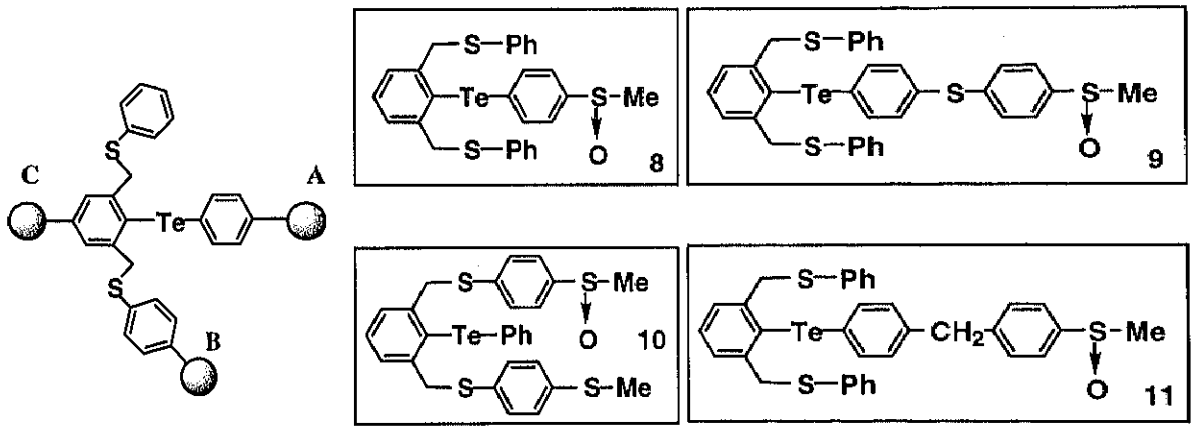
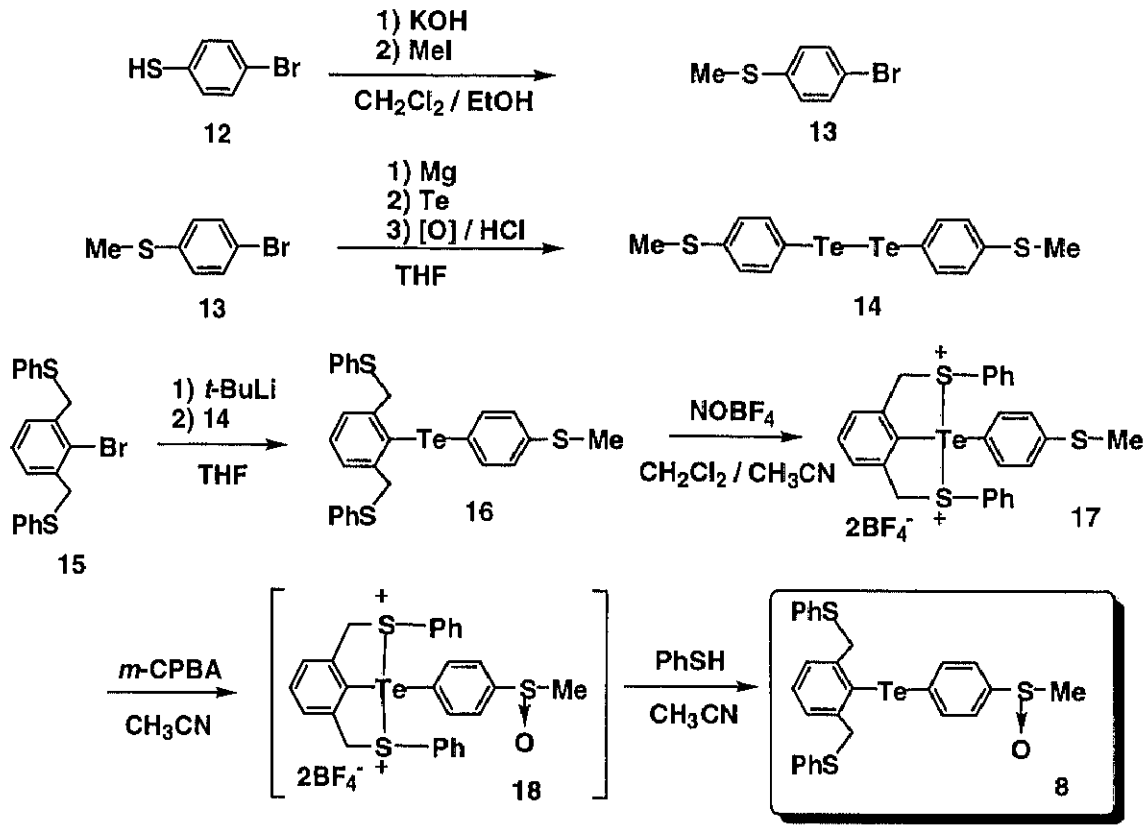


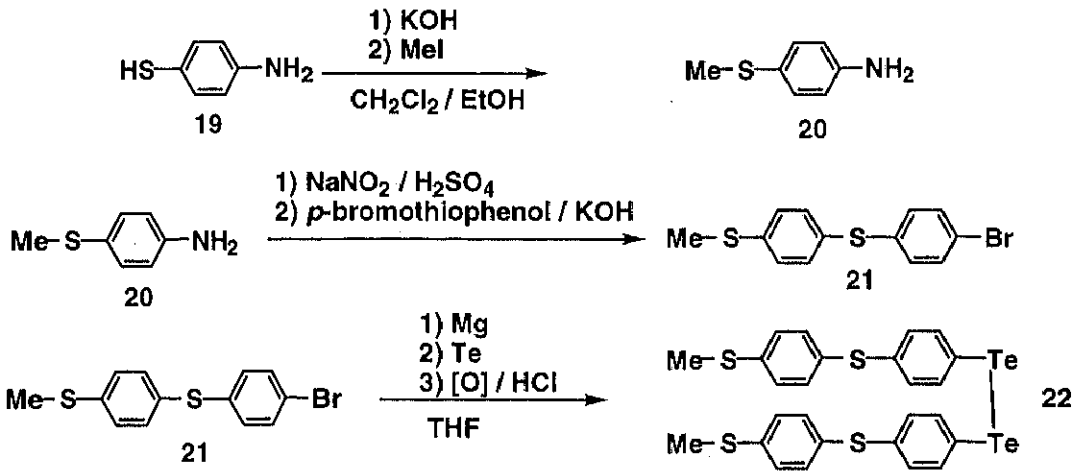
Figure 4-2

At first, the synthesis of 2,6-bis[(phenylthio)methyl]phenyl (4-methylsulfinyl)phenyl telluride **8** is shown in Scheme 4-4. Bis(4-methylthiophenyl) ditelluride **14** was synthesized from 4-bromo-methylthiobenzene **13** and then converted to 2,6-bis[(phenylthio)methyl]phenyl (4-methylthio)phenyl telluride **16**. Since 2,6-bis[(phenylthio)methyl]phenyl (4-methylthio) phenyl telluride **16** has four chalcogen atoms which are susceptible to oxidation, it is difficult to selectively oxidize only the sulfur atom of the methylthio group. Therefore, it was initially converted to the corresponding dicationic tellurane **17**, which was then treated with *m*-CPBA in order to oxidize the sulfur atom of the methylthio group to form **18**. The telluride **8** was obtained from the reduction of the dicationic tellurane **18** by adding two equivalents of thiophenol.



Scheme 4-4

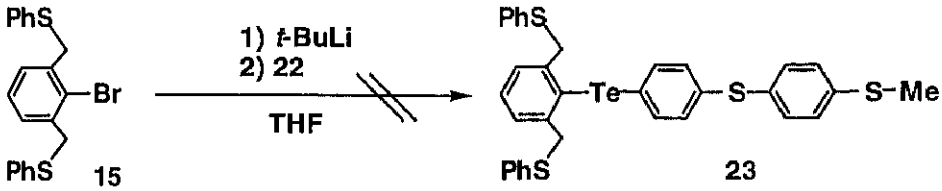
As a precursor of the telluride **9**, having the extended π-conjugated system, the ditelluride **22** was synthesized by the method shown in Scheme 4-5. The corresponding bromobenzene **21** was prepared from 4-methylthioaniline **20** and then converted to the ditelluride **22**.

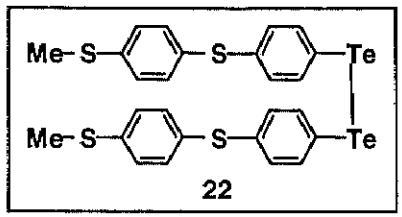


Scheme 4-5

The ditelluride **22** was treated with 2,6-bis[(phenylthio)methyl]-1-lithiobenzene to prepare

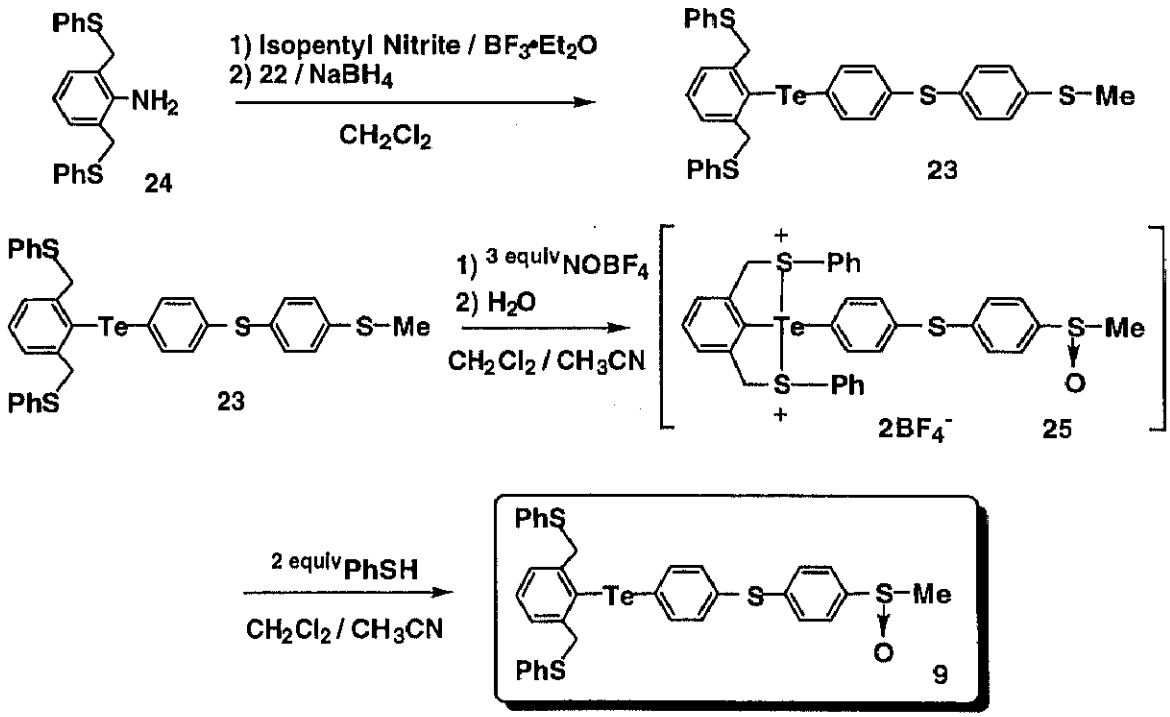
the telluride **23**. However only complex mixture was obtained, and the telluride **23** was produced. The reason of this result is not obvious but it is supposed to depend on the bulk of the ditelluride **22**.





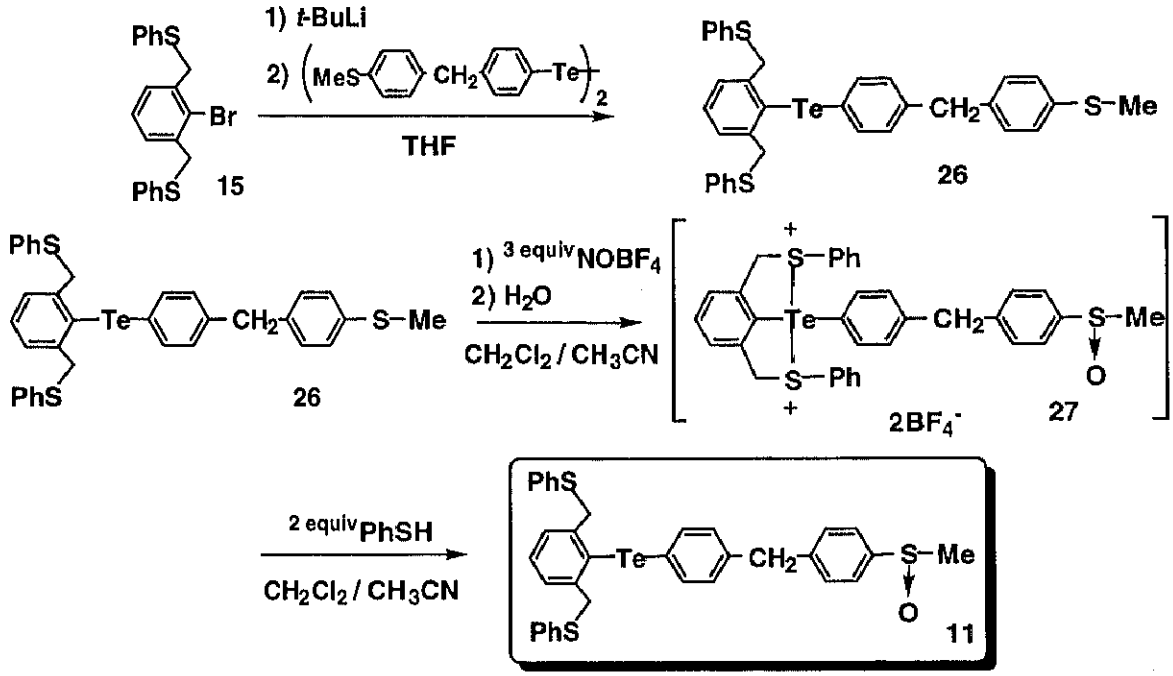
Scheme 4-6

Then the synthetic strategy was changed to the following method. Reduction of the ditelluride **22** with $NaBH_4$ gave the corresponding tellurolate ion, which was treated with 2,6-bis[(phenylthio)methyl]-1-diazobenzene to give the telluride **23** by nucleophilic attack of the tellurium atom. However, the yield of the reaction was 1%.

