Chapter 4

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

CONTENTS

I. Introduction
II. Remote Oxidation
III. Synthesis of Tellurides
IV. Synthesis of Dicationic Telluranes by Remote Oxidation
V. X-ray Crystallographic Analysis of Dicationic Tellurane (32)
VI. Further Investigation on the Reaction Mechanism of Remote Oxidation
   A. Necessity of π-Conjugated Spacer
   B. Intermolecular Oxidation
   C. Crossover Experiment
VII. Conclusion
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 NOBF₄ and NOPF₆, or (CF₃SO₂)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](image)

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 CF₃CO₂H. This reaction has been proposed to proceed not via the corresponding quinoid type intermediate but via the bis(dithia dication) dimer.²

![Scheme 4-2](image)

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 (CF₃SO₂)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](image_url)

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](image_url)
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 \( \pi \)-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 \( \pi \)-conjugated spacer such as thiophene, 4-phenyleneethynylene, 4-phenylene and so on. However it is difficult to introduce these \( \pi \)-conjugated spacers into the telluride, so many proposed substrates could not be synthesized.

In order to confirm the necessity of the \( \pi \)-conjugated spacer, the telluride 11, having no \( \pi \)-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](image)

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.
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.

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 NaBH₄ 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 NOBF₄. 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 methylsulfanyl group. As initiating reagents, triflic anhydride (Tf₂O) or triflic acid was used in the reaction.

Treatment of the telluride 8 with 1.2 equimolar amount of Tf₂O at -40 °C in CD₃CN afforded readily the corresponding stable dicationic tellurate 32 (Scheme 4-10). The reaction was carried out in an NMR tube and monitored by ¹H NMR. By adding Tf₂O 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 tellurate 32. This reaction proceeded quantitatively without any by-product.

The dicationic tellurate 32 was characterized by elemental and spectroscopic (EIMS, ¹H, ¹³C and ¹²⁵Te NMR) analyses. The ¹H NMR spectrum of the dicationic tellurate 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 tellurate 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 upfield from δ 2.57 to 2.43 by adding Tf₂O. This indicates that the sulfur atom of the methylsulfanyl group is reduced to form the methylthio group. The ¹²⁵Te signal of 32 appeared at δ 1343 which is similar to that of the corresponding dicationic tellurate 1b (δ 1331) without a 4-thiomethyl group.

![Scheme 4-10](image)

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 sulfurate 33b followed by the reaction with Tf₂O. Subsequently the corresponding dicationic compound 32 should be produced by the conformational change of the two phenylthiomethyl groups via the dicationic intermediate of the quinoid type 34, formed by the electron transfer from the tellurium atom to the sulfur atom in the methylsulfanyl group. However the reaction was too fast to detect the estimated intermediates 33a, 33b and 34 by ¹H, ¹³C or ¹²⁵Te NMR.
Triflic acid (TfOH) was also treated with the telluride 8 to form the dicationic tellurane (Scheme 4-12). When 1 or 2 equivmolar amount of triflic acid was added to the solution of the telluride 8, only hydroxysulfonium salt 35 was formed and further reaction did not occur. 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.
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 tellurate 32. In the $^1$H NMR spectrum of the dicationic tellurate 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.

![After adding 10 equiv of TFOH](image1)

![6 h later](image2)

![2 days later](image3)

**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](image)

The telluride 9, having the extended \(\pi\)-conjugated system, was also reacted with \(\text{Tf}_2\text{O}\) 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 \(\text{Tf}_2\text{O}\) 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](image)
The structure of this dicatonic tellurane 38 was assigned by EIMS, $^1$H, $^{13}$C and $^{125}$Te NMR. The $^1$H NMR spectrum of the dicatonic 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 $\delta$ 2.68 to 2.53 by adding Tf$_2$O 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 $\delta$ 1339.7.