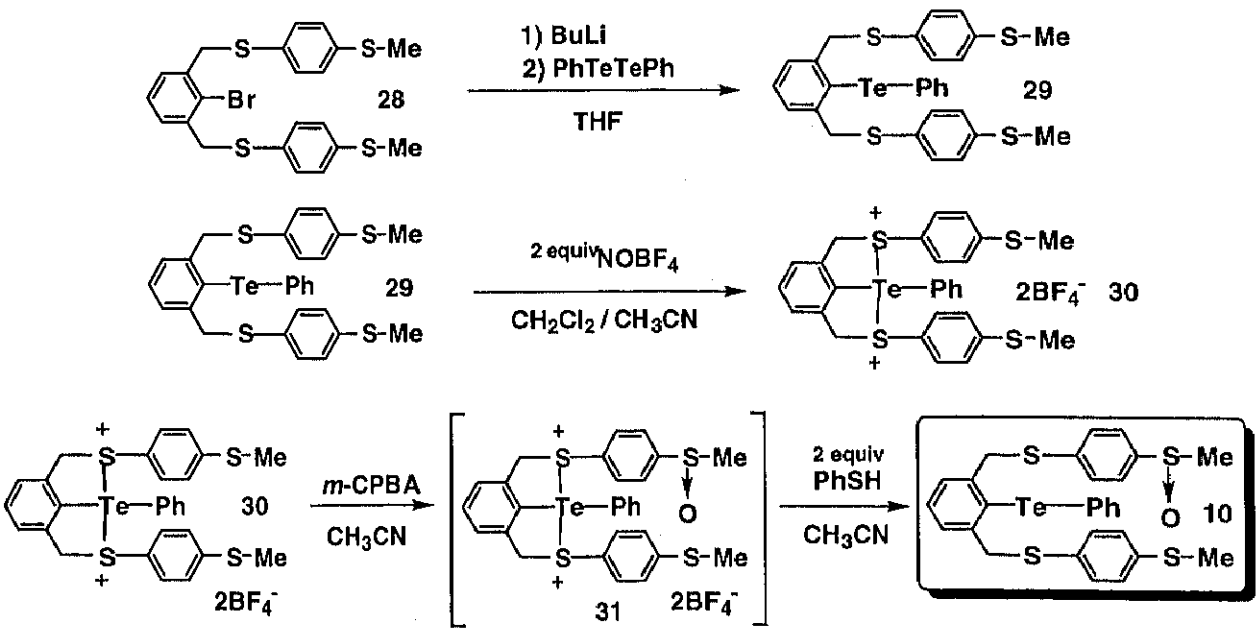


Scheme 4-7

The telluride **23** was directly oxidized to the dicationic tellurane **25** having methylsulfinyl group by adding three equivalents of $NOBF_4$. This dicationic tellurane **25** was converted to the telluride **9** by reduction of the tellurium atom with thiophenol. And the tellurides **10** and **11** were also synthesized by the method shown in Scheme 4-8 and 4-9 respectively.



Scheme 4-8



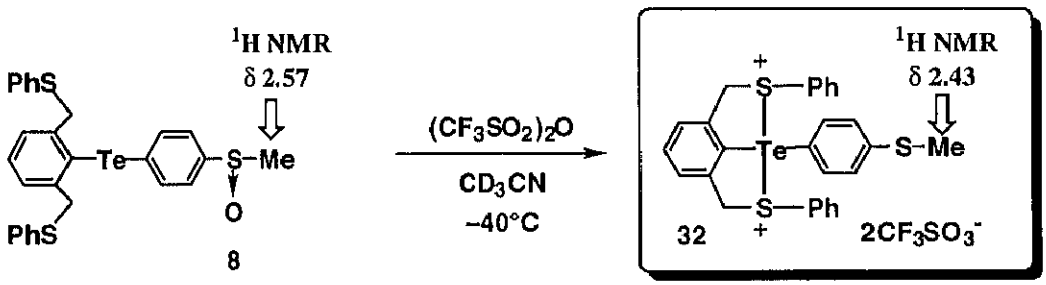
Scheme 4-9

IV. Synthesis of the Dicationic Telluranes by Remote Oxidation

In order to initiate the remote oxidation, it is necessary to add an acid or an acid anhydride to the solution of the tellurides having methylsulfinyl group. As initiating reagents, triflic anhydride (Tf_2O) or triflic acid was used in the reaction.

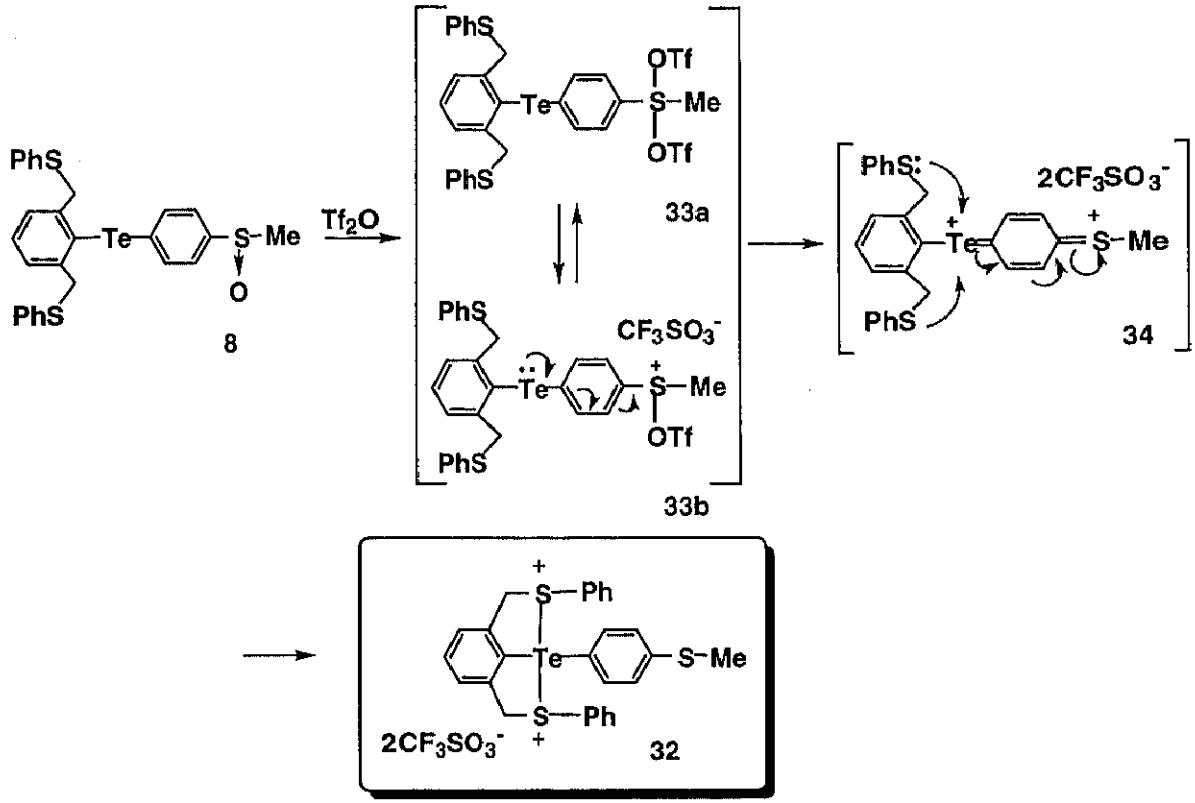
Treatment of the telluride **8** with 1.2 equimolar amount of Tf_2O at –40 °C in CD_3CN afforded readily the corresponding stable dicationic tellurane **32** (Scheme 4-10). The reaction was carried out in an NMR tube and monitored by ^1H NMR. By adding Tf_2O to the solution of the telluride, the color of the solution changed from colorless to wine red immediately. The ^1H NMR spectrum of the solution showed that of the dicationic tellurane **32**. This reaction proceeded quantitatively without any by-product.

The dicationic tellurane **32** was characterized by elemental and spectroscopic (EIMS, ^1H, ^{13}C and ^{125}Te NMR) analyses. The ^1H NMR spectrum of the dicationic tellurane **32** exhibits the benzylic methylene protons as two sets of AB quartet signals at δ 4.42, 5.26 (J = 18 Hz) and 4.90, 5.24 (J = 17 Hz) in a 1 : 1 ratio, respectively. These signals were assigned to the asymmetric bicyclic form of the dicationic tellurane as described in Chapter 1. These results demonstrate that the two sulfur atoms are directly coordinated to the central tellurium atom. The ^1H NMR signals of methyl protons are shifted up field from δ 2.57 to 2.43 by adding Tf_2O. This indicates that the sulfur atom of the methylsulfinyl group is reduced to form the methylthio group. The ^{125}Te signal of **32** appeared at δ 1343 which is similar to that of the corresponding dicationic tellurane **1b** (δ1331) without a 4-thiomethyl group.



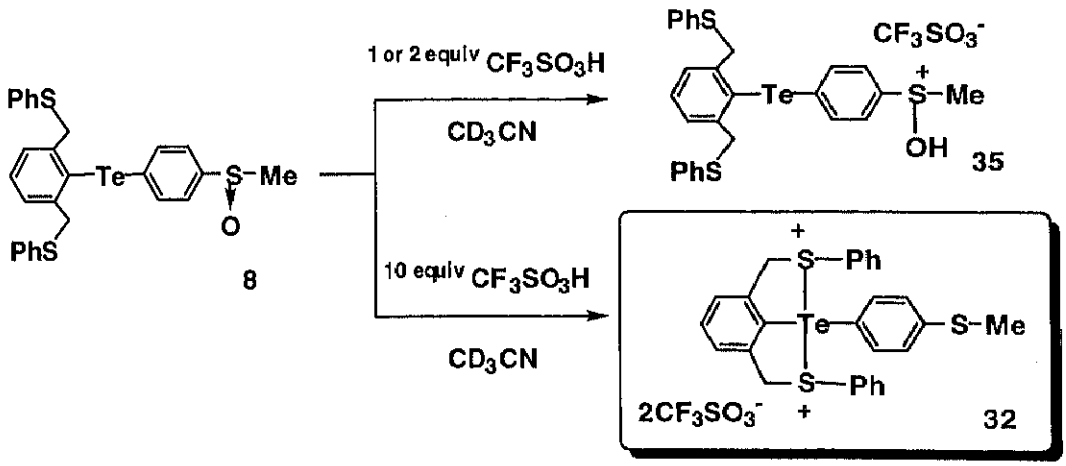
Scheme 4-10

This reaction is considered to proceed via the mechanism shown in Scheme 4-11. The mechanism for the present reaction may proceed initially by the formation of the sulfonium salt **33a** or the sulfurane **33b** followed by the reaction with Tf_2O. Subsequently the corresponding dicationic compound **32** should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic intermediate of the quinoide type **34**, formed by the electron transfer from the tellurium atom to the sulfur atom in the methylsulfinyl group. However the reaction was too fast to detect the estimated intermediates **33a**, **33b** and **34** by ^1H, ^{13}C or ^{125}Te NMR.



Scheme 4-11

Triflic acid (TfOH) was also treated with the telluride **8** to form the dicationic tellurane (Scheme 4-12). When 1 or 2 equimolar amount of triflic acid was added to the solution of the telluride **8**, only hydroxysulfonium salt **35** was formed and further reaction did not occurr. However the dicationic tellurane **32** was obtained in the case that 10 equivalents of triflic acid, namely excess amount to the substrate, was used. This result means that protonation of water, which should be formed from the reaction, is important to prevent the reverse reaction.



Scheme 4-12

The change of the ^{1}H NMR spectrum is shown in Figure 4-3. In the ^{1}H NMR spectrum just after adding 10 equivalents TfOH, two singlet peaks, which were assigned to one methyl and one benzyl group, were observed. It should be mentioned that the singlet peak of the methyl group was shifted down field from δ 2.57 to 3.31 by adding TfOH, because the oxygen atom of the sulfoxide was protonated. After 6 hours, the ^{1}H NMR spectrum changed to the complex pattern, suggesting that this reaction should have some intermediates. This reaction was completed after 2 days and the ^{1}H NMR spectrum only showed that of the dicationic tellurane **32**. In the ^{1}H NMR spectrum of the dicationic tellurane **32**, the singlet peak of the methyl group is shifted up-field to δ 2.43 compared with that of the telluride **8** (δ 2.57). This indicates the notion that the sulfur atom of the methylsulfinyl group is reduced to form the methylthio group.

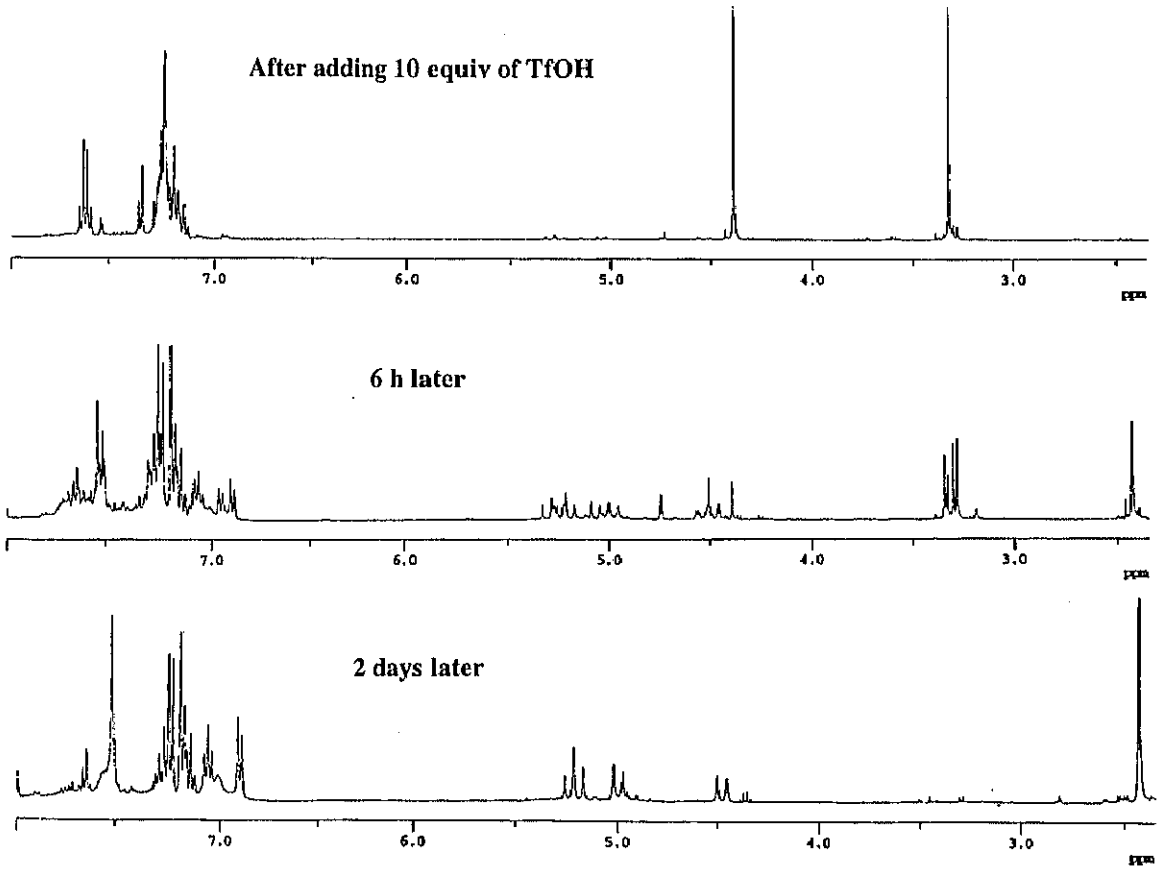
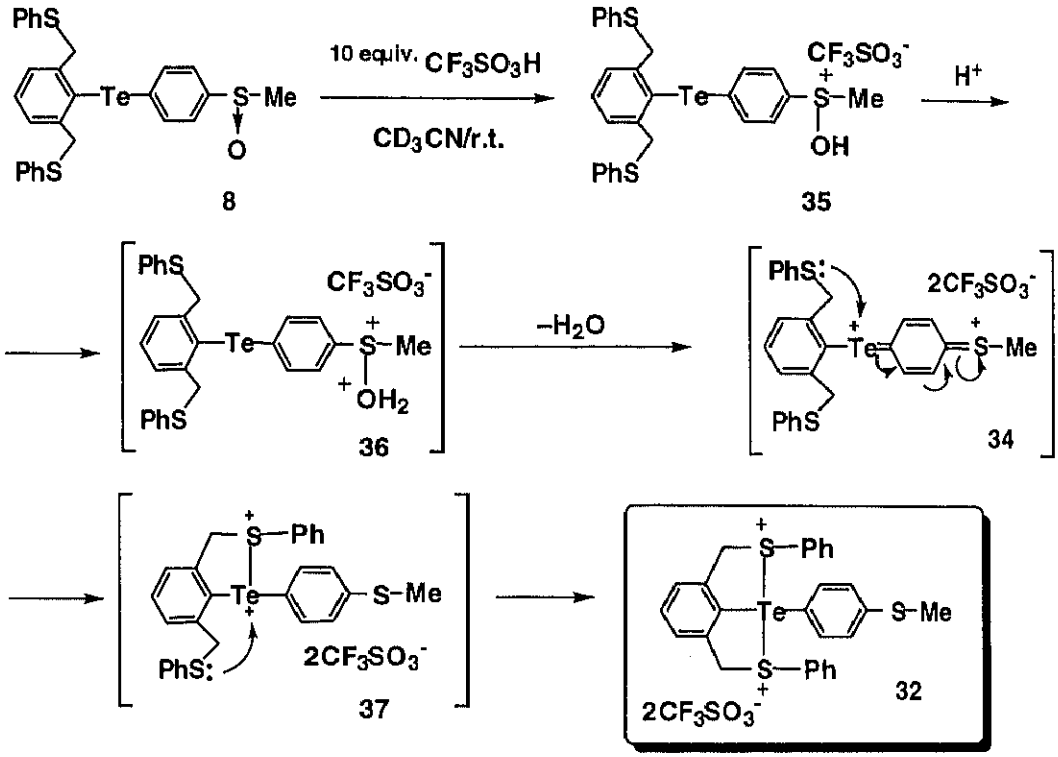


Figure 4-3

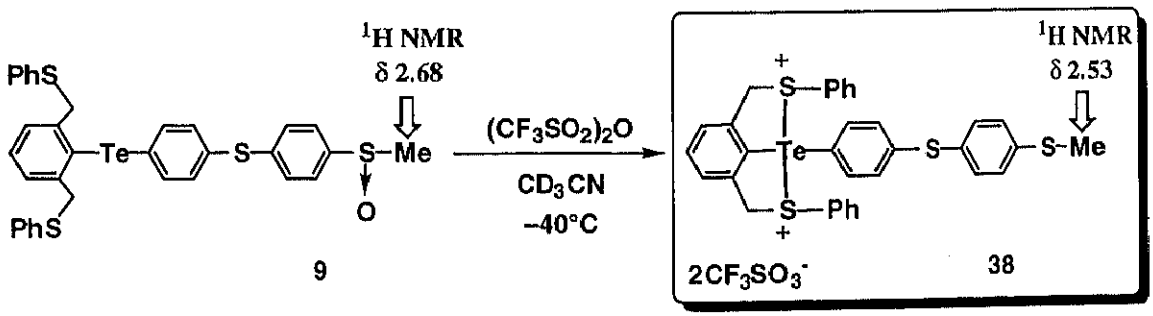
This reaction is predicted to proceed via the mechanism shown in Scheme 4-13. It is considered to be unmeasurably fast reaction in which the oxygen atom of the methylsulfinyl was protonated to form hydroxysulfonium salt **35** and this reaction was followed by ^{1}H NMR signal of the methyl protons. Subsequently the corresponding dicationic compound **32** should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic intermediate of the quinoide type **34**, formed by the electron transfer from the tellurium atom to

the sulfur atom in the methylsulfinyl group. However the ^{1}H NMR spectrum is too complicated to identify the structure of the intermediate although it is obvious that the reaction has two or three intermediates.



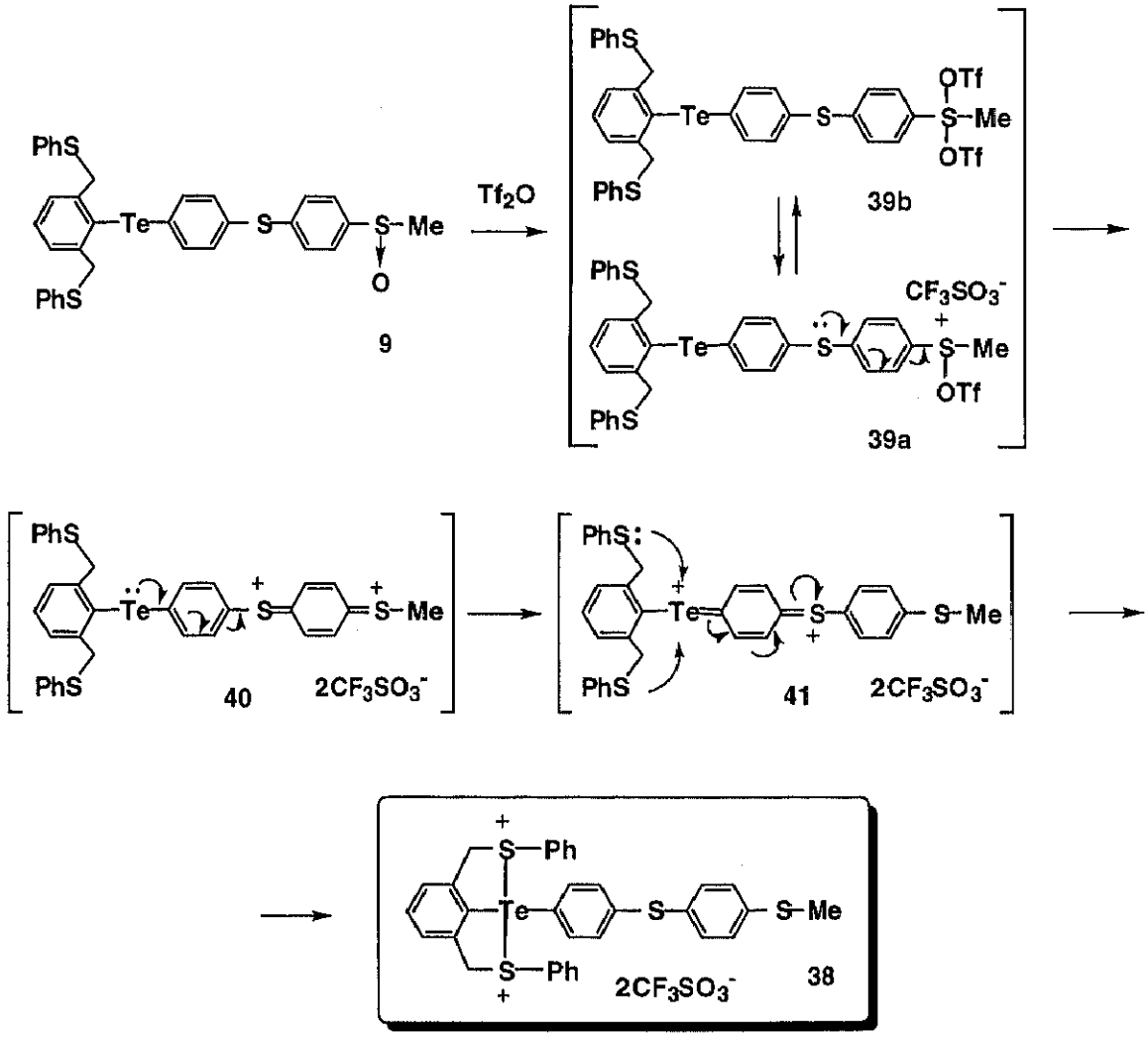
Scheme 4-13

The telluride **9**, having the extended π-conjugated system, was also reacted with Tf_2O to give the corresponding dicationic tellurane **38** with the reduced methylthio group (Scheme 4-14). The reaction was carried out in an NMR tube and monitored by ^{1}H NMR. By adding Tf_2O to the solution of the telluride **13**, the color of the solution changed from colorless to wine red immediately. The ^{1}H NMR spectrum of the solution showed that of the dicationic tellurane **38**. This reaction proceeded quantitatively without any by-product.



Scheme 4-14

The structure of this dicationic tellurane **38** was assigned by EIMS, ^{1}H, ^{13}C and ^{125}Te NMR. The ^{1}H NMR spectrum of the dicationic tellurane **38** also shows two sets of AB quartet signals shifted down-field compared with those of the telluride **9**. The ^{1}H NMR signals of methyl protons are shifted up-field from δ 2.68 to 2.53 by adding Tf_2O as the case of the telluride **8**. This indicates the notion that the sulfur atom of the methylsulfinyl group is reduced to form the methylthio group. And the ^{125}Te NMR signal of **38** was observed at δ 1339.7.

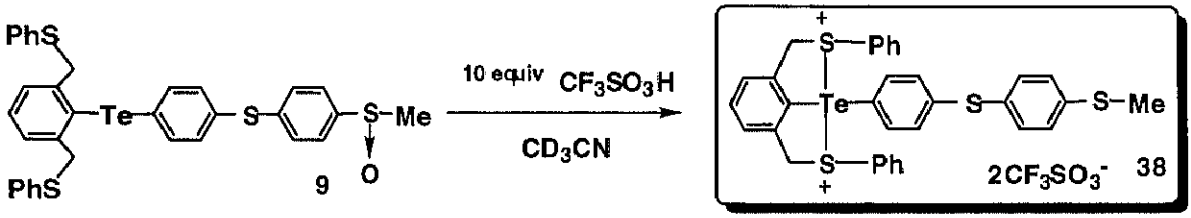


Scheme 4-15

The mechanism for the reaction may proceed initially by the formation of the sulfonium salt **39a** or the sulfurane **39b** followed by the reaction with Tf_2O. As shown in Scheme 4-15, the electrons shift from the tellurium atom to the sulfur atom of the methylsulfinyl group through an intramolecular π-conjugation in the benzene rings and the sulfur atom. Subsequently the corresponding dicationic compound **38** should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic intermediate of the quinoide types **40** and **41**,

formed by the electron transfer from the tellurium atom to the sulfur atom in the methylsulfinyl group. This sulfur atom is important to connect the π-conjugated system from the tellurium atom to the sulfur atom of the methylsulfinyl group. This reaction was too fast to detect the estimated intermediates **39a**, **39b**, **40** and **41** by ^{1}H, ^{13}C or ^{125}Te NMR.

The telluride **9** was also treated with 10 equimolar amounts of TfOH to produce the corresponding dicationic tellurane **38**. The reaction was carried out in an NMR tube and monitored by ^{1}H NMR. By adding TfOH to the CD_3CN solution of the telluride **9**, the ^{1}H NMR spectrum of the solution showed that of the hydroxysulfonium salt immediately. Subsequently the ^{1}H NMR spectrum changed to that of the corresponding dicationic tellurane **38** after one week at room temperature. In the ^{1}H NMR spectrum of the reaction mixture, at least three intermediates were observed before completing the reactions. However the structures of those intermediates were not identified yet.



Scheme 4-16

The change of the ^{1}H NMR spectrum is shown in Figure 4-4. In the ^{1}H NMR spectrum just after adding 10 equivalents TfOH, two singlet peaks, assigned to one methyl and one benzyl group, were observed. It should be mentioned that the singlet peak of the methyl group was shifted down field from δ 2.68 to 3.32 by adding TfOH, because the oxygen atom of the sulfoxide was protonated to produce the hydroxysulfonium salt. After 9 hours, the ^{1}H NMR spectrum changed to the complex pattern, which suggests that this reaction has some intermediates. This reaction was completed after one week and the ^{1}H NMR spectrum only showed that of the dicationic tellurane **38**. In the ^{1}H NMR spectrum, the singlet peak of the methyl group was shifted up field to δ 2.43. This indicates that the sulfur atom of the methylsulfinyl group is reduced to form the methylthio group.

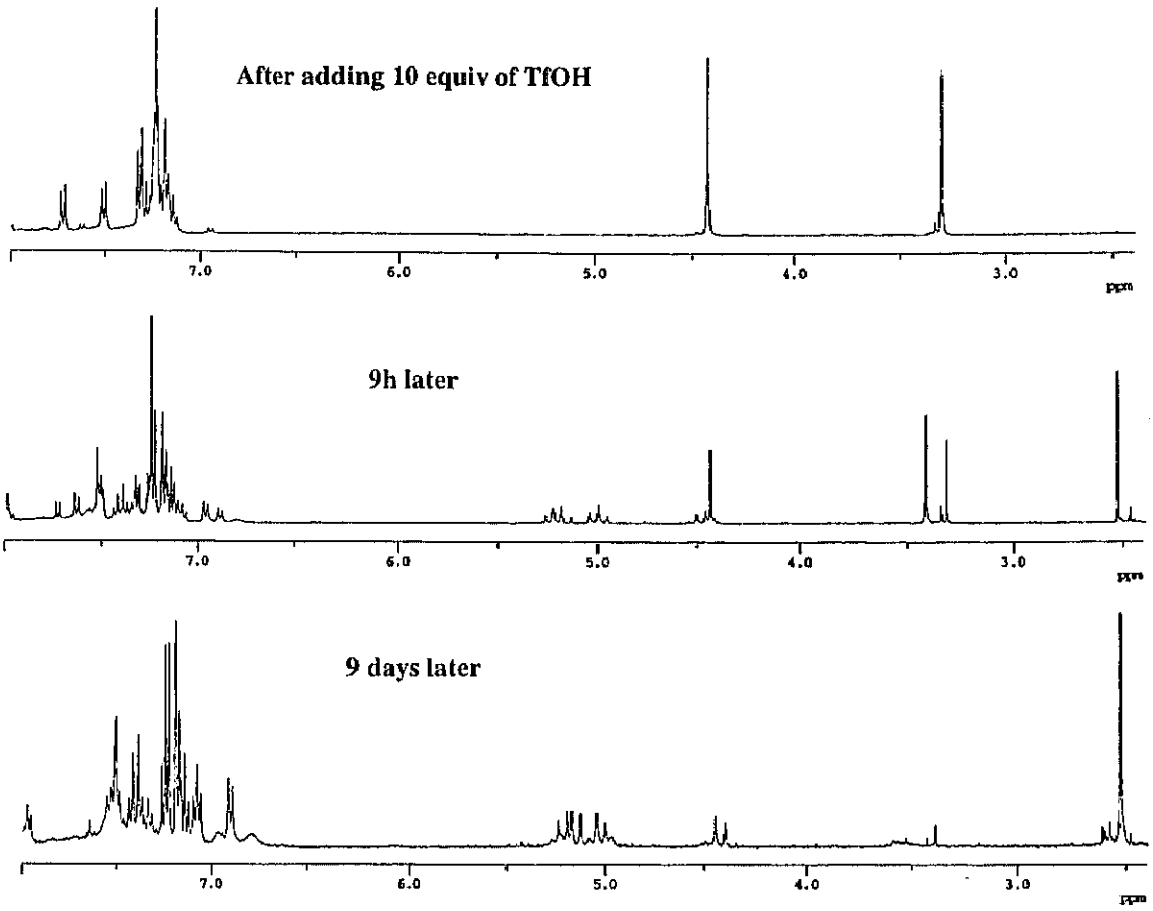
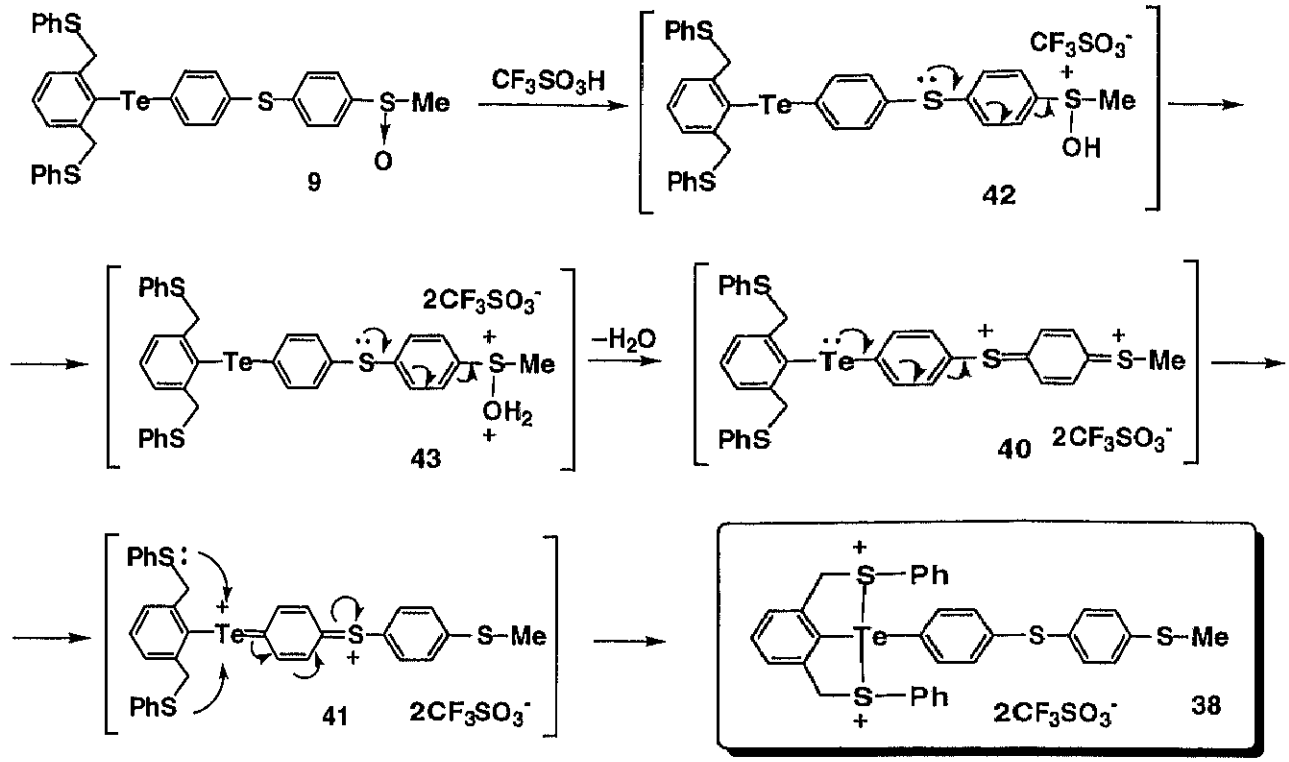