![Scheme 4-15](image)

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$_2$O. As shown in Scheme 4-15, the electrons shift from the tellurium atom to the sulfur atom of the methylsulfinyl group through an intramolecular $\pi$-conjugation in the benzene rings and the sulfur atom. Subsequently the corresponding dicatonic compound 38 should be produced by the conformational change of the two phenylthiomethyl groups via the dicatonic intermediate of the quinoide types 40 and 41.
formed by the electron transfer from the tellurium atom to the sulfur atom in the methylsulfanyl group. This sulfur atom is important to connect the \( \pi \)-conjugated system from the tellurium atom to the sulfur atom of the methylsulfanyl group. This reaction was too fast to detect the estimated intermediates 39a, 39b, 40 and 41 by \( ^1H \), \( ^{13}C \) 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 \( ^1H \) NMR. By adding TFOH to the CD\(_3\)CN solution of the telluride 9, the \( ^1H \) NMR spectrum of the solution showed that of the hydroxysulfonium salt immediately. Subsequently the \( ^1H \) NMR spectrum changed to that of the corresponding dicationic tellurane 38 after one week at room temperature. In the \( ^1H \) 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](image)

The change of the \( ^1H \) NMR spectrum is shown in Figure 4-4. In the \( ^1H \) 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 \( \delta 2.68 \) to \( \delta 3.32 \) by adding TFOH, because the oxygen atom of the sulfoxide was protonated to produce the hydroxysulfonium salt. After 9 hours, the \( ^1H \) NMR spectrum changed to the complex pattern, which suggests that this reaction has some intermediates. This reaction was completed after one week and the \( ^1H \) NMR spectrum only showed that of the dicationic tellurane 38. In the \( ^1H \) NMR spectrum, the singlet peak of the methyl group was shifted up field to \( \delta 2.43 \). This indicates that the sulfur atom of the methylsulfanyl group is reduced to form the methylthio group.
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 phenyllithiomethyl 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 $\pi$-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.
The telluride 10 was also treated with Tf$_2$O 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 $^1$H NMR. By adding Tf$_2$O to the solution of the telluride, 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 44. This reaction also proceeded quantitatively without any by-product.

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 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 \(\delta\) 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 \(\delta\) 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 \(\delta\) 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\(_2\)O, 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 \(\sigma\)-bond between them, because the methylsulfinyl group does not connect to the tellurium atom by a \(\pi\)-conjugated spacer. Finally the dicationic tellurane 44 should be produced by the formation of the 3e-4e bond (+S–Te–S+ bond).

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 dicaticonic 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 $\text{Tf}_2\text{O}$. 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 $\text{Tf}_2\text{O}$.

![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 dicaticonic tellurane 44. It was appeared that two stereoisomers of the dicaticonic 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 sulfanyl 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 possesses 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, wR=0.044.

The counter anions are omitted.

Bond Distances (Å)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Te(1)</td>
<td>2.637(1)</td>
</tr>
<tr>
<td>S(2)-Te(1)</td>
<td>2.730(1)</td>
</tr>
</tbody>
</table>

Bond Angles (deg)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Te(1)-S(2)</td>
<td>168.54(9)</td>
</tr>
<tr>
<td>S(1)-Te(1)-C(1)</td>
<td>81.3(1)</td>
</tr>
<tr>
<td>S(1)-Te(1)-C(9)</td>
<td>92.8(1)</td>
</tr>
<tr>
<td>S(2)-Te(1)-C(1)</td>
<td>80.0(1)</td>
</tr>
<tr>
<td>S(2)-Te(1)-C(9)</td>
<td>84.8(1)</td>
</tr>
</tbody>
</table>

Figure 4-5
VI. Further Investigation on the Reaction Mechanism of the Remote Oxidation

A. Necessity of \( \pi \)-Conjugated Spacer

In order to investigate the mechanism of the remote oxidation, the telluride 11, having no \( \pi \)-conjugated system between the tellurium atom and the sulfanyl group, was treated with \( \text{Tf}_2\text{O} \) or \( \text{TfOH} \). 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 \( \text{NOBF}_4 \) produced the corresponding dicationic tellurane.