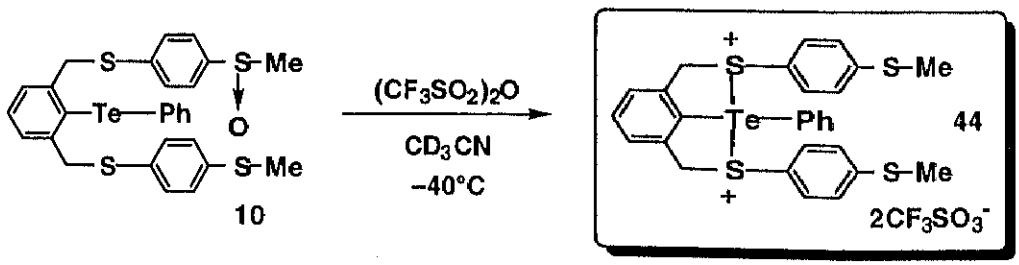
Figure 4-4

This reaction is predicted to proceed via the mechanism shown in Scheme 4-17. It is considered to be the fast reaction that the oxygen atom of the methylsulfinyl group should be protonated to form hydroxysulfonium salt **42** and this reaction has been followed by the ^{1}H NMR signal of the methyl protons. The next step should be the protonation of the hydroxysulfonium salt **42** and this step is considered to be slow. These double protonation of the oxygen atom of the sulfinyl group would make the facile sulfur-oxygen bond cleavage due to the elimination of a water molecule. Subsequently the corresponding dicationic compound **38** should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic intermediate of the quinoide types **40** and **41**, formed by the electron transfer from the tellurium atom to the sulfur atom through π-conjugated diphenyl sulfide spacer. In the end, the dicationic tellurane **38** was produced quantitatively without any by-product. It is obvious that this reaction has two or three intermediates by monitoring the ^{1}H NMR spectrum. However the ^{1}H NMR spectrum is too complicated to be identified the structures of the intermediates.



Scheme 4-17

The telluride **10** was also treated with Tf_2O to produce the corresponding dicationic tellurane **44** with the reduced methylthio group (Scheme 4-18). The reaction was carried out in an NMR tube and monitored by ^1H NMR. By adding Tf_2O to the solution of the telluride, the color of the solution changed from colorless to wine red immediately. The ^1H NMR spectrum of the solution showed that of the dicationic tellurane **44**. This reaction also proceeded quantitatively without any by-product.



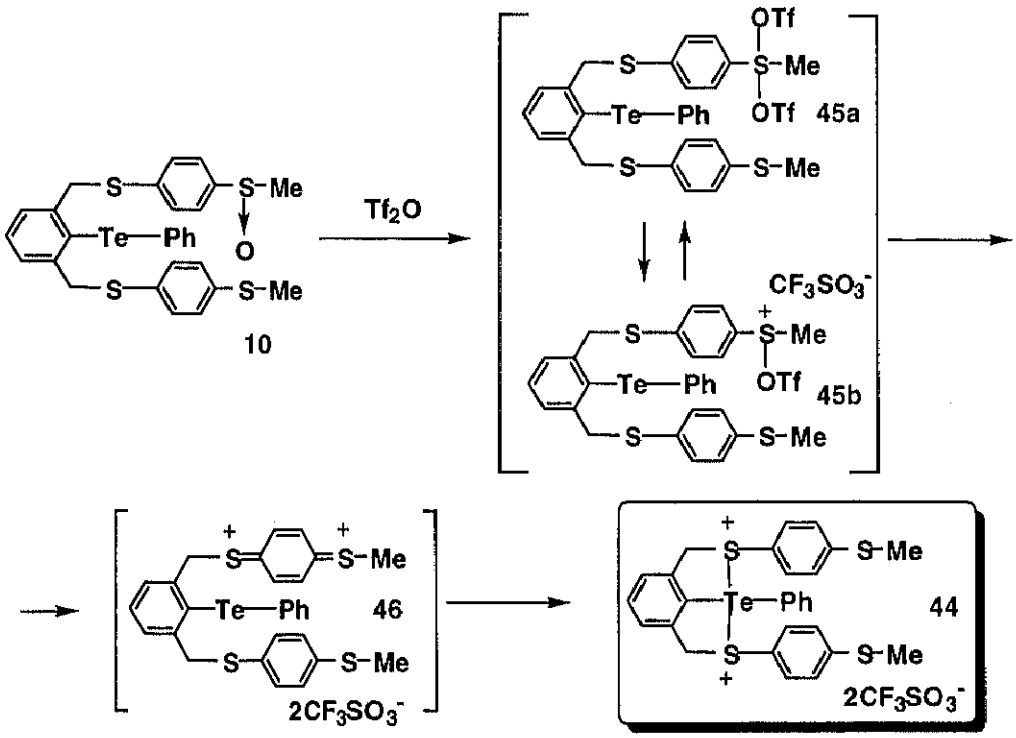
Scheme 4-18

In the structure of the telluride **10**, the methylsulfinyl group does not connect to the tellurium atom by a π-conjugated spacer. However the product of the reaction is the dicationic tellurane **44** with the reduced methylthio group as the case of the telluride **8** or **9**, in which the methylsulfinyl group directly connects to the central tellurium atom by a π-conjugated spacer. This result indicates the notion that the remote oxidation does not depend on the position of the

methylsulfinyl group.

The structure of the dicationic tellurane **44** was characterized by EIMS, ^{1}H, ^{13}C and ^{125}Te NMR. In the ^{1}H NMR of the dicationic tellurane **44**, two singlet peaks were observed at δ 2.38 to 2.47 in a 1 : 1 ratio. These signals are assigned to the two sets of the methylthio groups because the sulfinyl methyl protons were observed at δ 2.73 in the ^{1}H NMR spectrum of the telluride **10**. And these two sets of the methylthio protons indicate the notion that the dicationic tellurane **44** exists as an either *trans-cis* or *cis–trans* configuration, in which the two methylthio groups are nonequivalent. The ^{125}Te NMR signal of **16** was observed at δ 1330.7.

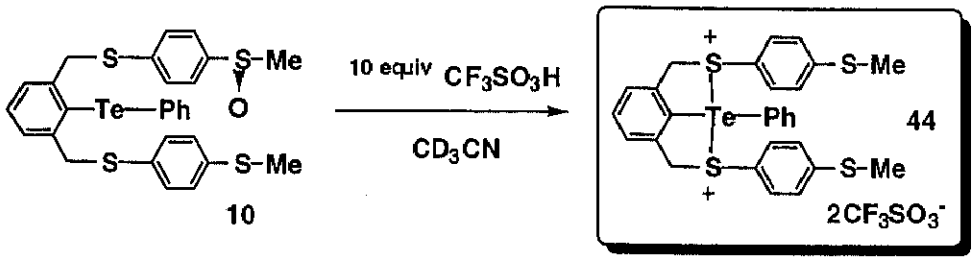
The mechanism of the reaction is predicted as shown in Scheme 4-19. It is a similar reaction mechanism as the case of the telluride **8** or **9** with Tf_2O, in which the quinoide type intermediate should be produced. However the electrons must shift from the central tellurium atom to the sulfur atom at the 2 or 6-benzylic position to make a σ-bond between them, because the methylsulfinyl group does not connect to the tellurium atom by a π-conjugated spacer. Finally the dicationic tellurane **44** should be produced by the formation of the 3c-4e bond (+S–Te–S+ bond).



Scheme 4-19

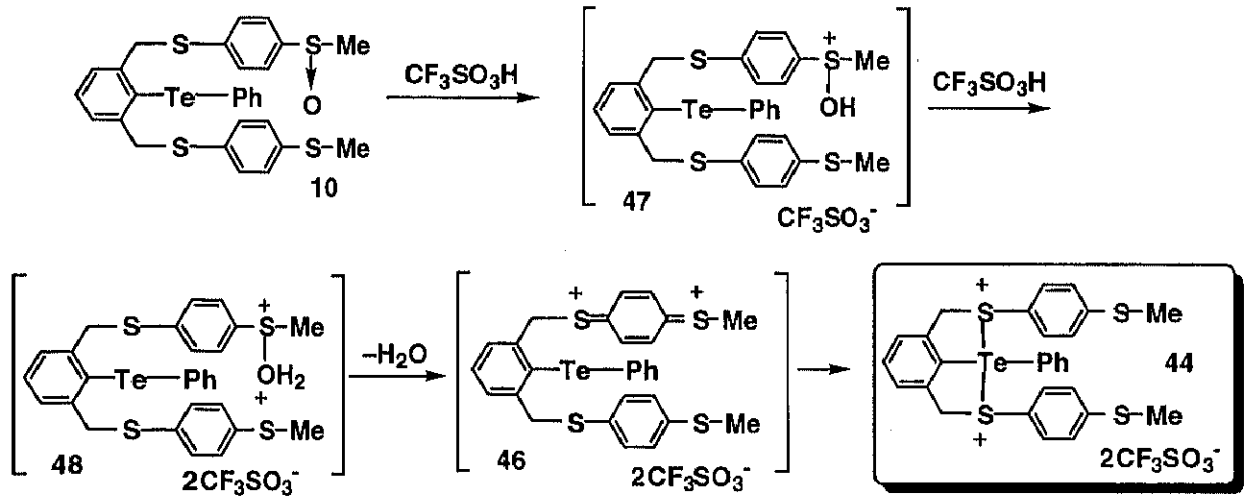
The reaction of the telluride **10** with 10 equimolar amounts of TfOH also gave the corresponding dicationic tellurane **44**. The reaction was also carried out in an NMR tube and monitored by ^{1}H NMR. By adding TfOH to the solution of the telluride, the color of the solution changed from colorless to wine red immediately. Only complex and broad signals

were observed in the ^{1}H NMR spectrum of the reaction mixture when it was observed at few hours later. However the ^{1}H NMR spectrum changed to those of the dicationic tellurane **44** after two days at room temperature. This reaction also proceeded quantitatively without any by-product.



Scheme 4-21

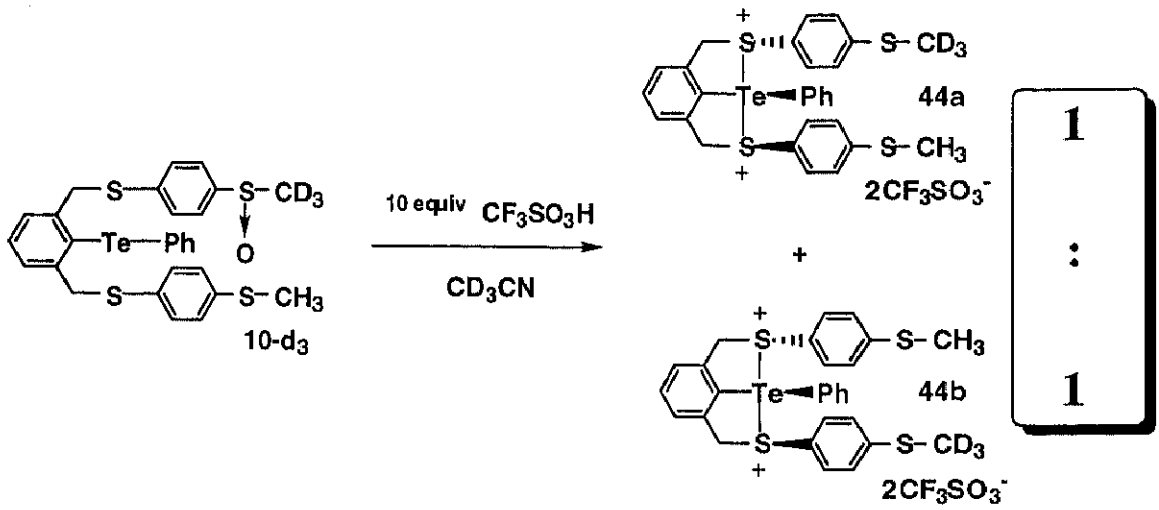
The mechanism of this reaction is predicted as shown in Scheme 4-22. Fundamentally this reaction mechanism is similar to that of the reaction using Tf_2O. However the double protonation of the oxygen atom of the sulfinyl group seemed to be difficult and slow, which makes the reaction slower compared with the case using Tf_2O.



Scheme 4-22

In order to investigate the mechanism of the reaction, deuterium-labeled experiment was carried out as shown in Scheme 4-23. The deuterium-labeled telluride **10-d$_3$** was treated with 10 equimolar amount of TfOH to produce the corresponding dicationic tellurane **44**. It was appeared that two stereoisomers of the dicationic tellurane, **44a** and **44b**, were obtained from the reaction. However it is difficult to prove that this result depends on the reaction mechanism, because it is possible to estimate an equilibrium between the two stereoisomers. Anyway it is

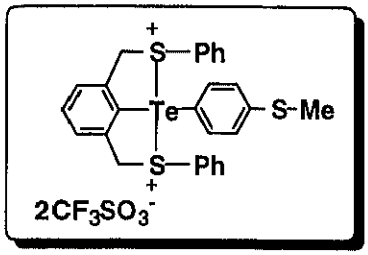
obvious that the conformation of the product does not depend on the position of the methyl sulfinyl group.

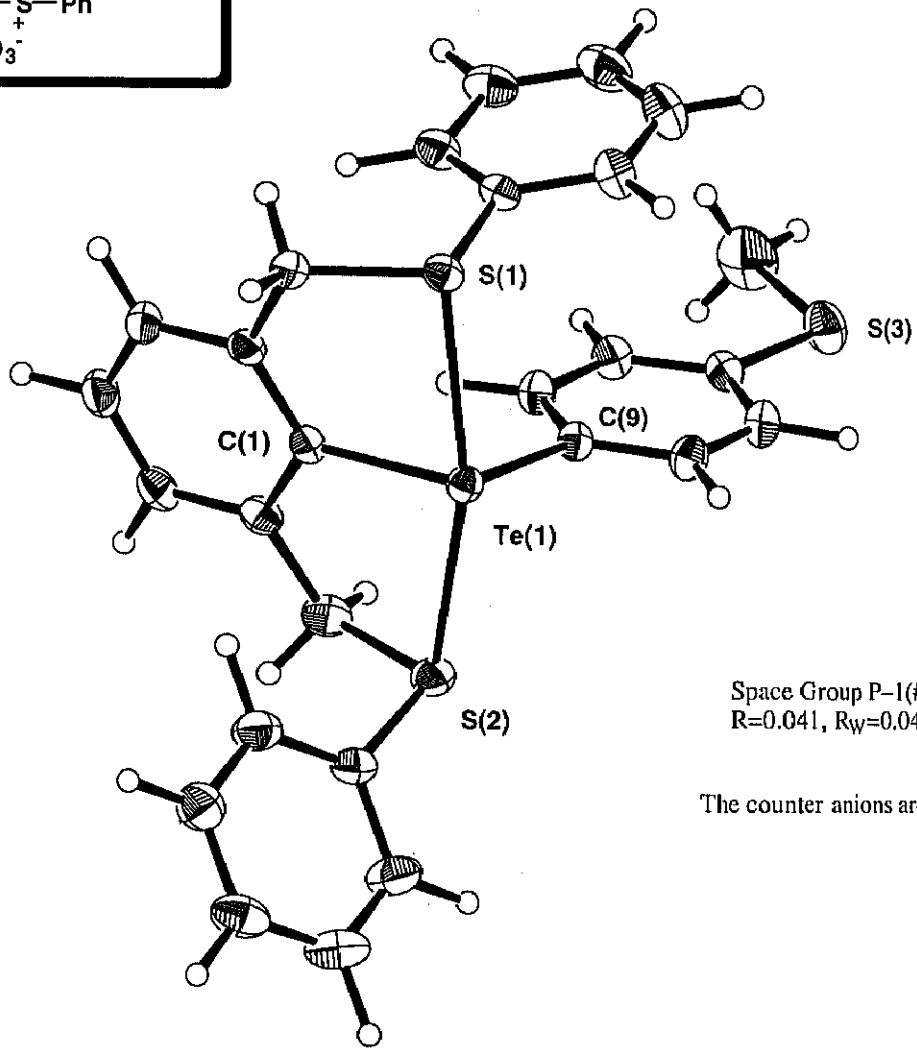


Scheme 4-23

V. X-ray Crystallographic Analysis of the Dicationic Tellurane (32)

Finally, the structure of the dicationic tellurane **32** was determined by X-ray analysis. An ORTEP view of the dicationic tellurane **32** is shown in Figure 4-5. The dicationic tellurane **32** posseses only one configurational form, namely, the three aryl groups on the chalcogen atoms which form the hypervalent bonding system, arrange in a *trans-cis* configuration similar to the dicationic telluranes **2a** and **2b**. Interestingly the *cis* oriented phenyl groups are arranged almost parallel each other and the distance between them is 3.24-3.98 Å, which is smaller than that of **2a** (3.25-4.28 Å). This fact indicates the notion that the π-π stacking should be stronger because of the electron-donating methylthio group. In addition, the respective bond lengths Te(1)–S(1) (2.637(1)) and Te(1)–S(2) (2.730(1)) are nearly identical to those of the dicationic telluranes, **1a** and **1b**.





Space Group P-1(#2)
R=0.041, R_W=0.044.

The counter anions are omitted.

Bond Distances (Å)

S(1)-Te(1) 2.637(1)
S(2)-Te(1) 2.730(1)

Bond Angles (deg)

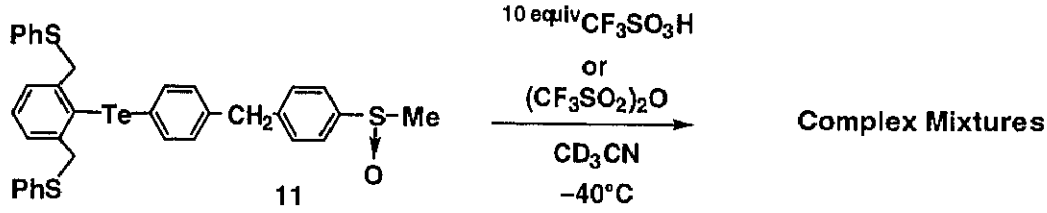
S(1)-Te(1)-S(2)	168.54(9)
S(1)-Te(1)-C(1)	81.3(1)
S(1)-Te(1)-C(9)	92.8(1)
S(2)-Te(1)-C(1)	80.0(1)
S(2)-Te(1)-C(9)	84.8(1)

Figure 4-5

VI. Further Investigation on the Reaction Mechanism of the Remote Oxidation

A. Necessity of π-Conjugated Spacer

In order to investigate the mechanism of the remote oxidation, the telluride **11**, having no π-conjugated system between the tellurium atom and the sulfinyl group, was treated with Tf_2O or TfOH. As the result of the each reactions, only complex mixtures were obtained and no dicationic tellurane was observed (Scheme 4-24), although the direct oxidation of telluride **26** with $NOBF_4$ produced the corresponding dicationic tellurane.



Scheme 4-24

This result supports the notion that the π-conjugated system is necessary to shift the electrons from the tellurium atom to the sulfur atom in the sulfinyl group and also rules out the intermolecular electron shift between the two molecules (Figure 4-6).

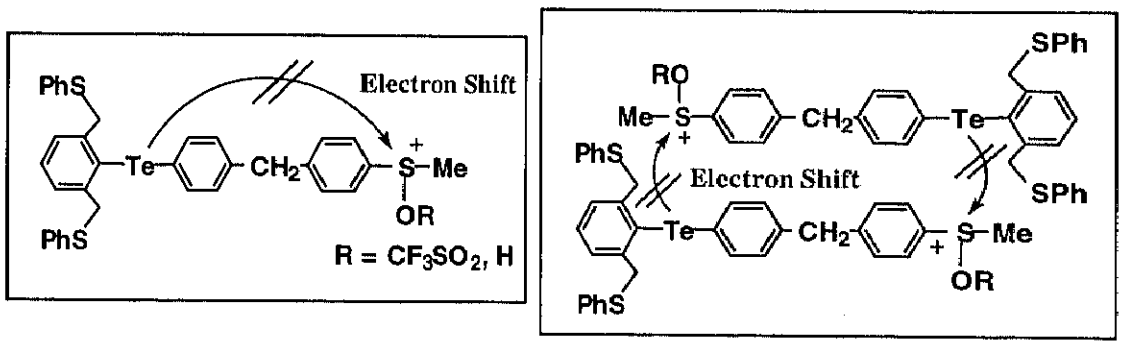
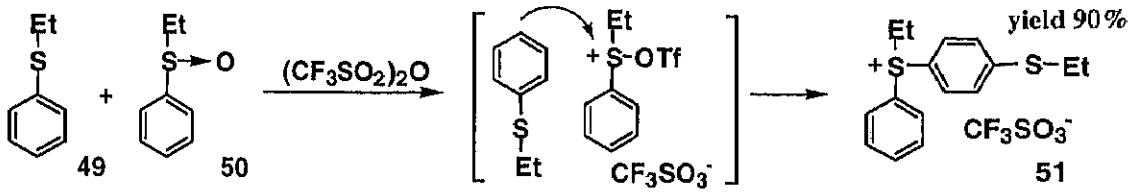


Figure 4-6

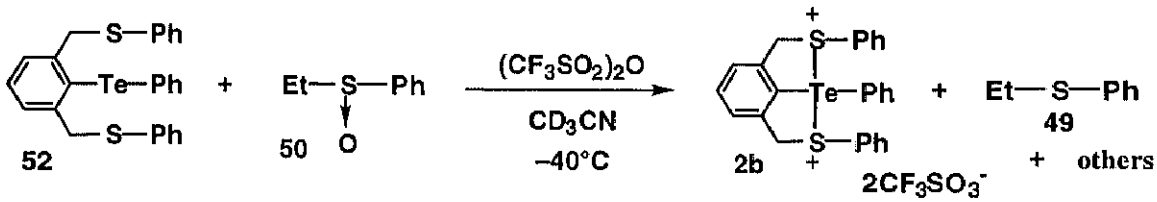
B. Intermolecular Oxidation

In recent paper[3], intermolecular reaction of ethyl phenyl sulfoxide **50** with ethyl phenyl sulfide **49** in the presence of the Lewis acid has been reported. In this reaction, sulfonium salt **51** was obatined by the reaction of the sulfoxide with Tf_2O. This sulfonium salt should be produced by the electrophilic substitution that the cationic sulfur atom would react with the aromatic carbon atom.



Scheme 4-25

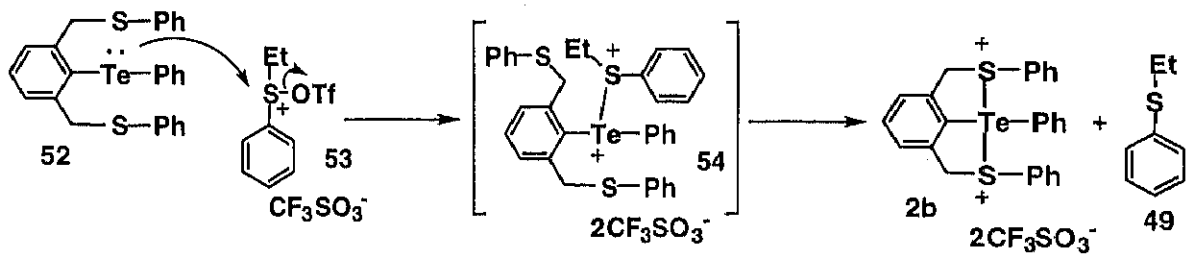
As applying this method to the oxidation of the corresponding telluride, it is possible to propose the intermolecular oxidation to produce the dicationic tellurane. At first a 1 : 1 mixture of the telluride **52** with ethyl phenyl sulfoxide **50** was treated with Tf_2O in CD_3CN. This reaction was carried out in an NMR tube and monitored by ^1H NMR. The resulting ^1H NMR spectrum of the reaction mixture showed the formation of the corresponding dicationic tellurane **2b** and also showed the reduction of ethyl phenyl sulfoxide **50** to ethyl phenyl sulfide **49** (Scheme 4-26). This result indicates the notion that the telluride **52** should be oxidized intermolecularly. However this reaction involves some by-products that depend on the intermolecular reaction.



Scheme 4-26

As the mechanism of this reaction, the intermolecular dicationic intermediate model and the electron transfer model should be predicted as shown in Scheme 4-27 and 4-28. In the intermolecular dicationic intermediate model, the sulfur atom of the sulfonium salt **53** should react with the tellurium atom to make a σ-bond. Subsequently ethyl phenyl sulfide **49** should be released by the intramolecular attack of the sulfur atom at the benzylic position. As a result of the reaction, the dicationic tellurane **2b** and reduced ethyl phenyl sulfide **49** should be produced in a 1 : 1 ratio.

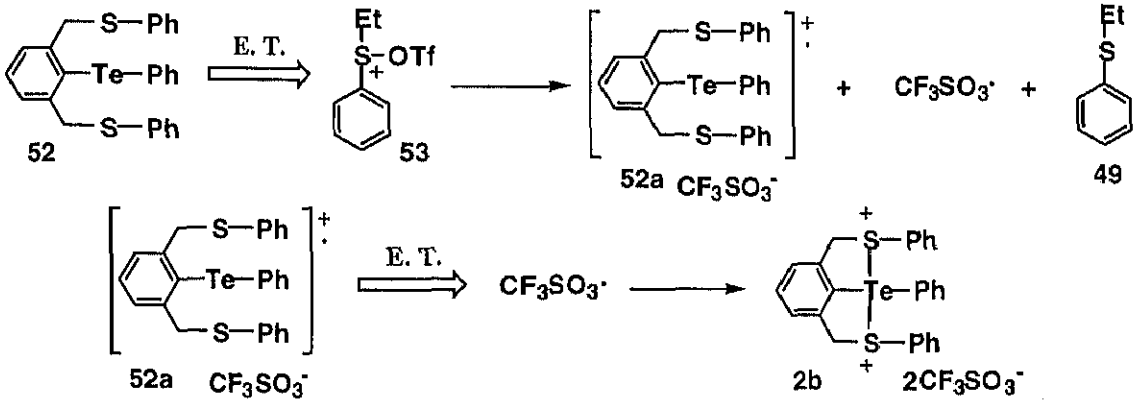
Intermolecular Dicationic Intermediate Model



Scheme 4-27

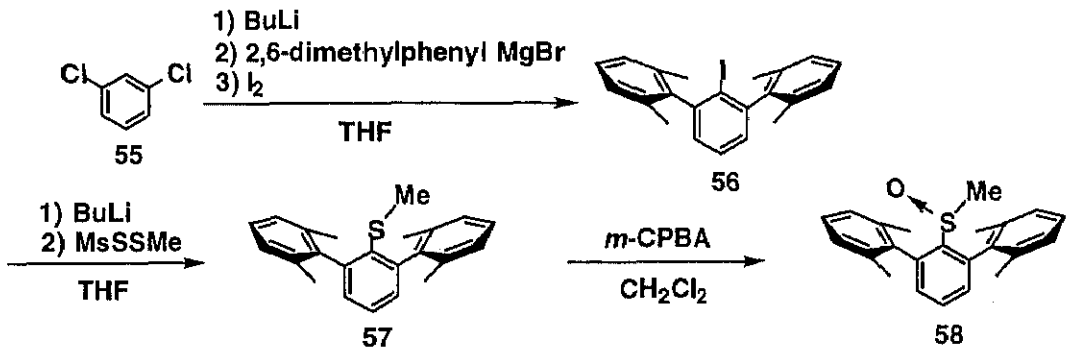
Besides the electron transfer mechanism is predicted as shown in Scheme 4-28. The first step of the reaction should be the single electron transfer from the telluride **52** to the sulfonium salt **53**. This electron transfer should produce the radical cation of the telluride **52a**, CF_3SO_3 radical and ethyl phenyl sulfide **49**. Subsequently another single electron transfer from the radical cation of the telluride to the CF_3SO_3 radical should give the dicationic tellurane **2b**.

Electron Transfer Model



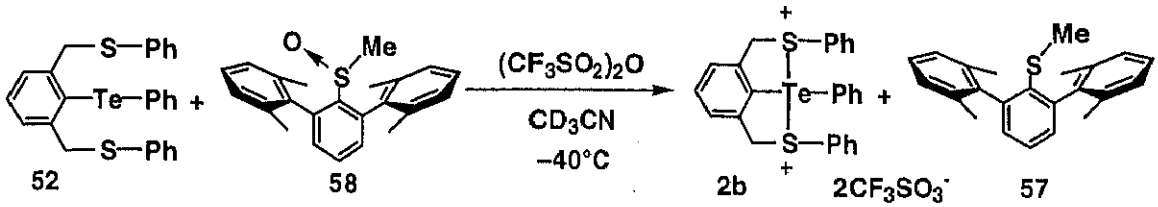
Scheme 4-28

In order to investigate the mechanism of this intermolecular oxidation, the bulky sulfoxide **58** was synthesized by the method shown in Scheme 4-29. This sulfoxide **58** should not make a complex with the telluride **52** as an intermediate because of its bulkiness.