![Scheme 4-24](image)

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

![Figure 4-6](image)

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 obtained by the reaction of the sulfoxide with \( \text{Tf}_2\text{O} \). This sulfonium salt should be produced by the electrophilic substitution that the cationic sulfur atom would react with the aromatic carbon atom.
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 Tf₂O in CD₃CN. 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.

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**
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$_3$SO$_3$ radical and ethyl phenyl sulfide 49. Subsequently another single electron transfer from the radical cation of the telluride to the CF$_3$SO$_3$ 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$_2$O 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 $^1$H NMR. This result means that this reaction should proceed via electron transfer not via dicationic intermediates.
For reference, only the sulfoxide 58 was treated with Tf₂O in CD₃CN under the same condition. This reaction was carried out in an NMR tube and monitored by ¹H NMR. By adding Tf₂O, 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.

By considering this result, the mechanism of the intermolecular reaction is predicted as shown in Scheme 4-32. The sulfoxide 58 should react with Tf₂O 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 CF₃SO₃ radical should react to produce the dicationic tellurane 2b.
C. Crossover Experiment

Furthermore the crossover experiment was carried out as follows. To the CD$_3$CN solution of the telluride 8 and the sulfoxide 50, two equivalents of Tf$_2$O 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$_2$O to form the dicationic tellurane by “intramolecular” remote oxidation and the intramolecular reaction should be predominant to the intermolecular reaction overwhelmingly.
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.
Experimental

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 CH₂Cl₂ (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH₂Cl₂ and the organic layer was dried over anhydrous MgSO₄. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, n-hexane-CHCl₃, 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, CDCl₃, room temperature) δ 4.25 (s, 4H, CH₂), 7.06–7.33 (m, 13H, ArH). ¹³C NMR (68 MHz, CDCl₃, 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 C₂₀H₁₇BrS₂: 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 Et₂O and the organic layer was dried over anhydrous MgSO₄. Recrystallization from EtOH gave white crystals, 4-bromothioanisole 13 (23 g) in 88 % yield.
4-Bromo-thio-anisole 13

$^1$H NMR (270 MHz, CDCl$_3$, room temperature) $\delta$ 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) $\delta$ 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-bromo-thio-anisole 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) $\delta$ 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) $\delta$15.4, 103.3, 126.9, 138.6, 139.5; $^{125}$Te NMR (126 MHz, CDCl$_3$, room temperature) $\delta$ 444.3 (relative to Me$_2$Te); MS (m/z) 202 (M$^+$).

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

t-BuLi (1.61 M, 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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-CHCl$_3$, 4 : 1) to give a pale yellow oil, telluride 16 (2.58 g) in 63% yield.

131
2,6-Bis[(phenylthio)methyl]phenyl 4-methylthiophenyl telluride 16

$^1\text{H NMR}$ (400 MHz, CDCl$_3$, room temperature) $\delta$ 2.40 (s, 3H, Me), 4.38 (s, 4H), 6.98–7.33 (m, 17H, Ar-H). $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$, room temperature) $\delta$ 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; $^{125}\text{Te NMR}$ (126 MHz, CDCl$_3$, room temperature) $\delta$ 449.4 (relative to Me$_2$Te); EIMS (m/z) 574 (M$^+$); Anal. Caled for C$_{27}$H$_{24}$S$_3$Te: 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$_3$CN (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$_2$Cl$_2$ (20mL) at -78°C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and recrystallization from CH$_2$Cl$_2$, CH$_3$CN 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.); $^1\text{H NMR}$ (270 MHz, CD$_3$CN, -40 °C) $\delta$ 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); $^{13}\text{C NMR}$ (100 MHz, CD$_3$CN, room temperature) $\delta$ 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; $^{125}\text{Te NMR}$ (126 MHz, CD$_3$CN, room temperature) $\delta$ 1342.9 (relative to Me$_2$Te); EIMS (m/z) 574 (M$^+$–2BF$_4^-$); Anal. Caled for C$_{27}$H$_{24}$B$_2$F$_6$S$_3$Te(CH$_2$Cl$_2$): C, 40.48; H, 3.15. Found: C, 40.86; H, 3.15.