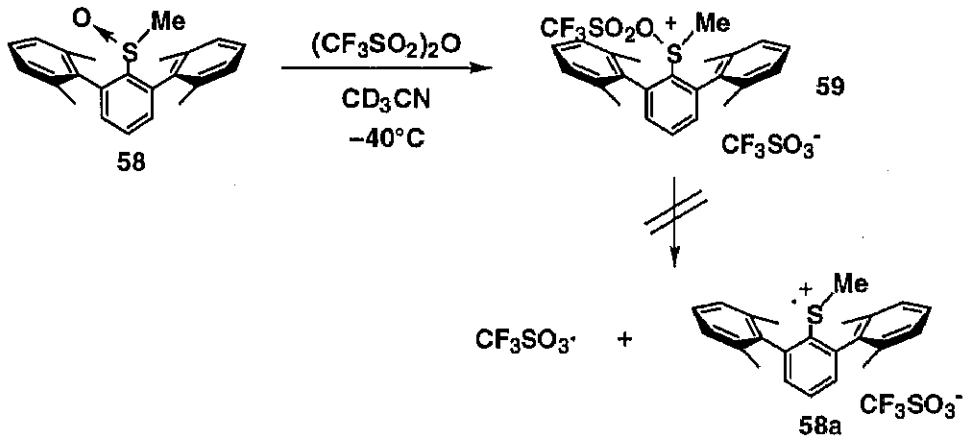
Scheme 4-29

Then the sulfoxide **58** was treated with Tf_2O in the presence of the telluride **52** under the same condition. As a result of the reaction, the corresponding dicationic tellurane **2b** and the sulfide **57** were produced in a 1 : 1 ratio, although some by-products were detected by ^1H NMR. This result means that this reaction should proceed via electron transfer not via dicationic intermediates.



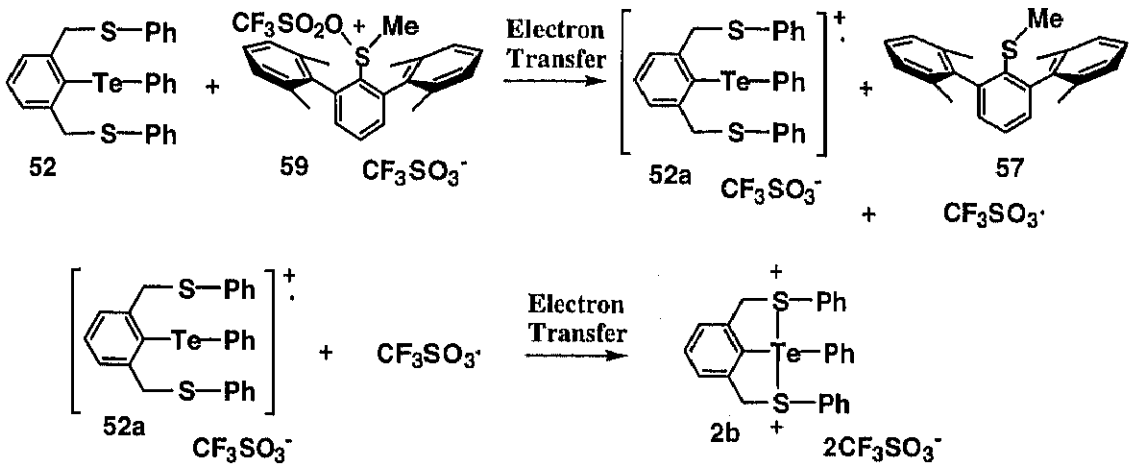
Scheme 4-30

For reference, only the sulfoxide **58** was treated with Tf_2O in CD_3CN under the same condition. This reaction was carried out in an NMR tube and monitored by ^1H NMR. By adding Tf_2O, the ^1H NMR spectrum of the sulfoxide **58** changed to that of the corresponding sulfonium salt **59**. This sulfonium salt was stable in solution during one day at room temperature and homolytic cleavage of the S–O bond was not observed. However it decomposed completely after one day.



Scheme 4-31

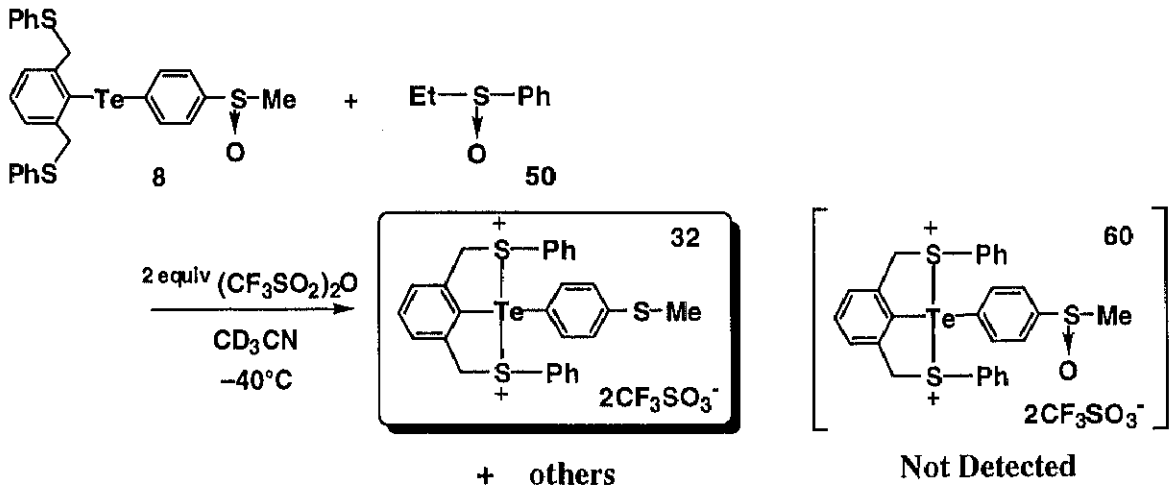
By considering this result, the mechanism of the intermolecular reaction is predicted as shown in Scheme 4-32. The sulfoxide **58** should react with Tf_2O to form the sulfonium salt **59**, which oxidizes the telluride **52** to produce the radical cation **52a** by single electron transfer. The resulting radical cation of the telluride **52** and CF_3SO_3 radical should react to produce the dicationic tellurane **2b**.



Scheme 4-32

C. Crossover Experiment

Furthermore the crossover experiment was carried out as follows. To the CD_3CN solution of the telluride **8** and the sulfoxide **50**, two equivalents of Tf_2O was added at –40 °C. As a result of the reaction, only the dicationic tellurane **32** with reduced methylthio group was observed and the dicationic tellurane **60** with methylsulfinyl group, which should originate from intermolecular reaction, was not produced. This result indicates the notion that the telluride **8** should react with Tf_2O to form the dicationic tellurane by "intramolecular" remote oxidation and the intramolecular reaction should be predominant to the intermolecular reaction overwhelmingly.



Scheme 4-33

VII. Conclusion

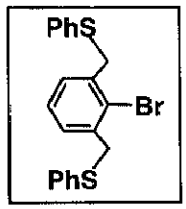
In conclusion, the author proposes a concept of remote oxidation as a new method to oxidize organic compounds. The word "remote" means that when the certain position of the molecule will be oxidized, the intramolecular electron shift will be caused through a π-conjugated system and then the other position will be oxidized indirectly. As applying this concept, new dicationic telluranes were synthesized by the oxidation reaction through π-conjugated bonds. This remote oxidation proceeds *via* intramolecular electron shift from the central tellurium atom to the methylsufinyl sulfur atom through a π-conjugated spacer.

At the same time, the intermolecular oxidation was also found to be possible to produce the dicationic tellurane. However the intramolecular oxidation is predominant to the intermolecular oxidation.

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 (^1H–^1H–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. The X-ray crystallographic analyses were performed on an Enraf-Nonius CAD4 diffractometer, a Rigaku AFC7S diffractometer and a Rigaku RAXIS II imaging plate area detector. 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 2,6-bis[(phenylthio)methyl]-1-bromobenzene 15

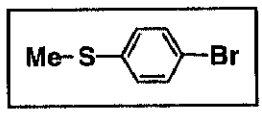


NaOH (0.39 g, 9.63 mmol) was added to a solution of thiophenol (1.06 g, 9.63 mmol) in ethanol (50 mL). This solution was added dropwise to a solution of 2,6-bis(bromomethyl)-1-bromobenzene (1.50 g, 4.38 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1) to give a colorless oil of 2,6-bis[(phenylthio)methyl]-1-bromobenzene **15** (1.54 g) in 88% yield.

2,6-Bis[(phenylthio)methyl]-1-bromobenzene 15

^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 4.25 (s, 4H, CH_2), 7.06–7.33 (m, 13H, ArH). ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 40.5, 126.7, 126.7, 126.9, 128.9, 129.6, 130.7, 135.7, 137.8; MS (m/z) 402 (M^+); Anal. Calcd for $C_{20}H_{17}BrS_2$: C, 59.85; H, 4.27. Found: C, 59.93; H, 4.32.

Synthesis of 4-bromothioanisole 13

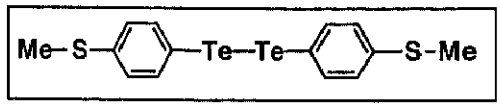


KOH (8.96 g, 160 mmol) was added to a solution of 4-bromothiophenol (25 g, 132 mmol) in ethanol (500 mL). Iodomethane (22 g, 160 mmol) was added dropwise to the solution at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with Et_2O and the organic layer was dried over anhydrous $MgSO_4$. Recrystallization from EtOH gave white crystals, 4-bromothioanisole **13** (23 g) in 88 % yield.

4-Bromothioanisole 13

^{1}H NMR (270 MHz, $CDCl_3$, room temperature) δ 2.48 (s, 3H, Me), 7.15 and 7.37 (ABq, J = 8.4 Hz, 4H, Ar-H). ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 15.3,119.3, 128.5, 133.8, 139.6; MS (m/z) 202 (M^+).

Synthesis of 4-methylthiophenyl ditelluride 14

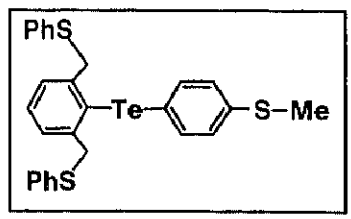


A solution of 4-methylthiophenyl magnesium bromide was obtained by adding 4-bromothioanisole **13** (8.0 g, 39.4 mmol) to a heterogeneous mixture of magnesium (1.2 g, 52.1 mmol) in dry THF (200 mL) under an argon atmosphere. Then dry powdered tellurium (6.1 g, 47.7 mmol) was added, and the reaction was allowed to proceed overnight. The mixture was then treated with 2.0 N aqueous HCl and oxidized with air for 48 h. Evaporation of the solvent, extraction with ether and water, and separation of the organic layer followed by concentration, gave a red solid that was purified by column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1). After recrystallization from $CHCl_3$, 4-methylthiophenyl ditelluride **14** (5.51 g) was obtained in 56% yield.

4-Methylthiophenyl ditelluride 14

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.47 (s, 6H, Me), 7.06 and 7.68 (ABq, J = 7.5 Hz, 8H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ15.4, 103.3, 126.9, 138.6, 139.5; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 444.3 (relative to Me_2Te); MS (m/z) 202 (M^+).

Synthesis of 2,6-bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluride 16

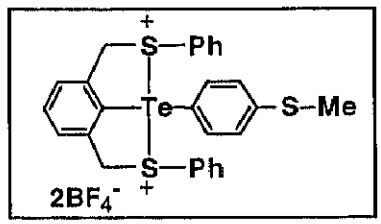


t-BuLi (1.61 mL, 1.70 M in *n*-hexane) was added to a dry THF (20 mL) solution of 2,6-bis[(phenylthio)methyl]-1-bromobenzene **15** (500 mg, 1.25 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of 4-methylthiophenyl ditelluride **14** (750 mg, 1.50 mmol) in dry THF (20 mL) using a transfer needle under the same conditions. 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, telluride **16** (2.58 g) in 63% yield.

2,6-Bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluride 16

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.40 (s, 3H, Me), 4.38 (s, 4H), 6.98–7.33 (m, 17H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 15.6, 45.8, 112.6, 123.9, 126.5, 127.5, 128.2, 128.8, 129.4, 130.2, 135.8, 136.2, 138.0, 144.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 449.4 (relative to Me_2Te); EIMS (m/z) 574 (M^+); Anal. Calcd for $C_{27}H_{24}S_3Te$: C, 56.67; H, 4.23. Found: C, 56.49; H, 4.03.

Synthesis of 2,6-bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluranyl bis(tetrafluoroborate) 17

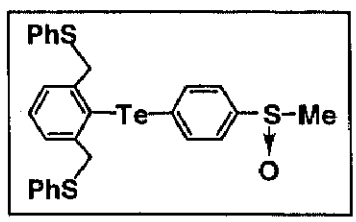


An anhydrous CH_3CN (10 mL) solution of $NOBF_4$ (421 mg, 3.60 mmol) was added dropwise to a solution of the telluride **16** (935 mg, 1.64 mmol) in anhydrous CH_2Cl_2 (20mL) at –78°C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH_2Cl_2, CH_3CN and ether gave wine red crystals of tellurane dication $2BF_4^-$ salt **17** (310 mg) in 68% yield.

2,6-Bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluranyl bis(tetrafluoroborate) 17

mp 162–166°C (decomp.); ^{1}H NMR (270 MHz, CD_3CN, –40 °C) δ 2.43 (s, 3H, Me), 4.42 and 5.26 (ABq, J = 18 Hz, 2H), 4.90 and 5.24 (ABq, J = 17 Hz, 2H), 6.86 – 8.23 (m,17H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN, room temperature) δ 14.5, 39.1, 39.9, 124.2, 124.9, 127.6, 128.7, 130.0, 131.0, 131.5, 132.2, 132.3, 132.8, 132.9, 134.8, 136.2, 147.5, 147.9, 150.5 ; ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 1342.9 (relative to Me_2Te); EIMS (m/z); 574 (M^+–$2BF_4^-$); Anal. Calcd for $C_{27}H_{24}B_2F_8S_3Te(CH_2Cl_2)$: C, 40.48; H, 3.15. Found: C, 40.86; H, 3.15 .

Synthesis of 2,6-bis[(phenylthio)methyl]phenyl 4-methylsulfinylphenyl telluride 8



The solution of *m*-CPBA (131 mg, 0.76 mmol) in CH_2Cl_2 (20 mL) was added to a CH_3CN (20 mL) solution of 2,6-bis[(phenylseleno)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) **17** (500 mg, 0.76 mmol) at 0 °C. The solution was stirred for 12 hours and then thiophenol (167 mg, 1.52 mmol) was added to the solution under the same condition. 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, EtOAc) to give a pale yellow crystals, the telluride 8 (215 mg) in 48% yield.

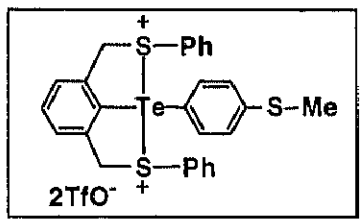
2,6-Bis[(phenylthio)methyl]phenyl 4-methylsulfinylphenyl telluride 8

mp 105-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.57 (s, 3H, Me), 4.29 (s, 4H), 7.13–7.38 (m, 17H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 43.9, 46.1, 122.4, 124.2, 124.3, 126.6, 126.7, 127.3, 128.4, 128.8, 129.9, 130.2, 130.4, 135.3, 135.4, 135.5, 144.4, 144.5; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 463.4 (relative to Me_2Te); EIMS (m/z) 590 (M^+); IR (NaCl) 1048 cm^{-1} (S–O); Anal. Calcd for $C_{27}H_{24}OS_3Te$: C, 55.13; H, 4.11. Found: C, 54.73; H, 4.30.

Reactions of the telluride 8 with trifluoromethanesulfonic anhydride

To a solution of the telluride **8** (14 mg, 0.02 mmol) in dry CD_3CN was added trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 5 μL, 0.02 mmol) at –40°C under an argon atmosphere. The color of the solution changed from pale yellow to wine red after addition. This solution was monitored by ^{1}H, ^{13}C and ^{125}Te NMR spectroscopy, which showed simple signals from dicationic tellurane.

2,6-Bis[(phenylseleno)methyl]phenyl phenyl telluranyl bis(trifluoromethanesulfonate) 32



mp 118–123°C (decomp.); ^{1}H NMR (270 MHz, CD_3CN, –40 °C) δ 2.43 (s, 3H, Me), 4.42 and 5.26 (ABq, J = 18 Hz, 2H), 4.90 and 5.24 (ABq, J = 17 Hz, 2H), 6.86 – 8.23 (m,17H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN, room temperature) δ 14.5, 39.1, 39.9, 124.2, 124.9, 127.6, 128.7, 130.0, 131.0, 131.5, 132.2, 132.3, 132.8, 132.9, 134.8, 136.2, 147.5, 147.9, 150.5 ; ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 1342.9 (relative to Me_2Te); EIMS (m/z); 574 (M^+–2TfO^-); Anal. Calcd for $C_{29}H_{24}F_6O_6S_5Te$: C, 40.02; H, 2.78. Found: C, 39.79; H, 2.99.

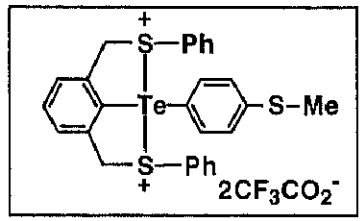
Reactions of the telluride 8 with trifluoromethanesulfonic acid

To a solution of the telluride **8** (7 mg, 0.01 mmol) in dry CD_3CN was added trifluoromethanesulfonic acid (CF_3SO_3H; 6 μL, 0.1 mmol) at –40°C under an argon atmosphere. The color of the solution changed from pale yellow to yellow after addition. This solution was monitored by ^{1}H and ^{125}Te NMR spectroscopy. It took one day to complete the reaction at room temperature. Finally, the signals of the corresponding dicationic tellurane were observed by ^{1}H and ^{125}Te NMR spectroscopy.

Reactions of the telluride 8 with trifluoroacetic anhydride

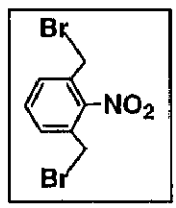
To a solution of the telluride **8** (3 mg, $5 \cdot 10^{-3}$ mmol) in dry CD_3CN was added trifluoroacetic anhydride ($(CF_3CO)_2O$; 1 μL, $6 \cdot 10^{-3}$ mmol) at –40°C under an argon atmosphere. The color of the solution changed from pale yellow to wine red after addition. This solution was monitored by ^1H, ^{13}C and ^{125}Te NMR spectroscopy. It took one day to complete the reaction at room temperature. Finally, the signals of the corresponding dicationic tellurane were observed by ^1H and ^{125}Te NMR spectroscopy.

2,6-Bis[(phenylseleno)methyl]phenyl phenyl telluranyl bis(trifluoromethanesulfonate) 32b



^1H NMR (270 MHz, CD_3CN, –40 °C) δ 2.54 (s, 3H, Me), 4.42 and 5.26 (ABq, J = 18 Hz, 2H), 4.90 and 5.24 (ABq, J = 17 Hz, 2H), 6.86 – 8.23 (m,17H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN, room temperature) δ 14.5, 39.1, 39.9, 124.2, 124.9, 127.6, 128.7, 130.0, 131.0, 131.5, 132.2, 132.3, 132.8, 132.9, 134.8, 136.2, 147.5, 147.9, 150.5 ; ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 1214.0 (relative to Me_2Te); EIMS (m/z); 574 (M^+–$2CF_3CO_2^-$).

Synthesis of 2,6-bis(bromomethyl)-1-nitrobenzene

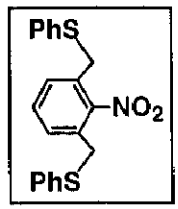


A solution of 2,6-dimethyl-1-nitrobenzene (52.9 g, 350 mmol) and N-bromosuccinimide (137 g, 770 mmol) in dry CCl_4 (800 mL) was stirred under an argon atmosphere at reflux conditions (70 °C), while being irradiated with a high-pressure mercury lamp for 15 h. The by-product succinimide could be removed by filtration, and for the removal of bromide, the filtrate was washed with aqueous sodium thiosulfate. The organic layer was separated, dried with anhydrous $MgSO_4$ and the crude product was obtained after evaporation of the solvent. Recrystallization from EtOH gave white crystals, 2,6-Bis(bromomethyl)-1-nitrobenzene (23 g) in 21% yield.

2,6-Bis(bromomethyl)-1-nitrobenzene

mp 120-121 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 4.50 (s, 4H, CH_2), 7.50-7.51 (m, 3H, ArH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.5, 130.8, 131.5, 131.8, 149.4; MS (m/z) 309 (M^+).

Synthesis of 2,6-bis[(phenylthio)methyl]-1-nitrobenzene



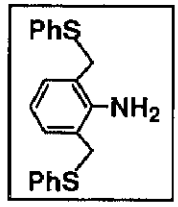
NaOH (0.26 g, 6.47 mmol) was added to a solution of thiophenol (0.67 mL, 6.47 mmol) in ethanol (50 mL). The solution was added dropwise to a solution of 2,6-bis(bromomethyl)-1-nitrobenzene (1 g, 3.23 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. After the removal of the solvent under vacuum at room temperature, the

crude product was subjected to column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1) to give a colorless oil of 2,6-bis[(phenylthio)methyl]-1-nitrobenzene (1.12 g) in 95% yield.

2,6-Bis[(phenylthio)methyl]-1-nitrobenzene

^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 4.10 (s, 4H, CH_2), 7.20–7.30 (m, 13H, ArH). ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 35.4, 127.3, 129.0, 129.0, 130.2, 130.6, 131.2, 134.5, 150.0; MS (m/z) 367 (M^+).

Synthesis of 2,6-bis[(phenylthio)methyl]-1-aminobenzene 24

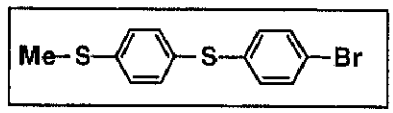


$NaBH_4$ (200 mg, 5.45 mmol) was added to a solution of 2,6-bis[(phenylthio)methyl]-1-nitrobenzene (200 mg, 5.45 mmol) in THF (50 mL). To this solution, selenium powder (200 mg) was added at 0 °C. The solution was stirred overnight at room temperature. After removal of the solvents, the residue was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1) to give a colorless oil of 2,6-bis[(phenylthio)methyl]-1-aminobenzene **24** (90 mg) in 49% yield.

2,6-Bis[(phenylthio)methyl]-1-aminobenzene 24

^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 4.07 (s, 4H, CH_2), 6.52–7.40 (m, 13H, ArH). ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 36.9, 117.9, 121.2, 126.7, 128.8, 130.4, 130.5, 135.5, 144.0; MS (m/z) 367 (M^+).

Synthesis of 4-methylthiophenyl 4-bromophenyl sulfide 21



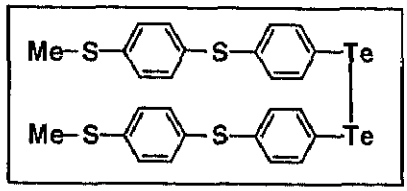
A 3 L beaker was charged with 4-aminothioanisole (17 g, 123 mmol), water (200 mL) and tetrafluoroboric acid (HBF_4; 50 mL,). The mixture was then placed in an ice-salt bath and cooled to 0 °C. Under mechanical stirring a solution of sodium nitrite (10.2 g, 150 mmol) in water (100 mL) was added dropwise, so that the temperature was kept below 5 °C. The resulting mixture was then poured slowly into a solution of potassium hydoxide (KOH; 10.5 g, 180 mol) and p-bromothiophenol (25 g, 132 mmol) in EtOH (500 mL) under vigorous stirring and cooling with ice. The brown-red mixture was stirred for 1h at 0 °C, 2 h at room temperature and finally 2 h at 80 °C in order to destroy remaining diazonium salt. After filtration and extraction with Et_2O, the crude product was obtained. Purification by column chromatography (silica gel; eluent, n-hexane) and recrytallization afforded a colorless crystals, the sulfide **21** (26.3 g) in 69% yield.

4-Methylthiophenyl 4-bromophenyl sulfide 21

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.49 (s, 3H, Me), 7.11 and 7.38 (ABq, J = 12.8 Hz, 4H, Ar-H), 7.21 and 7.31 (ABq, J = 12.8 Hz, 4H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$,

room temperature) δ 15.5, 120.4, 127.1, 130.2, 131.1, 132.1, 132.8, 136.2, 139.0 ; MS (m/z) 310 (M^+).

Synthesis of the ditelluride 22

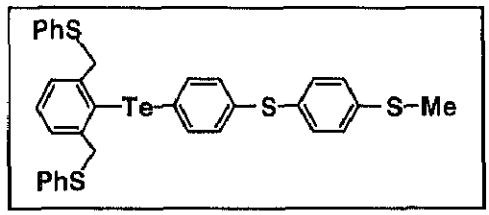


A solution of 4-methylthiophenyl 4-bromophenyl sulfide **21** (11.0 g, 35.3 mmol) in dry THF (20 ml) was added to a heterogeneous mixture of magnesium (1.0 g, 41.7 mmol) in dry THF (200 mL) under an argon atmosphere. This solution was refluxed for 12h. Then dry powdered tellurium (5.4 g, 42.2 mmol) was added, and the reaction was allowed to proceed overnight. The mixture was then treated with 2.0 N aqueous HCl and oxidized with air for 48 h. Evaporation of the solvent, extraction with ether and water, and separation of the organic layer followed by concentration, gave a red solid that was purified by column chromatography (silica gel; eluent, CH_2Cl_2). After recrystallization from CH_2Cl_2, the ditelluride **22** (8.88 g) was obtained in 70% yield.

Ditelluride 22

^1H NMR (270 MHz, $CDCl_3$, room temperature) δ 2.49 (s, 6H, Me), 7.02 and 7.65 (ABq, J = 8.2 Hz, 8H, Ar-H), 7.21 and 7.33 (ABq, J = 8.2 Hz, 8H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ15.5, 127.0, 129.7, 129.8, 133.2, 133.3, 138.1, 138.2, 138.5, 139.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 435.7 (relative to Me_2Te).

Synthesis of telluride 23

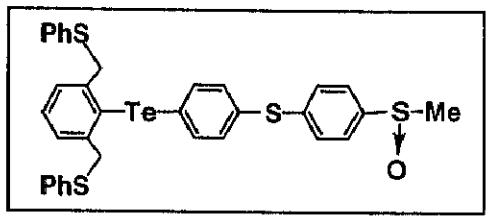


Isoamyl nitrite (1.0 mL, 8.55 mmol) was added to a dry CH_2Cl_2 (20 mL) solution of 2,6-bis[(phenylthio)methyl]-1-aminobenzene **24** (2.15 g, 6.38 mmol) at 0 °C under an argon atmosphere. The solution was stirred for 30 min and then a solution of ditelluride 22 (2.75 g, 3.8 mmol) reduced by sodium tetrahydroborate ($NaBH_4$; 302 mg, 8.0 mmol) in EtOH (20 mL) using a transfer needle under the same conditions. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with Et_2O. 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-CH_2Cl_2, 4 : 1) to give a pale yellow oil, the telluride **23** (43 mg) in 1% yield.

Telluride 23

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.45 (s, 3H, Me), 4.38 (s, 4H), 6.98–7.39 (m, 21H, Ar-H); ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 452.6 (relative to Me_2Te); FAB-MS (m/z) 682 (M^+).

Synthesis of the telluride 9

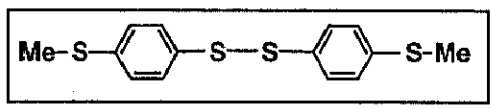


An anhydrous CH_3CN (10 mL) solution of $NOBF_4$ (22 mg, 0.19 mmol) was added dropwise to a solution of the telluride **23** (43 mg, 0.06 mmol) in anhydrous CH_2Cl_2 (20mL) at –78 °C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and CH_3CN (10 mL) was added to the solid. Then thiophenol (12 μL, 0.11 mmol) was added to the solution at 0 °C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with Et_2O. 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, EtOAc) to give a pale yellow oil, the telluride **9** (25 mg) in 68% yield.

Telluride 9

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.68 (s, 3H, Me), 4.39 (s, 4H), 7.16–7.48 (m, 21H, Ar-H); ^{13}C NMR (100 MHz, CD_3CN, room temperature) δ 43.9, 46.2, 118.5, 123.5, 124.3, 126.7, 128.4, 128.9, 129.4, 129.7, 160.4, 131.9, 133.9, 135.6, 136.1, 141.3, 143.4, 144.3; ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 457.2 (relative to Me_2Te); FAB-MS (m/z); 698 (M^+).

Synthesis of 4-methylthiophenyl disulfide

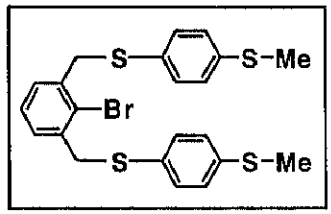


A solution of 4-methylthiophenyl magnesium bromide was obtained by adding 4-bromothioanisole (9.8 g, 48.4 mmol) to a heterogeneous mixture of magnesium (1.4 g, 61.8 mmol) in dry THF (200 mL) under an argon atmosphere. Then dry sulfur (2.3 g, 71.8 mmol) was added, and the reaction was allowed to proceed overnight. The mixture was then treated with 2.0 N aqueous HCl and oxidized with air for 48 h. Evaporation of the solvent, extraction with ether and water, and separation of the organic layer followed by concentration, gave a solid that was purified by column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1). After recrystallization from *n*-hexane, 4-methylthiophenyl disulfide (3.45 g) was obtained in 56% yield.

4-Methylthiophenyl disulfide

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.47 (s, 6H, Me), 7.17 and 7.39 (ABq, J = 8.5 Hz, 8H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 15.7, 127.0, 129.4, 131.6, 138.5 ; EIMS (m/z) 310 (M^+).

Synthesis of 2,6-bis[[(4-methylthiophenyl)thio]methyl]-1-bromobenzene 28

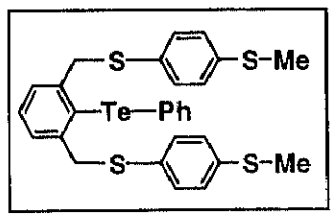


$NaBH_4$ (1.0 g, 26.9 mmol) was added to a solution of 4-methylthiophenyl disulfide (3.49 g, 11.2 mmol) in ethanol (50 mL) under an argon atmosphere. The solution was added dropwise to a solution of 2,6-bis(bromomethyl)-1-bromobenzene (3.22 g, 9.39 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, *n*-hexane- CH_2Cl_2, 4 : 1) to give a colorless oil of 2,6-bis[[(4-methylthiophenyl) thio]methyl]-1-bromobenzene **28** (1.16 g) in 95% yield.