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

The solution of m-CPBA (131 mg, 0.76 mmol) in CH$_2$Cl$_2$ (20 mL) was added to a CH$_3$CN (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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column
chromatography (silica gel; eluent, EtOAc) to give a pale yellow crystals, the telluride 8 (215 mg) in 48% yield.

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

mp 105-108 °C; 1H NMR (400 MHz, CDCl₃, room temperature) δ 2.57 (s, 3H, Me), 4.29 (s, 4H), 7.13-7.38 (m, 17H, Ar-H); 13C NMR (100 MHz, CDCl₃, 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; 125Te NMR (126 MHz, CDCl₃, room temperature) δ 463.4 (relative to Me₂Te); EIMS (m/z) 590 (M⁺); IR (NaCl) 1048 cm⁻¹ (S=O); Anal. Caled for C₂₇H₂₄O₅S₃Te: 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 CD₃CN was added trifluoromethanesulfonic anhydride ((CF₃SO₂)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 1H, 13C and 125Te 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.); 1H NMR (270 MHz, CD₃CN, -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); 13C NMR (100 MHz, CD₃CN, 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; 125Te NMR (126 MHz, CD₃CN, room temperature) δ 1342.9 (relative to Me₂Te); EIMS (m/z); 574 (M⁺-2TIO⁻); Anal. Caled for C₂₉H₂₄F₆O₆S₅Te: 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 CD₃CN was added trifluoromethanesulfonic acid (CF₃SO₂H; 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 1H and 125Te 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 125Te NMR spectroscopy.
Reactions of the telluride 8 with trifluoroacetic anhydride
To a solution of the telluride 8 (3 mg, 5.10^{-3} mmol) in dry CD_{3}CN was added trifluoroacetic anhydride ((CF_{3}CO)_{2}O; 1 \mu L, 6.10^{-3} mmol) at -40^\circ C under an argon atmosphere. The color of the solution changed from pale yellow to wine red after addition. This solution was monitored by \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{125}Te NMR spectroscopy. It took one day to complete the reaction at room temperature. Finally, the signals of the corresponding dicatonic tellurane were observed by \textsuperscript{1}H and \textsuperscript{125}Te NMR spectroscopy.

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

\textbf{32b}

\begin{equation}
\text{\textsuperscript{1}H NMR (270 MHz, CD_{3}CN, -40 ^\circ C) } \delta 2.54 (s, 3H, Me), 4.42 \text{ and } 5.26 (ABq, J = 18 Hz, 2H), 4.90 \text{ and } 5.24 (ABq, J = 17 Hz, 2H), 6.86 \text{ -} 8.23 (m, 17H, Ar-H); \text{\textsuperscript{13}C NMR (100 MHz, CD_{3}CN, room temperature) } \delta 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; \text{\textsuperscript{125}Te NMR (126 MHz, CD_{3}CN, room temperature) } \delta 1214.0 \text{ (relative to Me}_{2}\text{Te); EIMS (m/\text{z}) 574 (M}^+\text{--2CF}_{3}\text{CO}_{2}^\text{--})}.
\end{equation}

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

\textbf{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\textsubscript{4} (800 mL) was stirred under an argon atmosphere at reflux conditions (70 ^\circ 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\textsubscript{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.

\textbf{2,6-Bis(bromomethyl)-1-nitrobenzene}

mp 120-121 ^\circ C; \textbf{\textsuperscript{1}H NMR (270 MHz, CDCl\textsubscript{3}) } \delta 4.50 (s, 4H, CH\textsubscript{2}), 7.50-7.51 (m, 3H, ArH); \textbf{\textsuperscript{13}C NMR (67.8 MHz, CDCl\textsubscript{3}) } \delta 26.5, 130.8, 131.5, 131.8, 149.4; MS (m/\text{z}) 309 (M}^+).