2,6-Bis[[(4-methylthiophenyl)thio]methyl]-1-bromobenzene 28

^{1}H NMR (270 MHz, $CDCl_3$, room temperature) δ 2.46 (s, 6H, Me), 4.20 (s, 4H, Me), 7.03–7.24 (m, 11H, ArH); MS (m/z) 492 (M^+).

Synthesis of the telluride 29



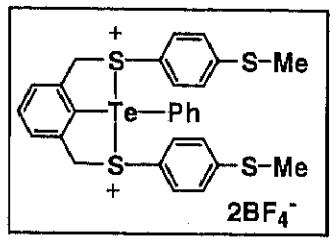
t-BuLi (3.3 mL, 1.56 M in *n*-hexane) was added to a dry THF (20 mL) solution of 2,6-bis[[(4-methylthiophenyl)thio]methyl]-1-bromobenzene **28** (1.16 g, 2.35 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of diphenyl ditelluride (1.15 mg, 2.82 mmol) in dry THF (20 mL) using a transfer needle under the same conditions. 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- CH_2Cl_2, 4 : 1) to give a pale yellow oil, telluride **29** (296 mg) in 20% yield.

2,6-Bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluride 29

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.37 (s, 3H, Me), 4.33 (s, 4H), 7.02–7.36 (m, 16H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 15.9, 46.5, 117.6, 124.1, 126.9, 127.3, 128.3, 129.5, 129.7, 131.5, 131.9, 135.3, 137.4, 144.4; ^{125}Te NMR (126 MHz,

$CDCl_3$, room temperature) δ 453.2 (relative to Me_2Te); EIMS (m/z) 620 (M^+); Anal. Calcd for $C_{28}H_{26}S_4Te$: C, 54.38; H, 4.24. Found: C, 54.47; H, 4.24.

Synthesis of the dicationic tellurane 30

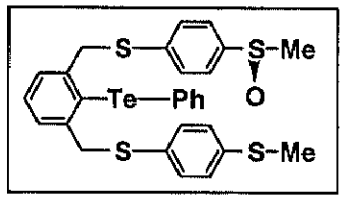


An anhydrous CH_3CN (10 mL) solution of $NOBF_4$ (42 mg, 0.36 mmol) was added dropwise to a solution of telluride **29** (106 mg, 0.17 mmol) in anhydrous CH_2Cl_2 (20mL) at –78°C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature to give wine red solid of tellurane dication $2BF_4^-$ salt **30** (100 mg) in 74% yield.

Dicationic Tellurane 30

^1H NMR (270 MHz, CD_3CN, room temperature) δ 2.38 (s, 3H, Me), 2.46 (s, 3H, Me), 4.51 and 5.24 (ABq, J = 18 Hz, 2H), 5.01 and 5.16 (ABq, J = 17 Hz, 2H), 6.74 – 8.19 (m, 16H, Ar-H); ^{125}Te NMR (126 MHz, CD_3CN, room temperature) δ 1330.5 (relative to Me_2Te); EIMS (m/z); 620 (M^+–$2BF_4^-$).

Synthesis of the telluride 10



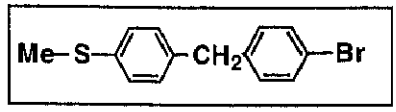
The solution of *m*-CPBA (20 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) was added to a CH_3CN (20 mL) solution of 2,6-bis[(phenylthio)methyl]phenyl phenyl telluranyl bis(tetrafluoroborate) **30** (100 mg, 0.12 mmol) at 0°C. The solution was stirred for 12 hours and then thiophenol (30 mg, 0.27 mmol) was added to the solution under the same condition. 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, EtOAc) to give a pale yellow oil, the telluride **10** (31 mg) in 39% yield.

Telluride 10

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.44 (s, 3H), 2.73 (s, 3H), 4.38 (s, 2H), 4.42 (s, 2H), 7.07–7.54 (m, 16H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 15.8, 43.7, 44.7, 46.7, 124.0, 124.1, 126.8, 127.3, 128.1, 128.2, 128.5, 129.2, 129.6, 129.7, 129.8, 130.1, 131.5, 131.7, 133.4, 135.3; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 447.1 (relative to Me_2Te); EIMS (m/z) 636 (M^+).

Synthesis of 4-methylthiophenyl 4-bromophenyl methane

A solution of 4-methylthiophenyl magnesium bromide was obtained by adding 4-bromothioanisole (10.2 g, 50.2 mmol) to a heterogeneous mixture of magnesium (1.4 g, 60.8 mmol) in dry THF (200 mL) under an argon atmosphere. This solution was stirred for 30 min and then added to a heterogeneous mixture of CuI (1.0 g, 5.26 mmol) and 4-bromobenzylbromide (12.5 g, 50.2 mmol) in dry THF (100 mL) using a transfer needle, and the reaction was allowed to proceed overnight. Evaporation of the solvent, extraction with ether and water, and separation of the organic layer followed by concentration, gave a oil that was purified by column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1). 4-methylthiophenyl 4-bromophenyl methane (3.68 g) was obtained in 25% yield.

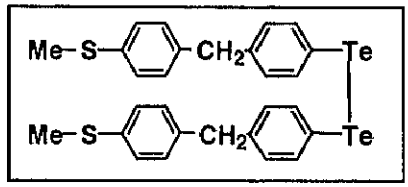


4-Methylthiophenyl 4-bromophenyl methane

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.46 (s, 3H, Me), 7.02-7.40 (m, 8H, Ar-H); MS (m/z) 292 (M^+).

Synthesis of ditelluride 22b

A solution of 4-methylthiophenyl 4-bromophenyl methane (3.7 g, 12.6 mmol) in dry THF (20 ml) was added to a heterogeneous mixture of magnesium (350 mg, 15.0 mmol) in dry THF (200 mL) under an argon atmosphere. This solution was refluxed for 12h. Then dry powdered tellurium (1.9 g, 15.1 mmol) was added, and the reaction was allowed to proceed overnight. The mixture was then treated with 2.0 N aqueous HCl and oxidized with air for 48 h. Evaporation of the solvent, extraction with ether and water, and separation of the organic layer followed by concentration, gave a red solid that was purified by column chromatography (silica gel; eluent, CH_2Cl_2). After recrystallization from CH_2Cl_2, the ditelluride **22b** (2.0 g) was obtained in 48% yield.

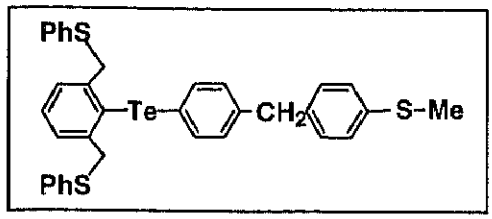


Ditelluride 22b

^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.44 (s, 6H, Me), 6.97 and 7.67 (ABq, J = 8.0 Hz, 8H, Ar-H), 7.07 and 7.17 (ABq, J = 8.3 Hz, 8H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 16.1, 40.9, 105.0, 127.0, 129.4, 129.8, 135.9, 137.7, 137.9, 138.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 424.8 (relative to Me_2Te).

Synthesis of the telluride 26

t-BuLi (4.3 mL, 1.54 M in *n*-hexane) was added to a dry THF (20 mL) solution of 2,6-bis[(phenylthio)methyl]-1-bromobenzene **15** (1.32 g, 3.29 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of the ditelluride **22b** (2.03 g, 2.99 mmol) in dry THF (20 mL) using a transfer needle under the same conditions.

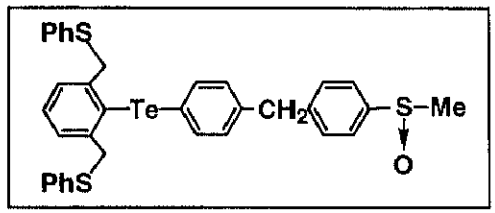


The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, *n*-hexane-$CHCl_3$, 4 : 1) to give white crystals, the telluride **26** (148 mg) in 7% yield.

Telluride 26

mp 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.44 (s, 3H, Me), 3.86 (s, 2H), 4.38 (s, 4H), 6.93–7.34 (m, 21H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 16.1, 41.0, 45.9, 114.3, 123.9, 126.5, 127.0, 128.2, 128.9, 129.4, 129.5, 130.1, 130.3, 135.8, 135.9, 135.9, 137.7, 140.3, 144.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 443.5 (relative to Me_2Te); EIMS (m/z) 664 (M^+); Anal. Calcd for $C_{34}H_{30}S_3Te$: C, 61.65; H, 4.56. Found: C, 60.71; H, 4.68.

Synthesis of the telluride 11



An anhydrous CH_3CN (10 mL) solution of $NOBF_4$ (86 mg, 0.74 mmol) was added dropwise to a solution of the telluride **26** (148 mg, 0.22 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 CH_3CN (10 mL) was added to the solid. Then thiophenol (24 μL, 0.22 mmol) was added to the solution at 0 °C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with Et_2O. 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, EtOAc) to give white crystals, the telluride **11** (107 mg) in 75% yield.

Telluride 11

mp 95-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.67 (s, 3H, Me), 3.93 (s, 2H), 4.38 (s, 4H), 6.93–7.52 (m, 21H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 41.1, 43.8, 45.8, 114.6, 123.7, 126.4, 128.1, 128.7, 129.3, 129.7, 130.1, 130.2, 135.7, 135.7, 139.2, 143.2, 144.0, 144.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 446.3 (relative to Me_2Te); FAB-MS (m/z) 680 (M^+); Anal. Calcd for $C_{34}H_{30}OS_3Te$: C, 60.20; H, 4.46. Found: C, 59.61; H, 4.57.

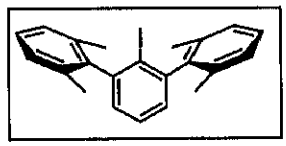
Reactions of the telluride 11 with trifluoromethanesulfonic anhydride

To a solution of the telluride **11** (32 mg, 0.5 mmol) in dry CD_3CN, trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 10 μL, 0.6 mmol) was added at –40°C under an argon atmosphere. The color of the solution changed from pale yellow to wine red after addition. This solution was monitored by ^1H and ^{125}Te NMR spectroscopy, which showed complicated signals. The products were too many to identify.

Reactions of the telluride 11 with trifluoromethanesulfonic acid

To a solution of the telluride **11** (5 mg, 0.01 mmol) in dry CD_3CN, trifluoromethanesulfonic acid (CF_3SO_3H; 6 μL, 0.1 mmol) was added at –40°C under an argon atmosphere. The color of the solution changed from pale yellow to yellow after addition. This solution was monitored by ^1H and ^{125}Te NMR spectroscopy, which showed complicated signals. The products were too many to identify.

Synthesis of 2'-iodo-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 56

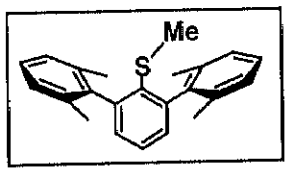


To a solution of (2,6-dimethylphenyl)magnesium bromide [prepared from 2,6-dimethylbromobenzene (3.7 g, 20 mmol) and magnesium (552 mg, 24 mmol) in 300 mL of anhydrous THF heated at reflux under an argon atmosphere], a solution of 2,6-dichlorobenzene (1.47 g, 10 mmol) in anhydrous THF was added. The resulting solution was heated at reflux for an additional 3h, cooled, quenched with a solution of iodine (3g, 12 mmol) in anhydrous THF. 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) to give colorless crystals, 2'-iodo-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl **56** (2.56 g) in 62% yield.

2'-Iodo-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 56

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.02 (s, 12H), 7.09–7.51 (m, 9H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 20.4, 106.7, 127.3, 127.6, 127.6, 129.0, 135.6, 144.7, 147.1; EIMS (m/z) 412 (M^+).

Synthesis of 2'-methylthio-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 57



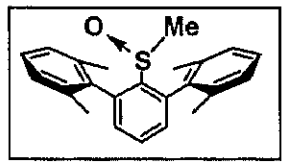
BuLi (5.0 mL, 1.58 M in *n*-hexane) was added to a dry THF (20 mL) solution of 2'-iodo-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl **56** (2.56 g, 6.21 mmol) at –78 °C under an argon atmosphere. The solution was stirred for 30 min and then added to a solution of dimethyl disulfide (703 mg, 7.48 mmol) in dry THF (20 mL) using a transfer needle under the same conditions. 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- CH_2Cl_2, 4 : 1) to give a colorless oil, 2'-Methylthio-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl **57** (1.15 g) in 54% yield.

2'-Methylthio-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 57

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 1.69 (s, 3H), 2.08 (s, 12H), 7.08–7.40 (m, 9H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 17.4, 20.8, 127.2, 127.2, 128.2, 129.2, 129.2, 135.9, 141.3, 145.1; EIMS (m/z) 332 (M^+).

Synthesis of 2'-methylsulfinyl-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 58



The solution of *m*-CPBA (640 mg, 3.70 mmol) in CH_2Cl_2 (20 mL) was added to the solution of 2'-methylthio-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl **57** (1.12 g, 3.36 mmol) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for overnight. The solvents were evaporated, and the residue was washed with aq. $NaHCO_3$ solution, then 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- CH_2Cl_2, 1 : 1) to give a colorless oil, **58** (31 mg) in 39% yield.

2'-Methylsulfinyl-2,6,2'',6''-tetramethyl-1,1':3',1''-terphenyl 58

^1H NMR (400 MHz, $CDCl_3$, room temperature) δ 2.06 (s, 6H), 2.14 (s, 6H), 2.38 (s, 3H), 7.10–7.62 (m, 9H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 21.2、21.3、38.3、100.2、127.2, 127.2, 127.9, 130.8, 131.7, 135.3, 136.8, 138.0, 141.7; EIMS (m/z) 348 (M^+).

Intermolecular reaction of the telluride 52 and ethyl phenyl sulfoxide 50

To a solution of the telluride **52** (5 mg, 0.01 mmol) and ethyl phenyl sulfoxide **50** (2 mg, 0.01 mmol) in dry CD_3CN, trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 3 μL, 0.03 mmol) was added at –40°C under an argon atmosphere. The colorless solution changed to clear yellow after addition. This solution was monitored by ^1H and ^{125}Te NMR spectroscopy, which showed formation of the dicationic tellurane **2b** and ethyl phenyl sulfide **49** in a 1 : 1 ratio. The ^1H NMR spectrum of the solution also showed formation of some by-products.

Intermolecular reaction of the telluride 52 and the sulfoxide 58

To a solution of the telluride **52** (10 mg, 0.02 mmol) and the sulfoxide **58** (8 mg, 0.02 mmol) in dry CD_3CN, trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 4 μL, 0.03 mmol) was added at –40°C under an argon atmosphere. The colorless solution changed to clear yellow after addition. This solution was monitored by ^1H and ^{125}Te NMR spectroscopy, which showed formation of the dicationic tellurane **2b** and the sulfide **57** in a 1 : 1 ratio. The ^1H NMR spectrum of the solution also showed formation of some by-products.

Crossover experiment

To a solution of the telluride **8** (14 mg, 0.02 mmol) and the sulfoxide **58** (8 mg, 0.02 mmol) in dry CD_3CN, trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 5 μL, 0.04 mmol) was added at –40°C under an argon atmosphere. This solution was monitored by ^1H and ^{125}Te NMR spectroscopy, which showed formation of the dicationic tellurane **32** and some by-products. The dicationic tellurane **60** was not observed.

Reference

1) a) Bergholdt, A. B.; Kobayashi, K.; Horn, E.; Takahashi, O.; Sato, S.; Furukawa, N.; Yokoyama, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1230–1236. b) Furukawa, N. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2571. c) Furukawa, N.; Kobayashi, K.; Sato, S.; Bergholdt, A. B.; Horn, E.; Takahashi, O. *Phosphorus Sulphur and Silicon* **1998**, *136-138*, 471.

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