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

\textbf{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\textsubscript{2}Cl\textsubscript{2} (10 mL) at 0 ^\circ C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH\textsubscript{2}Cl\textsubscript{2} and the organic layer was dried over anhydrous MgSO\textsubscript{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-CHCl₃, 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, CDCl₃, room temperature) δ 4.10 (s, 4H, CH₂), 7.20–7.30 (m, 13H, ArH). 13C NMR (68 MHz, CDCl₃, 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
NaBH₄ (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 CH₂Cl₂ and the organic layer was dried over anhydrous MgSO₄. After the removal of solvent under vacuum at room temperature, the crude product was subjected to column chromatography (silica gel; eluent, n-hexane-CHCl₃, 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, CDCl₃, room temperature) δ 4.07 (s, 4H, CH₂), 6.52–7.40 (m, 13H, ArH). 13C NMR (68 MHz, CDCl₃, 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 (HBF₄; 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 hydride (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 Et₂O, the crude product was obtained. Purification by column chromatography (silica gel; eluent, n-hexane) and recrystallization afforded a colorless crystals, the sulfide 21 (26.3 g) in 69% yield.

4-Methylthiophenyl 4-bromophenyl sulfide 21
1H NMR (400 MHz, CDCl₃, 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); 13C NMR (100 MHz, CDCl₃,
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 12 h. 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, CH₂Cl₂). After recrystallization from CH₂Cl₂, the ditelluride 22 (8.88 g) was obtained in 70% yield.

**Ditelluride 22**

¹H NMR (270 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, room temperature) δ15.5, 127.0, 129.7, 129.8, 133.2, 133.3, 138.1, 138.2, 138.5, 139.1; ¹²⁵Te NMR (126 MHz, CDCl₃, room temperature) δ 435.7 (relative to Me₂Te).

**Synthesis of telluride 23**

Isoamyl nitrite (1.0 mL, 8.55 mmol) was added to a dry CH₂Cl₂ (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 (NaBH₄; 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 Et₂O. The organic layer was dried over anhydrous MgSO₄, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-CH₂Cl₂, 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) $\delta$ 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) $\delta$ 452.6 (relative to Me$_2$Te); FAB-MS (m/z) 682 (M$^+$).

Synthesis of the telluride 9

An anhydrous CH$_3$CN (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$_2$Cl$_2$ (20 mL) at $-78 \, ^\circ$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$_3$CN (10 mL) was added to the solid. Then thiophenol (12 $\mu$L, 0.11 mmol) was added to the solution at 0 $^\circ$C. The resulting mixture was allowed to warm to room temperature overnight. The solvents were evaporated, and the residue was extracted with Et$_2$O. 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) $\delta$ 2.68 (s, 3H, Me), 4.39 (s, 4H), 7.16–7.48 (m, 21H, Ar-H); $^{13}$C NMR (100 MHz, CD$_3$CN, room temperature) $\delta$ 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$_3$CN, room temperature) $\delta$ 457.2 (relative to Me$_2$Te); 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) $\delta$ 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) $\delta$ 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$_2$Cl$_2$ (10 mL) at 0 °C. The solution was stirred overnight. After the removal of solvents, the residue was extracted with CH$_2$Cl$_2$ 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$_2$Cl$_2$, 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) $\delta$ 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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-CH$_2$Cl$_2$, 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) $\delta$ 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) $\delta$ 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,
CDCl₃, room temperature) δ 453.2 (relative to Me₂Te); EIMS (m/z) 620 (M⁺); Anal. Calcd for C₂₈H₂₆S₄Te: C, 54.38; H, 4.24. Found: C, 54.47; H, 4.24.

**Synthesis of the dicationic tellurane 30**

An anhydrous CH₃CN (10 mL) solution of NOBF₄ (42 mg, 0.36 mmol) was added dropwise to a solution of telluride 29 (106 mg, 0.17 mmol) in anhydrous CH₂Cl₂ (20 mL) 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 2BF₄⁻ salt 30 (100 mg) in 74% yield.

**Dicationic Tellurane 30**

¹H NMR (270 MHz, CD₃CN, 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); ¹²⁵Te NMR (126 MHz, CD₃CN, room temperature) δ 1330.5 (relative to Me₂Te); EIMS (m/z): 620 (M⁺–2BF₄⁻).

**Synthesis of the telluride 10**

The solution of m-CPBA (20 mg, 0.12 mmol) in CH₂Cl₂ (20 mL) was added to a CH₃CN (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 CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄, 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, CDCl₃, 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). ¹³C NMR (100 MHz, CDCl₃, 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, 133.4, 135.3; ¹²⁵Te NMR (126 MHz, CDCl₃, room temperature) δ 447.1 (relative to Me₂Te); EIMS (m/z) 636 (M⁺).

**Synthesis of 4-methylthiophenyl 4-bromophenyl methane**

139
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-CHCl₃, 4:1). 4-methylthiophenyl 4-bromophenyl methane (3.68 g) was obtained in 25% yield.

4-Methylthiophenyl 4-bromophenyl methane

¹H NMR (400 MHz, CDCl₃, 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, CH₂Cl₂). After recrystallization from CH₂Cl₂, the ditelluride 22b (2.0 g) was obtained in 48% yield.

Ditelluride 22b

¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, room temperature) δ 16.1, 40.9, 105.0, 127.0, 129.4, 129.8, 135.9, 137.7, 137.9, 138.1; ¹²⁵Te NMR (126 MHz, CDCl₃, room temperature) δ 424.8 (relative to Me₂Te).

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(phenylethio)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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane-CHCl$_3$, 4 : 1) to give 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$_2$Te); EIMS (m/z) 664 (M$^+$); Anal. Caled for C$_{34}$H$_{30}$S$_3$Te: C, 61.65; H, 4.56. Found: C, 60.71; H, 4.68.

**Synthesis of the telluride 11**

An anhydrous CH$_3$CN (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$_2$Cl$_2$ (20mL) at -78 °C under an argon atmosphere. When the addition was completed, the NO gas was removed under vacuum. After stirring overnight, the solvents were evaporated at room temperature and CH$_3$CN (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$_2$O. 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$_2$Te); FAB-MS (m/z) 680 (M$^+$); Anal. Caled for C$_{34}$H$_{30}$OS$_3$Te: 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 CD₃CN, trifluoromethanesulfonic anhydride ((CF₃SO₂)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 ¹²⁵Te 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 CD₃CN, trifluoromethanesulfonic acid (CF₃SO₂H; 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 ¹²⁵Te 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 3 h, cooled, quenched with a solution of iodine (3 g, 12 mmol) in anhydrous THF. The solvents were evaporated, and the residue was extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄, 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, CDCl₃, room temperature) δ 2.02 (s, 12H), 7.09–7.51 (m, 9H, Ar-H). ¹³C NMR (100 MHz, CDCl₃, 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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane- CH$_2$Cl$_2$, 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

$^1$H NMR (400 MHz, CDCl$_3$, room temperature) $\delta$ 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) $\delta$ 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$_2$Cl$_2$ (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$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and removal of the solvent at room temperature gave the crude product, which was subjected to column chromatography (silica gel; eluent, n-hexane- CH$_2$Cl$_2$, 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

$^1$H NMR (400 MHz, CDCl$_3$, room temperature) $\delta$ 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) $\delta$ 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$_3$CN, trifluoromethanesulfonic anhydride ((CF$_3$SO)$_2$O; 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 $^1$H and $^{125}$Te NMR spectroscopy, which showed formation of the dicaticonic tellurane 2b and ethyl phenyl sulfide 49 in a 1 : 1 ratio. The $^1$H 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$_3$CN, trifluoromethanesulfonic anhydride ((CF$_3$SO$_2$)$_2$O; 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 $^1$H and $^{125}$Te NMR spectroscopy, which showed formation of the dicationic tellurane 2b and the sulfide 57 in a 1:1 ratio. The $^1$H 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$_3$CN, trifluoromethanesulfonic anhydride ((CF$_3$SO$_2$)$_2$O; 5 µL, 0.04 mmol) was added at -40°C under an argon atmosphere. This solution was monitored by $^1$H 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

